

Magnetic Mirrors and Plasmonic Metasurfaces for Mid-infrared Graphene Photodetectors and Biosensors

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Submitted in partial fulfilment for the degree of

Doctor of Philosophy

To my parents, brother and sisters

Abstract

Magnetic Mirrors and Plasmonic Metasurfaces for Mid-infrared Graphene Photodetectors and Biosensors

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Graphene is the name given to a monolayer of carbon atoms arranged in a two-dimensional honeycomb lattice. Recently, there has been much interest concerning the use of graphene in photodetectors and biosensors due to its unique electronic and optical properties. Specifically, graphene is an attractive material for developing broadband and high-speed photodetectors because of its gapless band structure and ultrafast carrier dynamics. The high spatial confinement and electrical tunability of mid-infrared (MIR) graphene plasmon have also been used for biosensors which permit the quantification and identification of biomolecule monolayers. However, the realisation of high-performance graphene photodetectors operating in the MIR is hindered by the intrinsically low optical absorption ($< 2.3\%$) and short carrier lifetime (sub-picosecond) of this material. In addition, the sensitivity of graphene biosensors based on plasmons is limited by the relatively small field enhancement of graphene plasmons compared to that of conventional metal plasmons.

In this thesis, we present nano-optical approaches to enhance the performance of graphene-based photodetectors and biosensors operating in the MIR by employing magnetic mirrors and/or plasmonic metasurfaces.

First, we propose and experimentally demonstrate a long-wave infrared device that we termed a magnetic mirror, which consists of an array of amorphous silicon cuboids on a gold film. The device is demonstrated to reflect light with high reflectance and zero phase shift. A modified multipole analysis method is devised and employed to interpret the magnetic mirror behaviour. We investigate the use of this device in a graphene photodetector application and show that the light absorption by graphene placed on top can be boosted by more than three orders of magnitude compared to the absorption that would occur were the graphene instead placed on a gold mirror. This is achieved by producing a field distribution with enhanced intensity at the device surface.

Second, we design and experimentally demonstrate a mid-wave infrared polarization-independent graphene photodetector via the integration of plasmonic nanoantennas that we term Jerusalem-cross antennas (JC-antennas). The JC-antennas serve to concentrate the incident light onto graphene for strongly enhanced optical absorption, as well as to collect the photocarriers. We demonstrate mid-wave infrared detection both at room temperature and at cryogenic temperatures. Our device also shows a fast and broadband photoresponse that extends to visible and near-infrared wavelengths, thanks to the carrier collection by the JC-antennas.

Last, we propose and investigate a biosensor device that combines the strong field confinement and electrical tunability of graphene plasmons with the large field enhancement of metallic nanoantennas. The device consists of an array of plasmonic nanoantennas and graphene nanoslits on a resonant substrate. Systematic electromagnetic

simulations are performed to quantify the sensing performance of the proposed device. Our simulations show that the proposed device outperforms designs in which only plasmons from metallic nanoantennas or plasmons from graphene are utilized.

Declaration

This is to certify that

(i) this thesis comprises only my original work towards the degree of Doctor of

Philosophy except where indicated in the preface,

(ii) due acknowledgement has been made in the text to all other material used,

(iii) the thesis is less than 100,000 words in length, exclusive of tables, figures,

bibliographies and appendices.

Ming Ye

July 2020

Preface

This thesis is based on the works that I have done during my PhD candidature at The University of Melbourne. A list of publications and the contributions of the thesis author are presented below:

JOURNAL PAPERS

1. M. Ye, S. Q. Li, Y. Gao, and K. B. Crozier. Long-wave infrared magnetic mirror based on Mie resonators on conductive substrate. **Optics Express**, 28, 1472-1491 (2020)

- **M. Ye** designed the device, performed the simulations, fabricated and measured the devices and wrote the paper. S. Q. Li provided suggestions to the theoretical interpretation. Y. Gao provided suggestions to device fabrication. K. B. Crozier supervised the work.

My contribution to this work is 90% or more.

2. M. Ye, and K. B. Crozier. Metasurface with metallic nanoantennas and graphene nanoslits for sensing of protein monolayers and sub-monolayers. **Optics Express**, 28, 18479-18492 (2020)

- **M. Ye** conceived the idea, performed the simulations and wrote the paper. K. B. Crozier supervised the work.

My contribution to this work is 90% or more.

3. M. Ye*, Y. Gao*, J. J. Cadusch, S. Balendhran, and K. B. Crozier. Mid-wave infrared polarization-independent graphene photoconductor with integrated plasmonic nanoantennas operating at room temperature. (Submitted for publication to Advanced Optical Materials on June 23, 2020)

*- These authors contributed equally to this paper

- **M. Ye** performed the simulations, analysed the data, fabricated and measured the devices and wrote the paper. Y. Gao fabricated one of the graphene photodetector devices (Device #1), contributed to the simulations and helped review the draft. J. J. Cadusch and S. Balendhran helped with the device measurements. K. B. Crozier supervised the work.

My contribution to this work is about 45%.

4. S. Q. Li, W. Z Song, M. Ye, and K. B. Crozier. Generalized method of images and reflective color generation from ultra-thin multipole resonators. **ACS Photonics** 5, 2374-2383 (2018)

- **M. Ye** helped with characterization and discussed the results

CONFERENCE PROCEEDINGS

1. **M. Ye**, S. Q. Li, Y. Gao, V. R. Shrestha, and K. B. Crozier (2018 May). Mid-infrared Magnetic Mirror Based on a Hybrid Metal/Dielectric Metasurface. In **CLEO: QELS-Fundamental Science** (pp. FTh4J.6). Optical Society of America. (**Oral Presentation**)

- **M. Ye** did the oral presentation at the conference

My contribution to this work is 90% or more.

Chapter 3 is fully reproduced from the journal publication “**M. Ye**, S. Q. Li, Y. Gao, and K. B. Crozier. Long-wave infrared magnetic mirror based on Mie resonators on conductive substrate. **Optics Express**, 28, 1472-1491 (2020)”.

Chapter 4 is written with modifications based on the work “**M. Ye***, Y. Gao*, J. J. Cadusch, S. Balendhran, and K. B. Crozier. Mid-wave infrared polarization-independent graphene photoconductor with integrated plasmonic nanoantennas operating at room temperature”, submitted for publication to *Advanced Optical Materials* on June 23, 2020. The texts on pages 98, 102-107, 109-115 of chapter 4 are from the publication “**M. Ye***, Y. Gao*, J. J. Cadusch, S. Balendhran, and K. B. Crozier. Mid-wave infrared polarization-independent graphene photoconductor with integrated plasmonic nanoantennas operating at room temperature”. **M. Ye** performed the simulations, analysed the data, fabricated and measured the devices and wrote the paper. Y. Gao fabricated one of the graphene photodetector devices (Device #1), contributed to the simulations and helped review the draft. J. J. Cadusch and S. Balendhran helped with the device measurements. K. B. Crozier supervised the work. My contribution to the work presented in chapter 4 is 60%.

Chapter 5 is fully reproduced from the journal publication “**M. Ye**, and K. B. Crozier. Metasurface with metallic nanoantennas and graphene nanoslits for sensing of protein monolayers and sub-monolayers. **Optics Express**, 28, 18479-18492 (2020)”.

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Some of the figures used in this dissertation have been taken from published papers. In these instances, the appropriate reference has been inserted at the end of the figure caption to acknowledge the source and permission obtained from the publisher for reproduction.

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It is just as fresh in my mind now as years ago a picture of Isaac Newton holding a prism from which emerges a rainbow of light. To me, the four years of research training and learning that I have had at the University of Melbourne are like a “prism” sorting out the many aspects of life with simple and colourful experiences. For the things I have learned and achieved, I am genuinely grateful for all the helps and supports offered by those both near and far. The opportunity for my graduate study would not be possible without the financial support generously provided by the Melbourne Research Scholarship at The University of Melbourne. I am deeply impressed by the free, open and supportive academic community here at The University of Melbourne. I am proud that I could be a part of it just as I am sure that many of other international students will feel the same way.

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Ming Ye
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List of Abbreviations

2D	two-dimensional
SLG	single-layer graphene
FLG	few-layer graphene
TM	transverse magnetic
SEM	scanning electron microscopy
SNOM	scanning near-field optical microscopy
SPPs	surface plasmon polaritons
MIR	mid-infrared
MWIR	mid-wave infrared
LWIR	long-wave infrared
MCT	mercury cadmium telluride
InSb	indium antimonide
PbSe	lead selenide
CQDs	colloidal quantum dots
CVD	chemical vapor deposition
MGM	metal-graphene-metal
GDPRs	graphene-disk plasmonic resonators
GNRs	graphene nanoribbons

NNH	nearest-neighbour hopping
TCE	thermal-carrier excitation
GQD	graphene quantum dot
LSPs	localized surface plasmons
PEC	perfect electric conductor
PMC	perfect magnetic conductor
FEM	finite element method
FDTD	finite difference time domain
FTIR	Fourier transform infrared spectrometer
QCL	quantum cascade laser

Chapter 1

Introduction

1.1 Overview

Graphene has drawn much attention in recent years as a candidate material for the development of novel photonic and optoelectronic devices, due to its unique electronic and optical properties.¹ In particular, there has been much interest concerning the use of graphene for high-performance, low cost and environmentally-friendly photodetectors operating in the mid-infrared (MIR, wavelength: $\sim 2.5\text{-}25\ \mu\text{m}$). Commercially available MIR photodetectors are largely based on conventional narrow-bandgap semiconductors such as HgCdTe (MCT),^{2, 3} indium antimonide (InSb),⁴ and lead selenide (PbSe),⁵ and other technologies such as quantum wells⁶ and type-II superlattices.⁷⁻⁹ However, these devices are often expensive and bulky due to complex growth/fabrication processes and cryogenic cooling, respectively. In addition, many of the semiconductor materials used for MIR detection are toxic and hazardous to the environment. Graphene provides promising platform to address these issues for several reasons. First, it is a well-established principle for MIR photodetectors that reduction in the volume of the photosensitive material results in reduced detector noise associated with the thermal generation of charge carriers.¹⁰ This motivates investigation into graphene because a photodetector based on it will in some sense represent a limiting case of this volume reduction principle as it is only one layer of atoms thick. Second, the growth of uniform graphene films over large areas can be achieved by chemical vapor deposition (CVD), and show excellent crystal quality and physical properties that are comparable to mechanically-exfoliated graphene. Third, graphene is non-toxic and environmentally

friendly. Furthermore, graphene is an attractive material for developing high-speed and broadband photodetectors because of its ultrafast carrier dynamics and gapless band structure.¹¹⁻¹⁴ Despite these advantages, graphene photodetectors generally suffer from low responsivity,^{15, 16} due to the intrinsically low optical absorption ($< 2.3\%$) and short photocarrier lifetime (sub-picosecond) of this material. This poses challenges to the realization of high-performance graphene detectors operating in the MIR due to the resulting low signal-to-noise ratio, especially at room temperature.

It has been shown that graphene supports plasmons in the MIR with strong spatial confinement.^{17, 18} In addition, graphene plasmons are electrically tuneable via external gating.^{19, 20} These properties have been used in biosensors for the quantification and identification of biomolecules down to monolayers.²¹⁻²³ The strong spatial confinement of graphene plasmons provides excellent overlap between the local electric field and the nanometre-sized biomolecules, thereby increasing the absorption in biomolecules. In addition, the graphene plasmon could be electrically tuned to overlap with molecular fingerprints in different spectral regions. This can be done by electrostatic modulation of the graphene Fermi level. However, the sensitivity of biosensors based on graphene plasmons is limited by the relatively small field enhancement of graphene plasmons compared to that of conventional metal plasmons. This poses challenges to the detection of biomolecules in sub-monolayer forms.

In this thesis, we present nano-optical approaches for enhancing the performance of graphene-based photodetectors and biosensors operating in the MIR by improving the light-graphene interaction. These include the experimental demonstration of a long-wave infrared (LWIR) magnetic mirror and the investigation of its use in a graphene photodetector application as an optical back-reflector for absorption enhancement of graphene; experimental demonstration of mid-wave infrared (MWIR) polarization

independent graphene photodetectors with integrated plasmonic nanoantennas operating at room temperature; and an investigation of a graphene biosensor with metallic nanoantennas and graphene nanoslits for the sensing of protein monolayers and sub-monolayers.

This thesis is organized as follows:

Chapter 1 presents details on the key properties of graphene and a literature review of graphene for photodetectors and biosensors. First, we will review graphene properties relevant to this work, including its electronic band structure, the ambipolar electric field effect, its linear optical absorption properties and tuneable graphene plasmons. Then, we will present the research background and motivation via a literature reviews of graphene photodetectors and biosensors operating in the MIR. Last, we will present the basic concepts of magnetic mirrors and show how they can be used in graphene photodetectors for absorption enhancement.

Chapter 2 describes the simulation, nanofabrication and characterization methods employed in this thesis. We will first present details on simulations performed using the finite difference time domain method (FDTD Solutions, Lumerical) and finite element method (FEM, COMSOL Multiphysics). In particular, the modelling of graphene and multipolar analysis of the scattering of magnetic mirrors will be discussed. Then, we will describe the graphene growth and transfer methods, and the device fabrication processes for both magnetic mirrors and graphene photodetectors. Finally, we will describe the experimental setups that we used for device characterization including for determination of the reflectance and phase shift of the magnetic mirrors, and the photoresponse of graphene photodetectors.

Chapter 3 presents the results of our work on experimental demonstration of a LWIR magnetic mirror, which is fully reproduced from my refereed journal publication entitled “Long-wave infrared magnetic mirror based on Mie resonators on conductive substrate” that is published in *Optics Express*. In this work, we harness the high reflectance of a conductive substrate (gold film) and the versatile scattering properties of high index Mie resonators (a-Si, i.e. amorphous silicon, cuboids) to achieve a thin LWIR magnetic mirror with high reflectance. We experimentally demonstrate a LWIR magnetic mirror consisting of an array of a-Si cuboids (1.1 μm thick) on gold substrate, with measured zero-phase shift and high reflectance of $\sim 90\%$ at a wavelength of 8.4 μm . A modified multipole analysis method is devised and employed to study the multipolar scattering properties of an a-Si cuboid above a perfect electric conductor (PEC) and provides insights into the physical mechanism of the magnetic mirror behaviour. We further show by simulation that the optical absorption in monolayer graphene placed on our structure can be enhanced by more than three orders of magnitude compared to the absorption that would result were the graphene instead placed on a gold mirror. The demonstrated magnetic mirror structure represents an attractive substrate for graphene photodetectors by enhancing the graphene absorption and providing an electrical contact for electrostatic gating.

Chapter 4 presents the results of the second work of this thesis, on the demonstration of a MWIR graphene photodetector. In this work, we demonstrate a polarization-independent graphene photoconductor with integrated plasmonic nanoantennas which we term Jerusalem-cross nanoantennas (JC-antennas). Unlike methods that rely on charge trapping centres or photogating effects for photoresponsivity enhancement, our approach, in which JC-antennas are used to increase optical absorption and improve photocarrier collection, does not hinder the detector speed. The rise time of

our device is measured to be 11.4 μs . Our JC-antennas, with their elongated ends (~ 270 nm) and narrow gaps (~ 40 nm) between adjacent antennas, also render a stronger optical absorption enhancement in the graphene, with a simulated absorption of 16.4% in the MWIR at 4.12 μm , which is 64% and 167% larger than that occurring in the rod-antenna configuration of a previous study²⁴ for polarized and unpolarized light, respectively. Moreover, this absorption is polarization-independent due to the highly symmetric shape (four-fold symmetry) of the JC-antennas. Our device shows significant MWIR photoresponse, with measured maximum responsivities of 4.6 mA/W (corresponding to 14.5 V/W) at room temperature and 1.9 A/W (corresponding to 4.4×10^3 V/W) at 78 K. Notably, our device also shows a strong and broadband photoresponse that extends to visible and near-infrared wavelengths, due to the improved carrier collection by the JC-antennas.

Chapter 5 reports our third work, which is a simulation study of a graphene biosensor. In this work, we present a sensing strategy that employs a nanostructured surface that consists of an array of plasmonic nanoantennas and graphene nanoslits on a resonant substrate. By combining the strong field confinement of graphene plasmons with the large field enhancement of metallic nanoantennas, light-molecule interaction is enhanced in the proposed device, allowing the detection of biomolecules with densities down to sub-monolayers. Systematic electromagnetic simulations are performed to quantify the sensing performance of the proposed device and show that it outperforms designs in which only plasmons from metallic nanoantennas or plasmons from graphene are utilized. In these simulation studies, we consider the model system of a representative protein - goat anti-mouse immunoglobulin G (IgG) – in monolayer or sub-monolayer form. Our simulation shows that the proposed device is able to detect the protein IgG with densities down to a surface percentage coverage of 0.11%.

Chapter 6 summarizes the important findings of this thesis as well as making the suggestions for some future research directions.

1.2 Graphene

Graphene is the name given to a monolayer of sp^2 -hybridized carbon atoms arranged in a two-dimensional (2D) honeycomb lattice. It is the basic building block of other important allotropes including graphite, carbon nanotube and fullerenes. The theoretical study of graphene has a long history. In 1947,²⁵ P. R. Wallace first theoretically predicted the bandstructure of graphene and showed the unusual semi-metallic behaviour of graphene. In 2004, graphene was first experimentally isolated from graphite using a scotch-tape technique by A. K. Geim and co-workers.²⁶ Since then, there have been intensive studies on graphene, both theoretical and experimental. It has been reported that many of its properties surpass those of other materials. These include it having an extremely high carrier mobility (of $2.5 \times 10^5 \text{ cm}^2/\text{Vs}^{27}$), being very strong mechanically (Young's modulus of 1 TPa and an intrinsic strength of 130 GPa²⁸), having a high thermal conductivity (exceeding 3000 W/mK^{29, 30}), having an optical absorption that is very high considering the fact that it is just a single layer of atoms ($\sim 2.3\%$ in the infrared limit¹²), being completely impermeable to gases³¹ and being able to sustain extremely high densities of electric current (a million times higher than copper³²). In addition, as discussed, graphene supports plasmons in the mid-infrared with high spatial confinement and electrical tunability. The superior properties of graphene have attracted enormous interest for both fundamental physics and practical applications, especially for photonic devices. Graphene-based mid-infrared photodetectors and biosensors represent two examples of such opportunities and are pursued in this thesis. In this section, we will review the fundamental electronic and optical properties of graphene, including the basics of graphene plasmons.

1.2.1 Unique Electronic and Optical Properties

Electronic properties. In the hexagonal lattice of graphene, the $2S$, $2P_x$ and $2P_y$ electrons form the in-plane σ -bonds between adjacent carbon atoms, while the $2P_z$ electrons form the out-of-plane π -bonds. The electronic band structure of monolayer graphene can be described using a tight-binding Hamiltonian.^{25, 33} Making the π -band approximation and considering both the nearest-neighbour and next-nearest-neighbour hopping, the electronic dispersion relation is given as follows³⁴

$$E^{\pm}(k_x, k_y) = \pm t \sqrt{3 + f(k_x, k_y)} - t' f(k_x, k_y) \quad (1.1)$$

$$f(k_x, k_y) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right) \quad (1.2)$$

where t is the nearest-neighbour hopping energy (~ 2.8 eV), t' is the next-nearest-neighbour hopping energy, a is the carbon-carbon distance (~ 1.42 Å), the plus and minus sign apply to the upper (π^*) and lower (π) band respectively, and (k_x, k_y) are the momentum vectors in the first Brillouin zone that constitute the ensemble of available electronic momenta.

If we neglect the next-nearest-neighbour hopping energy, the dispersion relation (Eqn. (1.1)) can be further simplified to be as follows

$$E^{\pm}(k_x, k_y) = \pm t \sqrt{3 + 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right)} \quad (1.3)$$

The electronic band structure is shown in Fig. 1.1(a).³⁵ It can be seen that the band structure is symmetric around zero energy. With one $2P_z$ electron per atom in the π - π^* model and the other $2S$, $2P_x$ and $2P_y$ electrons filling the low-lying σ -band, the valence band (negative energy branch) is fully occupied, whereas the conduction band (positive energy branch) is totally empty. These occupied and unoccupied bands meet at the K and

K' points at the corners of the Brillouin zone. These points are called the Dirac points. Expanding Eqn. (1.3) at the K and K' points yields the linear electronic dispersion relation for massless Dirac fermions³⁴

$$E^{\pm}(k_x, k_y) = \pm \hbar v_F \sqrt{k_x^2 + k_y^2} \quad (1.4)$$

where v_F is the Fermi velocity in graphene ($v_F \approx 10^6$ m/s). This dispersion relation is plotted in Fig. 1.1(b). It can be seen that it has a cone shape (known as the Dirac cone) and that the conduction and valence bands cross at the Dirac point. Consequently, electrons propagating through monolayer graphene behave as massless Dirac fermions and exhibit electronic properties for a 2D gas of charged particles described by the relativistic Dirac equation with electrons mimicking particles with zero mass and an effective “speed of light” of around 10^6 m/s. This unique electronic band structure results in graphene having many exceptional properties, including superior carrier mobility, ultra-wideband electrical tunability and ultra-wideband optical absorption.

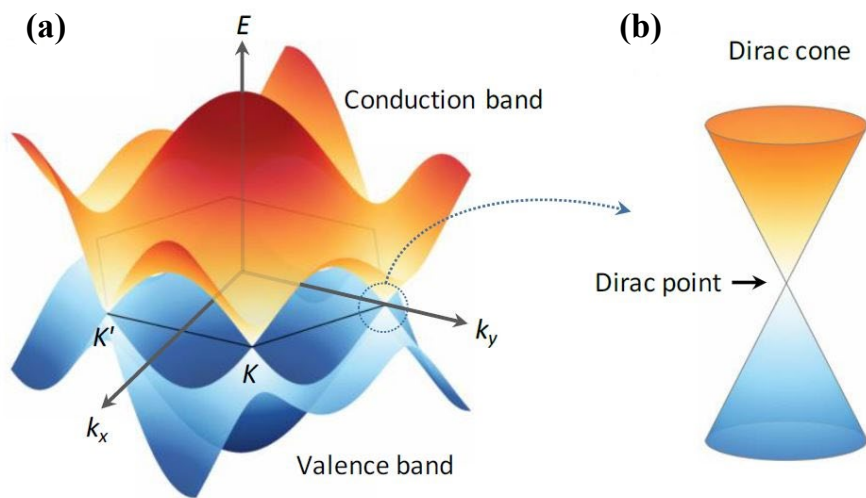


Figure 1.1. Electronic band structure neglecting next-nearest-neighbour hopping. (a) in the honeycomb lattice of graphene and (b) at the Dirac points. Reproduced from ref. 35

Ambipolar electric field effect. The linear electronic dispersion relation of monolayer graphene renders a strong ambipolar electric field effect³⁶ (Fig. 1.2(a)) that permits tuning of its carrier concentration to be as high as 10^{13} cm^{-2} by applying an electric field. Figure 1.2(a) shows the tuning of the Fermi level and resistivity of graphene in a field-effect configuration by applying a gate voltage, as a result of the modulation of electron (hole) concentration. The rapid decrease in resistivity on increasing carrier concentration (Fig. 1.2(a)) indicates a high carrier mobility of $\sim 5000 \text{ cm}^2/\text{Vs}$. The strong electrical tuning of the carrier concentration in graphene, and the resultant tuneable optical properties, hold great promise for achieving active photonic and optoelectronic devices, e.g. via tuneable optical absorption and local refractive index change in graphene.

Linear optical absorption. Graphene also shows an optical absorption of $\sim 2.3\%$ in the infrared limit (wavelength: $< 3 \text{ }\mu\text{m}$), which is remarkably high when one considers that graphene comprises a single layer of atoms. This allows graphene to be seen in a standard optical microscope by eye when it is on a layer of SiO_2 on an Si substrate.^{37, 38} The optical contrast scales with the number of graphene layers and can be maximized by optimizing the spacer (i.e. SiO_2 layer) thickness or by appropriate choice of wavelength, e.g. via filters in a regular optical microscope.^{37, 38} In the thin-film limit of the Fresnel equations, the transmittance of single-layer graphene (SLG) is given by¹²

$$T = (1 + 0.5\pi\alpha)^{-2} \approx 1 - \pi\alpha \approx 97.7\% \quad (1.5)$$

where $\alpha = e^2/(4\pi\epsilon_0\hbar c) \approx 1/137$ is the fine structure constant. In the visible region, the reflectance of SLG suspended in air is less than 0.1% ,¹² and rises to around 2% for ten graphene layers on an SiO_2 (300 nm)/Si substrate.³⁸ In fewer-layer graphene (FLG) samples, there is little perturbation from adjacent layers and each layer can be seen as a

2D electron gas. Consequently, FLG samples are optically equivalent to a superposition of SLGs that are almost non-interacting.³⁸ Thus, the optical absorption of FLG in the visible region is proportional to the number of layers, with an absorption of $\sim 2.3\%$ ($A = 1 - T$) for each layer.¹² Figure 1.2(b) shows an optical image of a suspended graphene monolayer and of a bilayer covering an aperture in air,¹² showing optical absorptions of $\sim 2.3\%$ and $\sim 4.6\%$ respectively.

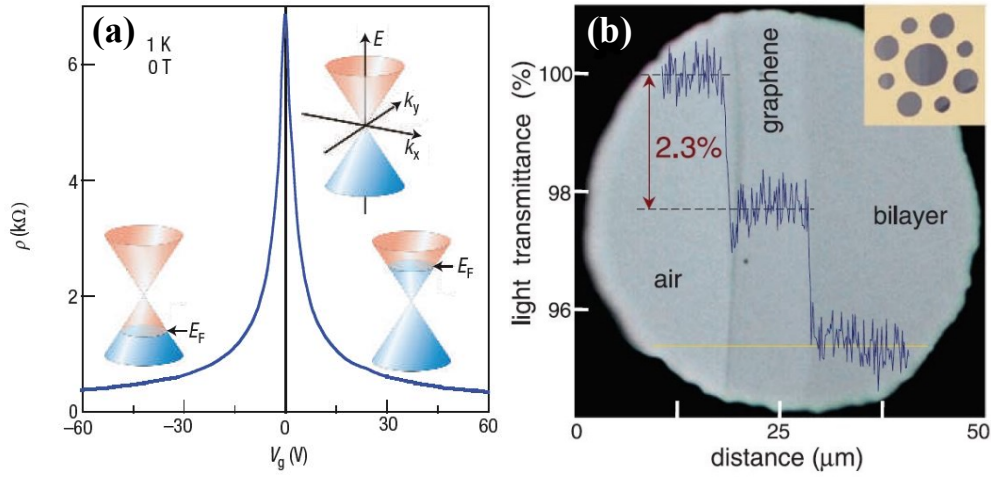


Figure 1.2. Ambipolar electric field effect and linear optical absorption in graphene. (a) Ambipolar electric field effect in monolayer graphene in field-effect devices with a dielectric layer of 300-nm thick SiO_2 .^{26, 39} Insets show schematic illustrations of the energy diagram. Reproduced from ref. 36. (b) Optical image of graphene monolayer and bilayer on a 50-μm aperture. The line scan profile shows the intensity of transmitted white light along the yellow line. Inset, a 20-mm-thick metal support structure with several apertures with different diameters covered with graphene flakes. Reproduced from ref. 12.

1.2.2 Graphene Plasmons

Dispersion relation. As mentioned previously, graphene supports plasmons in the mid-infrared regime.¹⁷ More importantly, graphene plasmons possess much stronger field confinement than noble metal plasmons and are tuneable by adjusting the carrier concentration through external gate bias.²² Graphene plasmons have also been reported to exhibit sub-picosecond lifetimes^{40, 41} These unique properties of graphene plasmons make them attractive platforms for emerging mid-infrared applications such as mid-infrared photodetectors and mid-infrared vibrational spectroscopy.

Similar to noble metals, graphene supports transverse magnetic (TM) surface plasmons modes, where the incident electric field parallel to the plasmon propagating direction is coupled to the free carriers in graphene and induces collective carrier oscillation. The graphene plasmon propagating along the surface of graphene is highly confined to the graphene and decays exponentially along the perpendicular directions. The dispersion relation of TM-mode graphene plasmons in an insulator-graphene-insulator system is given by^{17, 42, 43}

$$\frac{\varepsilon_{r1}}{\sqrt{k_p(\omega)^2 - \varepsilon_{r1}\omega^2/c^2}} + \frac{\varepsilon_{r2}}{\sqrt{k_p(\omega)^2 - \varepsilon_{r2}\omega^2/c^2}} = -i \frac{\sigma(\omega)}{\omega \varepsilon_0} \quad (1.6)$$

where ε_0 is the permittivity in free space, ε_{r1} and ε_{r2} are the relative permittivities of media above and below the graphene respectively, $\sigma(\omega)$ is the frequency dependent surface conductivity of graphene neglecting spatial dispersion (for a uniform graphene layer), ω is the frequency of light, k_p is the wavenumber of graphene plasmon and c is the speed of light in vacuum. The surface conductivity of graphene based on a semi-classical Drude model is given by Eqn. (1.7). By substituting Eqn. (1.7) into Eqn. (1.6), the dispersion relation of graphene in a quasi-static regime ($k_p \gg \omega/c$) is expressed as⁴²

$$\sigma(\omega) \approx i \frac{e^2 |E_F|}{\pi \hbar^2 (\omega + i\tau^{-1})} \quad (1.7)$$

$$k_p(\omega) \approx \frac{\pi \hbar^2 \epsilon_0 (\epsilon_{r1} + \epsilon_{r2})}{e^2 |E_F|} \left(1 + \frac{i}{\tau \omega}\right) \omega^2 \quad (1.8)$$

where E_F and τ are the Fermi level and intrinsic relaxation time of graphene respectively. The intrinsic relaxation time is caused by defects, impurities and scattering processes in graphene and is thus indicative of the quality of graphene. It can be seen from the dispersion relation of Eqn. (1.8) that graphene plasmons can be tuned by adjusting the graphene Fermi level. More specifically, the graphene plasmon wavelength is proportional to the graphene Fermi level. In the mid-infrared frequency range, under typical graphene doping conditions, the graphene plasmon wavevector can be two orders of magnitude smaller than that in free space,¹⁷ indicating an extreme spatial confinement. This is illustrated in Fig. 1.3 (a), where the near-field enhancement distributions of localized resonant plasmons (frequency 1600 cm⁻¹) from a gold dipole-antenna array and a graphene ribbon array are compared.²² Figure 1.3(b) shows the percentage of space-integrated near-field intensity confined within a volume extending a distance d outside the nanoantenna and graphene nanoribbon, from which we can see that 90% of the mode energy is confined within 15 nm from the graphene surface, whereas the same percentage is spread over a distance 500 nm from the gold surface.

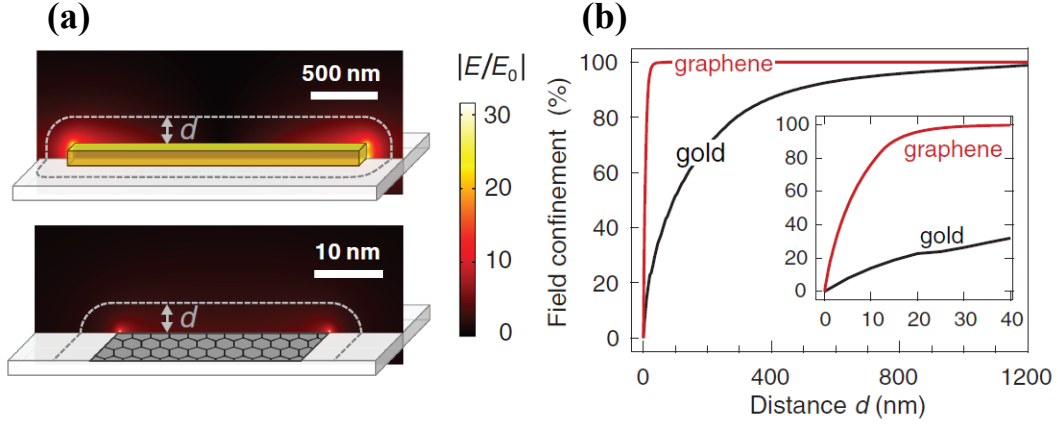


Figure 1.3. Comparison between the field confinement between graphene plasmon and noble metal plasmon. (a) Near-field enhancement distribution $|E/E_0|$ at 1600 cm^{-1} resonance frequency in a gold dipole-antenna array and a graphene ribbon array. (b) Percentage of space-integrated near-field intensity confined within a volume extending a distance d outside the nanoantenna and graphene ribbon. Inset shows a zoom-in for distance d between 0 and 40 nm. Reproduced from ref. 22.

Excitation of graphene plasmons. It has been demonstrated that localized graphene plasmons can be excited by patterning graphene into micro- to nanoribbons and into nanodisk arrays.^{40, 44, 45} The excited plasmons can be observed through absorption peaks in transmission spectroscopy measurements. Graphene ribbon arrays are widely employed to study the basic properties of graphene plasmons due to their simple geometry, as this facilitates physical interpretation. It was shown that the plasmonic response of an individual graphene ribbon in an array is unaffected by the array periodicity when it is greater than twice of the ribbon width,⁴⁶ indicating negligible inter-ribbon coupling effect in this limit. Thus, plasmonic resonances within an individual ribbon occur when $k_p = (2n + 1)\pi/W$, where W is the ribbon width and n is a natural number. Figure 1.4(a) shows the transmission measurement scheme for graphene

nanoribbons on a diamond-like carbon substrate as described in ref. 19, with excitation light from a broadband mid-infrared source. Figure 1.4(b) shows a scanning electron microscope (SEM) image of an array of graphene nanoribbons. The excited plasmonic resonances can be identified by the peaks in the measured extinction spectra in Fig. 1.4(c), which is here defined as $1 - T_{\text{per}}/T_{\text{par}}$, where T_{per} and T_{par} are the transmission values for light with electric field perpendicular and parallel to the nanoribbons, respectively. The plasmonic resonance frequency is shown to be tuned with varying ribbon width. When the actual width of the ribbons is replaced by an effective electrical width, there is a good agreement between the measured plasmon frequency as a function of wavevector and the fitted curve based on the relation described in Eqn. (1.8), as shown in Fig. 1.4(d).

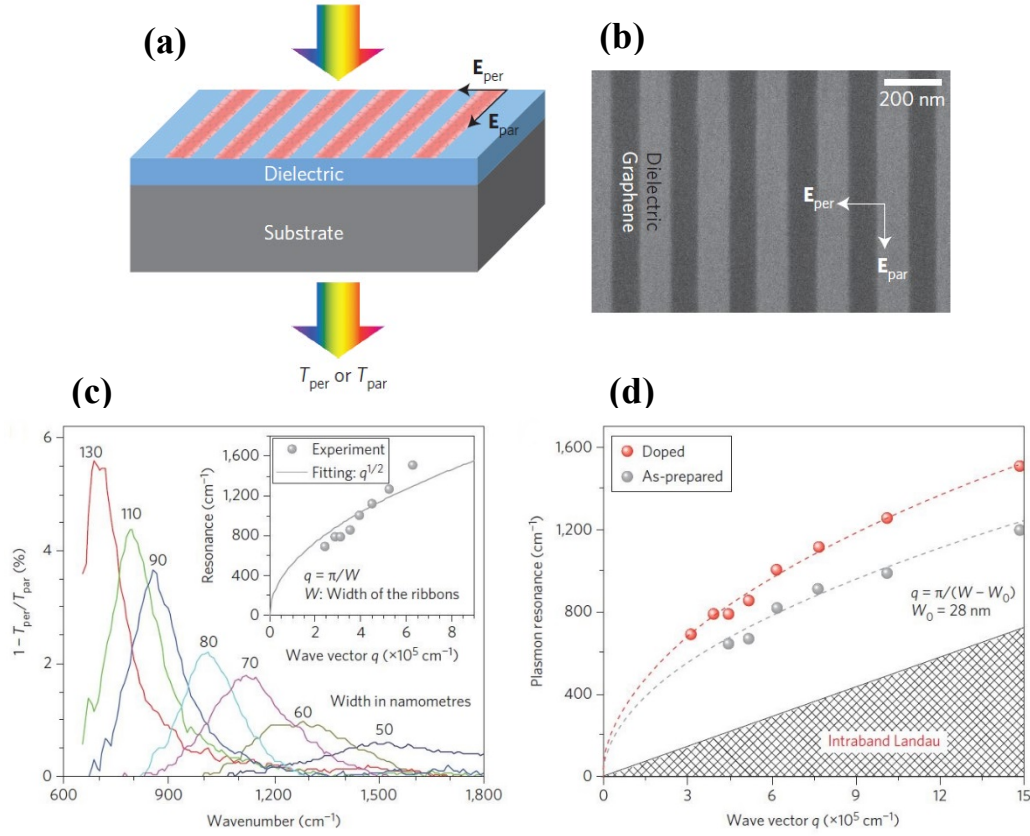


Figure 1.4. Plasmons in graphene nanoribbon array on diamond-like carbon substrate. (a) Schematic of the transmission measurement scheme for graphene nanoribbons. T_{per} and T_{par} correspond to the transmission for light with electric field perpendicular and parallel to the nanoribbons respectively. (b) SEM image of a typical array of graphene nanoribbons with ribbon width of 100 nm. (c) Measured extinction spectra ($1 - T_{\text{per}}/T_{\text{par}}$) of graphene nanoribbon arrays with different ribbon widths. Inset, measured and fitted plasmon resonance frequency as a function of wave vector. (d) Plasmon resonance frequency plotted as a function of wave vector $q = \pi/W_e$, with a corrected ribbon width $W_e = W - W_0$, where W_0 is 28 nm. Reproduced from ref. 40.

Infrared nanoimaging of graphene plasmons. Scanning near-field optical microscopy (SNOM)⁴⁷ has been widely used for the direct imaging of surface plasmon polaritons (SPPs) on metal surfaces, by which characteristics of the plasmons such as

reflection, interference and damping can be elucidated.⁴⁸ Similar techniques have been used for the direct imaging of the infrared graphene plasmons with a scattering-type SNOM.^{49, 50} Figure 1.5 shows an example,⁴⁹ in which the graphene plasmons were launched by illuminating the sharp tip of an atomic force microscope (AFM) with a focused infrared beam (Fig. 1.5(a)). The sharp tip, with a curvature radius of 25 nm, scattered the beam (wavelength: 11.2 μm) and allowed the coupling to SPPs on the graphene. The imaging results are plotted in Fig. 1.5(b-e), showing variations in the near-field amplitude as a function of the tip position. Elongated elliptical patterns were produced by line defects (Fig. 1b). Circular patterns can be observed near the point and circular defects (Fig. 1.5(d)). Furthermore, fringes can be seen at the graphene-SiO₂ interface (Fig. 1.5(b)), SLG and bilayer graphene boundaries (Fig. 1.5(c)) and graphene corners and edges Fig. 1.5(e). The graphene plasmon wavelength was found to be $\sim 200\text{nm}$, which is two orders of magnitude smaller than the free space wavelength.

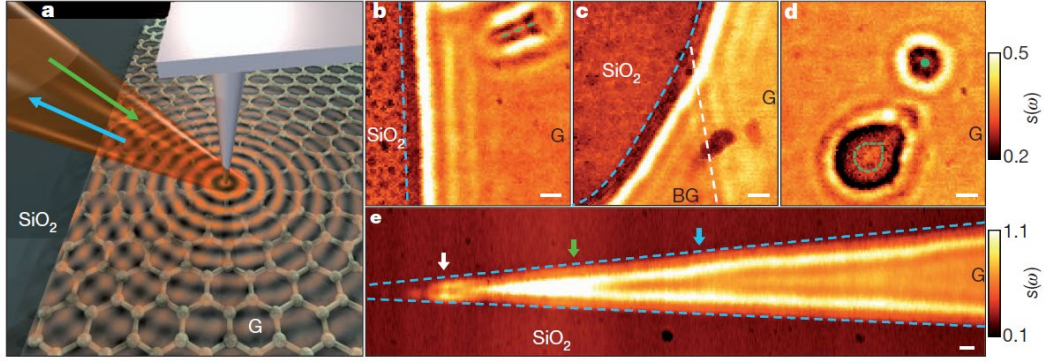


Figure 1.5. Infrared nanoimaging of graphene plasmons. (a) Schematic of an infrared scattering-type SNOM measurement setup for graphene plasmon on SiO₂ substrate. (b-e) Images of infrared graphene plasmon interference patterns (at frequency 892 cm⁻¹) close to graphene edges (blue dashed lines) and defects (green dashed lines and green dot), and at the boundary between single and bilayer graphene (white dashed line). Locations of boundaries and defects were determined from AFM topography taken simultaneously with the nearfield data. Scale bars, 100 nm. Reproduced from ref. 49.

1.3 Graphene for Mid-infrared Photodetectors

The use of graphene for developing high-speed and broadband photodetectors has attracted much interest due to its unique electronic and optical properties. The two properties that are important for photodetectors are as follows. First, graphene possesses a gapless band structure. This enables a broadband optical absorption in graphene over a wide spectral region, including the ultraviolet, visible, infrared and terahertz. Second, graphene exhibits ultrafast carrier dynamics ($\sim$ sub-picosecond carrier lifetime),^{51, 52} which makes it possible to realize high-speed photodetectors. This thesis will focus on graphene photodetectors that operate in the mid-infrared (MIR) regime. In this section, we will first discuss current technologies for MIR photodetectors based on traditional semiconductors. Then we will review some of the basic detection mechanisms that have

been used to realize pure graphene-based photodetectors, as well as the challenges these detectors face. Finally, we will review recent progress in improving the responsivity of graphene photodetectors for MIR detection.

1.3.1 Mid-infrared Photodetection with Traditional Semiconductors

The detection of MIR light, especially those portions of this spectral band that lie within the two atmospheric windows (mid-wave infrared (MWIR): 3-5 μm , long-wave infrared (LWIR): 8-12 μm),⁵³ is highly desired for a wide range of applications that include biosensing,^{22, 54} security,⁵⁵ IR spectroscopy⁵⁶ and thermal imaging.⁵⁷⁻⁵⁹ Commercially available MIR photodetectors are mainly based on traditional narrow-bandgap semiconductors such as HgCdTe (MCT),^{2, 3} indium antimonide (InSb),⁴ lead selenide (PbSe),⁵ and other technologies such as quantum wells⁶ and type-II superlattices.⁷⁻⁹ However, they are often quite expensive and bulky due to their complex growth/fabrication processes and cryogenic operation. Colloidal quantum dots (CQDs) have been explored due to their high absorption efficiency and ease of fabrication.⁶⁰⁻⁶² So far, only a few works^{63, 64} have reported MIR photodetection based on CQDs because most of the known CQDs have relatively large bandgaps that do not allow absorption in the MIR. While bolometers have been employed for room temperature infrared detection, their application is ultimately limited by their slow response, with typical rise time of several milliseconds.⁶⁵ In addition, most of the current semiconductor materials used for MIR detection are toxic and hazardous to environment.

1.3.2 Graphene-based Photodetectors and Their Challenges

In recent years, there has been much interest in the development of new materials for high-performance, low-cost, and environmentally-friendly MIR photodetectors. Two-dimensional (2D) materials provide a promising platform to achieve these goals for

several reasons. First, 2D materials represent a drastic reduction in the volume of the active (photosensitive) material. A major challenge for achieving room temperature detection of MIR light lies in the large detector noise associated with the thermal generation of charge carriers in small-bandgap semiconductor materials.¹⁰ One way to mitigate the thermal generation is to reduce the volume of the active material.¹⁰ Second, a few 2D materials (*i.e.* graphene²⁴, PtSe₂⁶⁶, PdSe₂⁶⁷, black phosphorus⁶⁸, *etc.*) have already shown great potential for MIR detection. Some of these materials, such as graphene and PtSe₂, have been reported to show MIR response only when they are in 2D-forms (*i.e.* monolayer or bilayer) because of their unique band structures. Third, some MIR sensitive 2D materials, including graphene, are non-toxic and environmentally-friendly. However, so far, the fabrication of most high-quality 2D materials other than graphene is primarily based on manual exfoliation from pure crystals, and the growth of uniform 2D films over large areas is still very challenging. In contrast, wafer-scale graphene has been grown by chemical vapor deposition (CVD)^{69, 70}, and shows excellent crystal quality and physical properties that are comparable to mechanically-exfoliated graphene samples. Based on different mechanisms, graphene photodetectors have been demonstrated in a broad spectral range from the visible to the terahertz wavelength regimes,⁷¹⁻⁷⁵ and with bandwidths up to 40 GHz for optical communications.^{72, 76} Below, we will review some of the basic mechanisms that have been employed for the realisation of graphene photodetectors in field effect transistor configurations.

Photovoltaic effect. For photodetectors operating by the photovoltaic effect, photogenerated charge carriers are separated by built-in electric fields.⁷⁷⁻⁷⁹ These built-in electric fields originate from the fact that the graphene doping can be made to vary as a function of position by local chemical doping,⁸⁰ by local electrostatic gating,^{77, 81} or by the metallic doping effect. The later arises from the work-function difference between the

contacting metal and graphene.^{77-79, 82} Among these approaches, metallic doping is relatively easy to implement in practice. One of the early experimental demonstrations based on this effect was a metal-graphene-metal (MGM) photodetector with asymmetric metal contacts as shown in Fig. 1.6.⁷⁶ As the photocurrent occurs only in the submicrometre-wide region near the metal-graphene interface, inter-digitated electrodes were employed to increase the effective photodetection area (Fig. 1.6(a)). An asymmetric metallization scheme with palladium (Pd) source electrodes and titanium (Ti) drain electrodes was employed to enable zero-bias operation. Due to the fact that the doping under the two types of electrodes are different, the photocurrent near both electrodes can flow in the same direction, facilitating the collection of photocurrent at zero source-drain voltage. Upon illumination at a telecommunication wavelength of 1.55 μm , photogenerated electron-hole pairs were collected under the built-in electric fields near both source and drain electrodes, which constituted the photocurrent. A responsivity of 1.5 mA/W was obtained under zero-bias for incident powers up to around 10 dBm (Fig. 1.6(b)). Due to the ultrafast carrier dynamics in graphene, the MGM graphene detector showed a relatively high 3-dB bandwidth of ~ 16 GHz (Fig. 1.6(c)). The device was also deployed in a 10 Gbit s⁻¹ optical data link, showing an error-free data recovery with a completely open eye in the eye-diagram (inset of Fig. 1.6(c)).

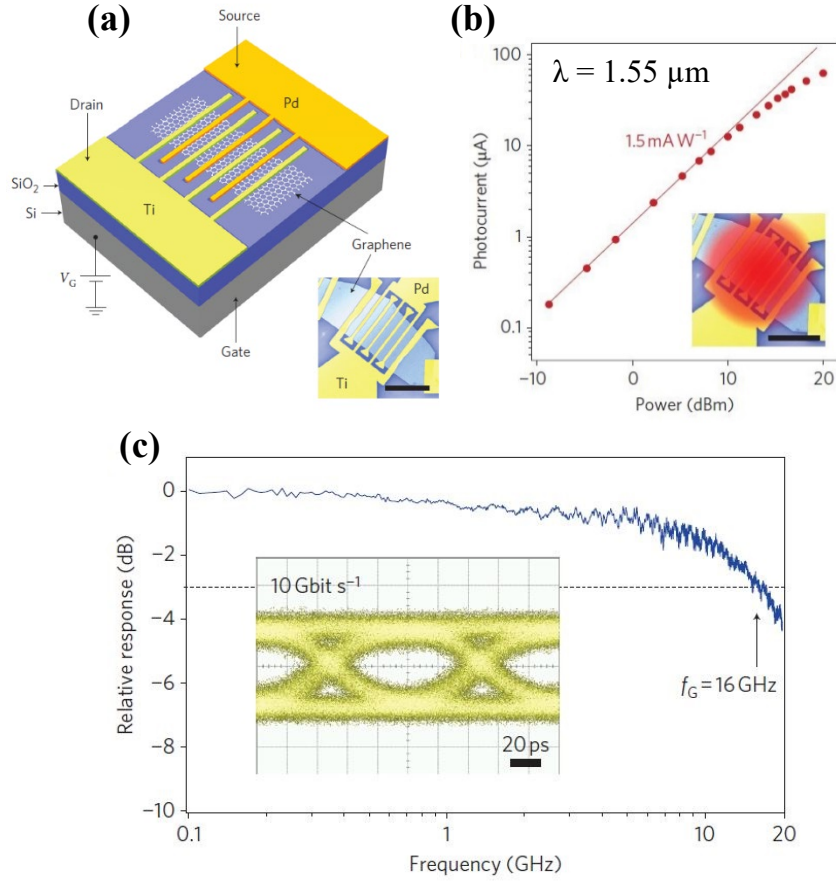


Figure 1.6. Photovoltaic effect-based metal-graphene-metal (MGM) photodetectors with asymmetrically inter-digitated electrodes. (a) Schematic illustration of the MGM photodetector. Bottom right: SEM image of the MGM photodetector. Scale bar, 5 μm . (b) Measured photocurrent as a function of the incident power under a gate voltage of -15 V and zero source-drain bias. The responsivity before saturation is 1.5 mA/W. Inset: schematic of the device under illumination. Scale bar, 5 μm . (c) Relative photoresponse as a function of the modulation frequency of excitation light. Inset: receiver eye-diagram obtained by deploying the MGM photodetector in a 10 Gbit s⁻¹ optical data link. Reproduced from ref. 76.

Photo-thermoelectric (PTE) effect. It has been reported that hot-carrier-assisted transport can play an important role in the optoelectronic response of graphene.^{15, 83-85} Due to the strong electron-electron interactions,⁸⁶ the photoexcited electron-hole pairs

will give rise to heating of carriers in graphene within an ultra-short timescale (~ 10 -50 fs).⁸⁷⁻⁹⁰ The hot carriers remain at a temperature (T_e) higher than that of the lattice for several picoseconds and slowly reach an equilibrium with the lattice on a nanosecond scale via scattering processes between the charge carriers and acoustic phonons.^{91, 92} In the PTE effect, the light-induced temperature difference associated with hot-carrier excitation results in a voltage via Seebeck effect. This voltage is termed the thermoelectric voltage (V_{PTE}). The thermoelectric voltage (V_{PTE}) can be calculated by integrating the local electric field along the channel generated by a photo-induced temperature gradient with a spatially varying Seebeck coefficient (S): $V_{PTE} = \int S \cdot \nabla T_e dx$. Graphene photodetectors based on PTE effect have been demonstrated, with the temperature gradient being generated by light absorption by the graphene,^{15, 93} by light-excited graphene plasmons⁹⁴ or by light-excited substrate phonons.¹⁶

Figure 1.7(a-c) show a work in which a dual-gated graphene p-n junction device was reported to exhibit photoresponse to a laser with an operating wavelength of 850 nm.¹⁵ The p-n junctions are controlled by a global bottom gate and by a local top gate as shown in Fig. 1.7(a). Tuning the bottom and top gate voltages respectively permit independent control of the carrier density of electrons and holes in each region (region 1 and 2 as indicated in Fig. 1.7(a)), resulting in the formation of various kind of junctions. Upon light excitation, electron-hole pairs decay rapidly into a thermal distribution of hot carriers with a local temperature that is higher than the lattice temperature. The difference between the temperature of the laser-illuminated region and the temperature of its surroundings gives rise to a thermoelectric current, the magnitude and sign of which depend on the carrier type and densities. In uniformly doped graphene, the thermal current is isotropic and the net thermoelectric current is zero. On the other hand, when a p-n junction is formed in graphene, the symmetry of the thermal current due to the electrons

and holes is broken. This leads to a non-zero net thermoelectric current. The magnitude and sign of the photovoltage caused by this current are determined by the Seebeck coefficient and temperature gradient in both the p-type and n-typed doped graphene regions. Figure 1.7(b) shows the photocurrent map of the device measured at temperature of 40 K for an optical power of 50 μ W under zero source-drain bias. A p-n junction is formed in the graphene along the edge of the top gate contact for $V_{BG} = -5$ V and $V_{TG} = 2$ V. The map shows a strong photocurrent at the interface of the p-n junction, with a maximum responsivity of 5 mA/W. Unlike the photovoltaic effect, the PTE induced photocurrent displays a six-fold photovoltage pattern as a function of the bottom and top gate voltages (Fig. 1.7(c)). The sign reversals that occur in the bipolar p-n junctions and in the unipolar p^+p or nn^- junctions are due to the sign change in the transconductance and the electric field respectively. These provide strong evidence of the PTE effect playing a dominant role to the photoresponse in graphene devices. Figure 1.7(d-e) show a similar graphene photodetector based on PTE effect of graphene p-n junctions.⁹³ To optimize the photovoltage collection for incident radiation with a Gaussian profile, several p-n junctions were created and connected in series. The photovoltages were collected in the radial direction, using a nanopatterned electrolyte gating technique (Fig. 1.7(d)). Every other graphene segment was covered with a PMMA mask so that each segment was p- or n-doped in an alternating fashion by the patterned top electrolyte gate (via PMMA masking) and the global bottom gate. In doing so, photovoltages of neighbouring p-n junctions point in opposite directions (Seebeck coefficient has opposite signs) and all the photovoltages can be added up to give the total photovoltage. This device geometry facilitates the detection for an incident Gaussian radiation because the photovoltage is collected in the direction of temperature gradient, i.e. in the radial direction. The

maximum responsivity of this device was 26.2 mV/W at $\lambda = 8.58 \mu\text{m}$, when eight voltage segments were included in the device, as can be seen in Fig. 1.7(e).

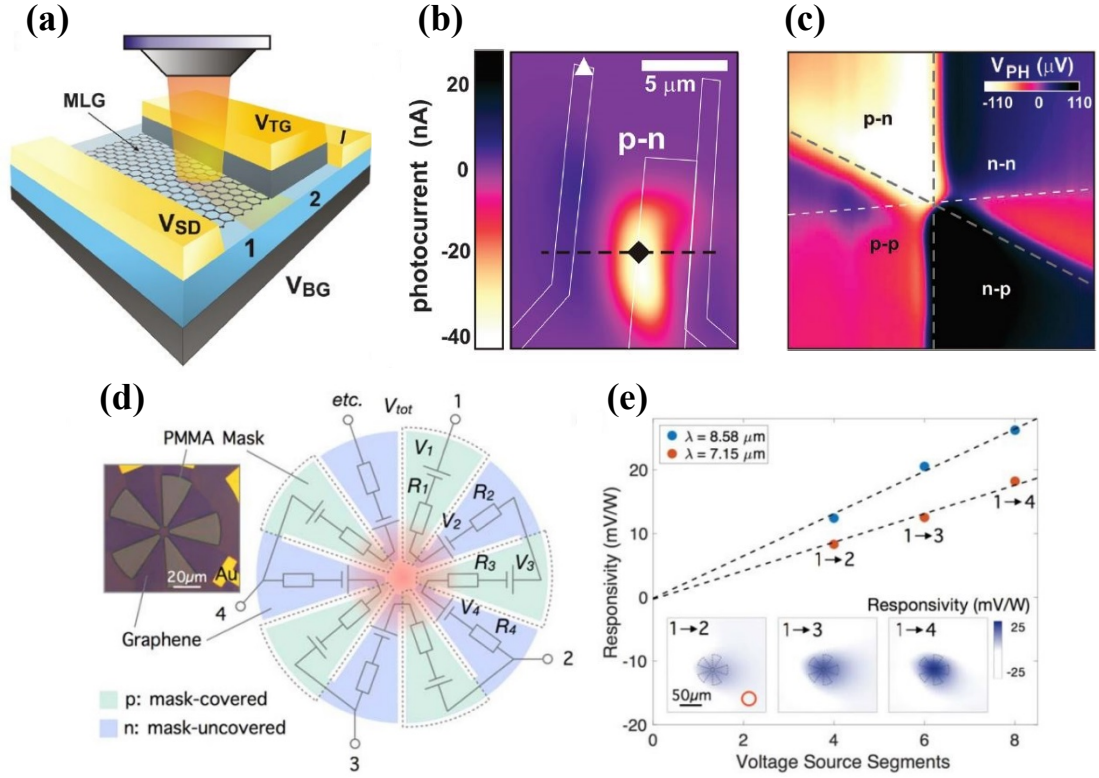


Figure 1.7. Photo-thermoelectric (PTE) effect induced photoresponse in graphene p-n junction devices. (a) Experimental schematic of a dual-gated graphene device. Reproduced from ref. 15. (b) Photocurrent map of the device measured at temperature of 40 K for an optical power of 50 μ W. $V_{BG} = -5$ V, $V_{TG} = 2$ V, $V_{DS} = 0$ V. Reproduced from ref. 15. (c) Photovoltage as a function of V_{BG} and V_{TG} at $T = 40$ K, measured at the location marked by the triangle in (b). Gray dashed lines are lines of high resistance from transport characteristics. The white dashed line indicates equal carrier densities in the two regions of the doped graphene. Reproduced from ref. 15. (d) Equivalent circuit diagram and optical image of a graphene thermopile design. Graphene is etched into a circular channel with a meandering shape, with each segment being p- or n-doped in an alternating fashion. Reproduced from ref. 93. (e) Responsivity of the thermopile measured at the centre of the device as a function of the number of voltage source segments included in the circuit at $\lambda = 8.58$ μ m and $\lambda = 7.15$ μ m. Inset: Responsivity spatial mappings measured at $\lambda = 8.58$ μ m, with 4, 6 and 8 voltage source segments included in the circuit, respectively. The red circle indicates the FWHM of the laser spot which is ~ 30 μ m. Reproduced from ref. 93.

The temperature difference can also be induced by the excitation of graphene plasmons, as is shown in Fig. 1.8(a) in a graphene photoconductor with graphene-disk plasmonic resonators (GDPRs) connected by quasi-1D graphene nanoribbons (GNRs).⁹⁴ Following optical excitation, highly confined graphene plasmons in the GDPRs decay rapidly and lead to hot charge carriers which thermalize at an elevated temperature within tens of femtoseconds. The hot carriers then relax to a lower temperature within a few picoseconds via lattice vibration and eventually evolve towards ambient temperature by heat dissipation through the surround materials. The GDPRs serve as the source of hot carriers as they support plasmonic resonance upon light illumination. The conductance of the channel is dominated by the quasi-1D GNRs as they are much narrower than the GDPRs. In addition, the edge roughness and charge impurities in the GNRs resulting from the lithographic process introduce disordered localized states. The localized potential barriers associated with these disordered states produce a drastic temperature dependence of the charge carrier transport (large thermoelectric coefficient) and enable the detection of hot carriers upon excitation of plasmonic resonance. Figure 1.8(b-e) illustrate two carrier transport mechanisms whose occurrence depends on whether resonant plasmons are excited. Without plasmon excitation, carriers at a moderately-elevated temperature transport by nearest-neighbour hopping (NNH, Fig. 1.8(e)) between neighbouring localized states, leading to a small thermal smearing of the carrier distribution (Fig. 1.8(b)). The excitation of plasmonic resonance produces hot carriers at elevated temperature (thermal carrier excitation (TCE), Fig. 1.8(d)), resulting in greater thermal smearing of the carrier distributions, which facilitates their transport through the potential barriers (Fig. 1.8(c)). It was argued that the latter mechanism was prevalent in the measurements.⁹⁴ Photocurrent was measured for laser excitation at a wavelength of 12.2 μm as a function of temperature with incident powers of 230 μW (blue symbols) and 660

μW (red symbols), as shown in Fig. 1.8(f). A photoresponsivity of 16 mA/W was obtained at room temperature.

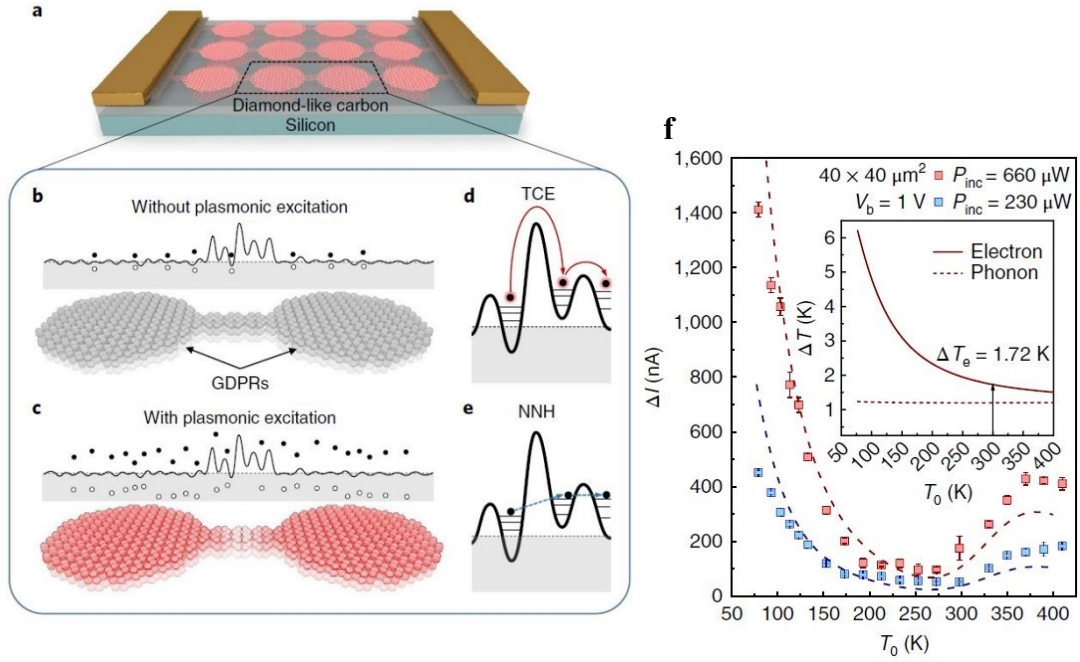


Figure 1.8. Plasmon-assisted PTE photoresponse in a graphene photoconductor. (a) Schematic of the device, consisting of graphene-disk plasmonic resonators (GDPRs, red circles) connected by quasi-1D graphene nanoribbons (GNRs). (b-c) Cartoon illustration of the disorder potential (solid curve) around the chemical potential and carrier thermal smearing before (b) and after (c) photoexcitation at room temperature. (d-e) Cartoon illustration of thermal-carrier excitation (TCE) transport (d), in which electrons with higher thermal energy can overcome the localized potential barriers and nearest-neighbour hopping (NNH) transport (e), in which thermalized electrons evanescently hop between neighbouring localized states under the driving external electric field. (f) Photocurrent measured as a function of temperature under $12.2 \mu\text{m}$ excitation with incident power of $230 \mu\text{W}$ (blue symbols) and $660 \mu\text{W}$ (red symbols). Dashed curves: calculated photocurrent. Inset: calculated electron (solid curve) and phonon (dashed curve) temperature increases under incident power of $660 \mu\text{W}$. The incident light is polarized parallel to the GNRs. Reproduce from ref. 94.

It has also been demonstrated that temperature gradients in graphene can be induced through the excitation of substrate phonons.¹⁶ Figure 1.9 shows such an example in which phonon-mediated PTE photoresponse was observed in a graphene photoconductor on a polar (SiO₂) substrate. A photoresponsivity of around 58.5 nA/W was measured close to the edges of the electrodes at a frequency of 1080 cm⁻¹ (wavelength of 9.26 μm) for incident light polarized parallel to the edge of the contact, as shown in Fig. 1.9(a, c). This photocurrent generation is based on an indirect mechanism, where the incident light is absorbed by the substrate phonons (transverse (TO) phonon band of SiO₂ is centred around 1065.5 cm⁻¹), leading to local heating of the charge carriers in graphene which generates a PTE photovoltage and causes a current flow. That this mechanism occurs was supported by the fact that the device shows photocurrent across a large area, even when the light spot is outside the graphene region (Fig. 1.9(a)). This mechanism is different from PTE photoresponse reported near metallic contacts⁹⁵ or p-n junctions^{15, 81} in the visible and near-infrared regions. When the excitation wavelength is 1390 cm⁻¹, i.e. far from the substrate TO phonon band, the device shows photocurrent in a much smaller area close to the edges of contacts (Fig. 1.9(b)), since heating of the graphene charge carriers is caused by direct light absorption in graphene and is limited by the laser spot size. The PTE photocurrent generated by direct light absorption in graphene was greatly enhanced for incident light polarized perpendicular to the edge of the electrodes, when substrate surface phonons were excited (close to frequency of 1170 cm⁻¹, red symbol in Fig. 1.9(d)), producing a strongly enhanced electric fields and large absorption in graphene.

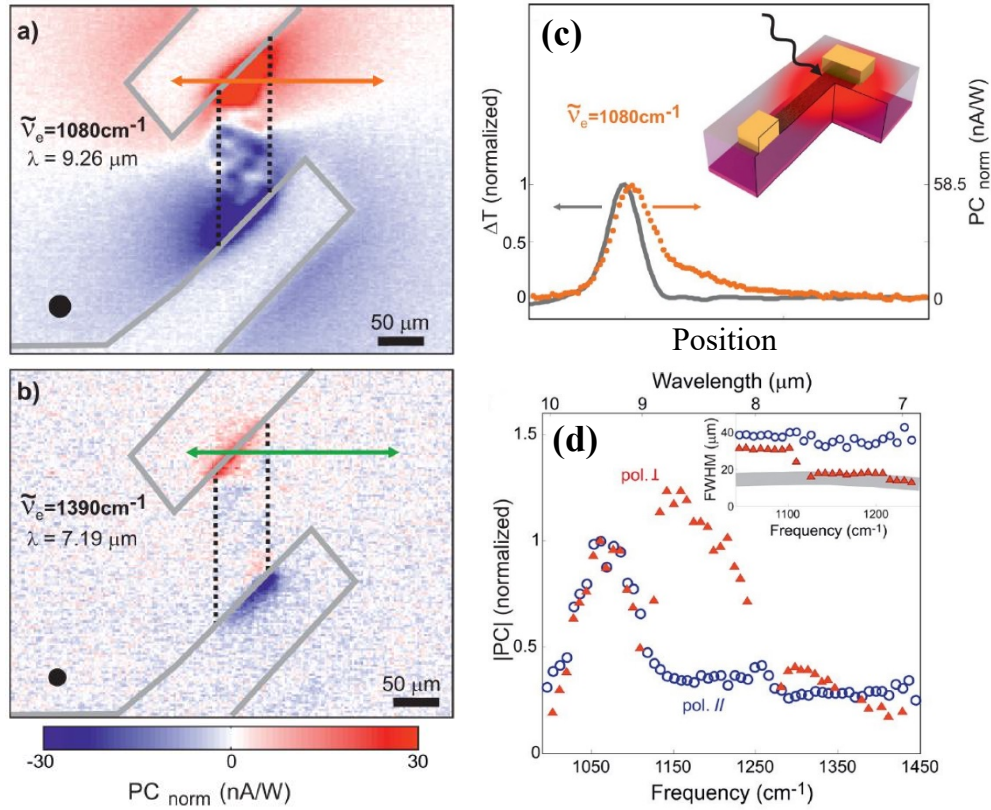


Figure 1.9. Phonon-mediated PTE photoresponse in a graphene photoconductor on a polar substrate. (a-b) Photocurrent maps upon excitation with wavelength $\lambda = 9.26 \mu\text{m}$ (1080 cm^{-1}) (a), and $\lambda = 7.19 \mu\text{m}$ (1390 cm^{-1}) (b). The gray lines depict the structure of contacts. The black dotted lines indicate the graphene position. The black circle at the bottom left represents the beam spot size (FWHM $22 \mu\text{m}$ (a) and $14 \mu\text{m}$ (b)). The light polarization is parallel to the contacts. (c) Photocurrent (orange curve) at 1080 cm^{-1} along the orange arrow in (a). The gray curve represents the laser spot size obtained from the spatial derivative of optical transmission measurement. (d) Photocurrent spectra for incident light polarized perpendicular (red triangles) and parallel (blue circles) to the contact edge. Inset: corresponding FWHM of the photocurrent signal. The gray line indicates the width of the laser spot. Reproduced from ref. 16.

Pyroresistive effect. Graphene can be combined with pyroelectric materials, where changes in spontaneous polarization can produce strong doping in graphene. This effect could be used for developing uncooled MIR photodetectors.^{96, 97} The basic

operation principle of photodetectors based on this effect is as follows. Light absorption induced heating and temperature increase in the pyroelectric material produce a variation of its spontaneous polarization due to the pyroelectric effect. The bound (polarization) surface charges of the pyroelectric material induce free charges in the graphene, resulting in a change of the resistance of the graphene. This phenomenon can be termed the pyroresistive effect. Detectors based on the pyroresistive effect have characteristics that are somewhere between those of pyroelectric detectors and bolometers as they use pyroelectricity of the pyroelectric material to induce doping (as in pyrodetectors) while read-out is based on resistance change in graphene (as in bolometers). Figure 1.10 shows a room-temperature MIR photodetector that combines a dual-gated SLG amplifier with a pyroelectric material.⁹⁶ The device architecture and the corresponding electrical model is shown in Fig. 1.10(a). The device consists of a graphene field-effect transistor on a pyroelectric substrate (500 μm -thick z-cut lithium niobate crystal, LiNbO_3). A 10 nm-thick Al_2O_3 dielectric layer isolates the graphene from an H-shaped floating Au structure. The lateral pads of the floating Au structure are placed in direct contact with the substrate. The floating metallic structure is designed to concentrate the pyroelectric charges on the top-gate capacitor of the graphene channel, leading to a temperature coefficient of the resistance of up to $900\% \text{K}^{-1}$. The gain of the SLG amplifier is controlled by the geometric ratio of the areas of the capacitors C_3 and C_2 , which is a result of the conservation of charge. Consequently, the pyroelectric response of the LiNbO_3 crystal is transduced with high gain (up to 200) into resistivity modulation for graphene. The modulation of the channel drain current under MIR radiation at 1100 cm^{-1} ($\sim 9\text{ }\mu\text{m}$) is shown in Fig. 1.10(b) over nine ON/OFF illumination cycles. A responsivity of 0.27 mA/W is obtained under a source-drain bias voltage of 10 mV . Figure 1.10(c) shows the photocurrent maps of the device measured by chopping the beam at different frequencies. The two peaks in the

photocurrent map become progressively resolved as the frequency increases and match the location of the lateral pads when the frequency is above 500 Hz. This trend can be understood by the fact that at higher frequencies, there is less time for the heat to laterally spread from the illuminated spot. This means that the temperature increase in the substrate at locations away from the pads contributes little to the charge doping of the graphene channel.

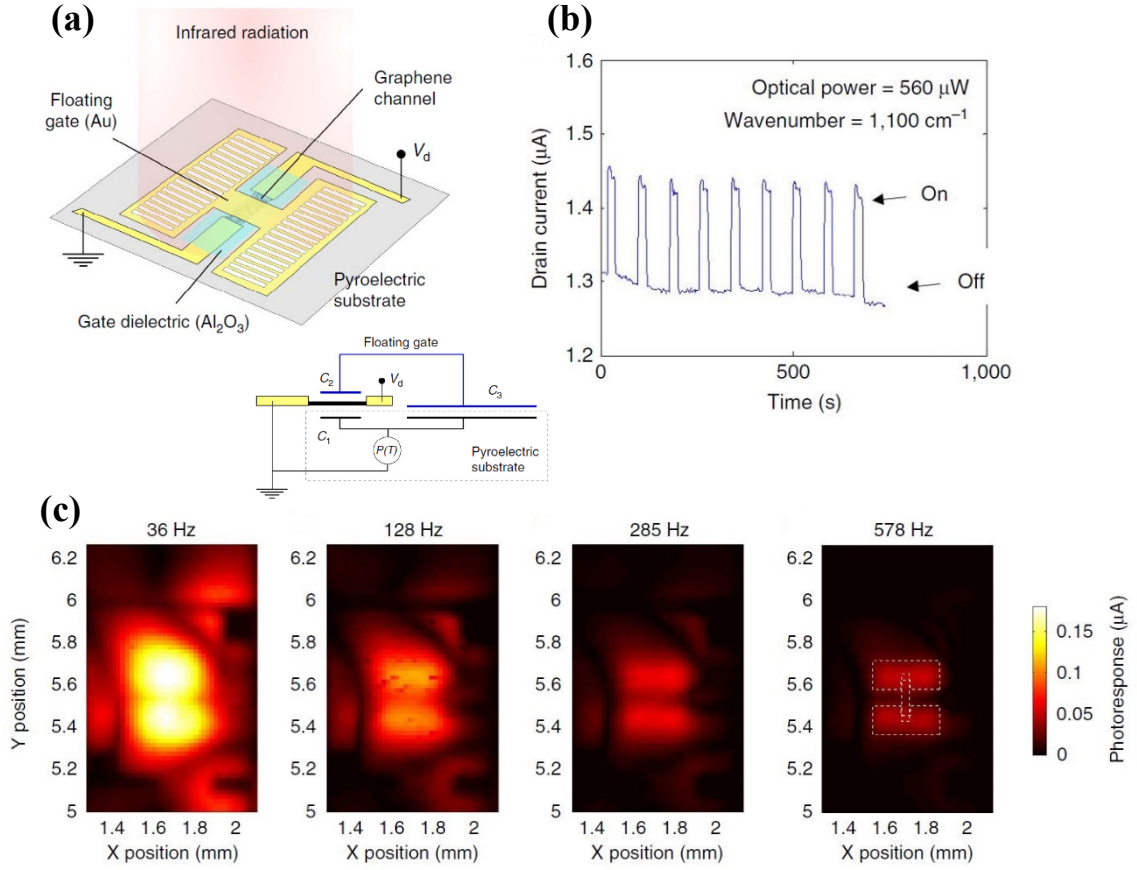


Figure 1.10. Graphene photodetector based on pyroresistive effect. (a) Schematic of the device with a dual-gated SLG amplifier on a pyroelectric substrate (500 μm -thick z-cut lithium niobate crystal, LiNbO_3). A floating metallic structure is fabricated on top of the Al_2O_3 coated graphene channel and the substrate to concentrate the pyroelectric charges on the top-gated graphene channel. Bottom right shows the corresponding electrical model. (b) Photoresponse of the device under MIR illumination at 1100 cm^{-1} ($\sim 9 \mu\text{m}$) with a source-drain bias voltage of 10 mV. (c) Photocurrent maps measured with illumination power of 1.8 mW at 1100 cm^{-1} for different frequencies. Reproduced from ref. 96.

Despite the demonstrations of graphene photodetectors based on the various detection mechanisms discussed above, a challenge that remains to be addressed is the relatively low responsivity of these photodetectors ($\sim$ several mA/W). This is mainly due to the intrinsically low optical absorption in graphene ($\sim 2.3\%$) and the fact that the area

over which photodetection occurs is small ⁷⁹ as a result of the ultrashort carrier lifetime ($\sim$ ps) in graphene. This means that MIR graphene photodetectors, especially those operating at room temperature, can have low signal-to-noise ratios.

1.3.3 Responsivity Enhancement for Mid-infrared Photodetection

Several strategies for enhancing the responsivity of graphene photodetectors have been demonstrated. In the following paragraphs, we will discuss these approaches. Band structure engineering and the introducing of trapping centres in graphene have been shown to enhance the optical absorption and photoconductive gain. For example, Zhang et al demonstrated a MIR graphene photodetector comprising a graphene quantum dot (GQD) array (Fig. 1.11), with a responsivity of 0.4 A/W under a source-drain bias voltage of 20 mV.⁹⁸ By patterning the graphene into GQD structures (Fig. 1.11 (a)), a midgap states band (MGB) was introduced and a bandgap was created due to quantum confinement effects. Figure 1.11(b) depicts the band diagram of unpatterned single layer graphene (left panel) and GQD including MGB (right panel). In unpatterned single layer graphene, the lifetime of photogenerated electrons is usually very short due to the high interband and intraband recombination rates. In a GQD structure, on the other hand, the introduced MGB allows carrier multiplication to occur which leads to generation of secondary electrons, thereby increasing the overall electron generation efficiency. In addition, the existence of the MGB effectively mitigates electron-phonon scattering,⁹⁹ as the generated electrons can be trapped in the MGB. The efficient electron generation and subsequent trapping in the MGB give rise to a very high photoconductive gain, which enables the photodetection in the MIR (Fig. 1.11(c)). However, the response time of the detector was limited by the long lifetime of the trapped electrons ($\sim$ tens of seconds) as can be seen from Fig. 1.11(c). Also, the detector operation was restricted to low temperature ($\sim$ 10 K)

because the responsivity is smaller at higher temperatures as a result of shortened carrier lifetime.

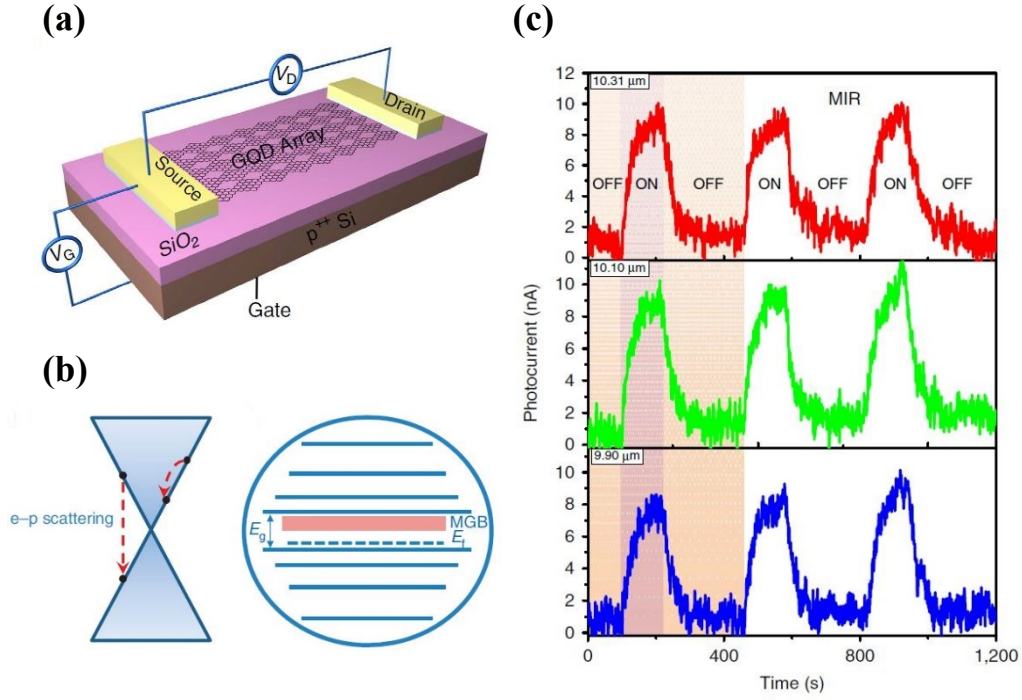


Figure 1.11. Band structure engineering in a graphene quantum dot photodetector. (a) Schematic of the graphene quantum dots photodetector. (b) Band structure diagram of a pure graphene sheet (left) and a graphene quantum dot array (right) with midgap states band (red shadowed region). Red dashed arrows indicate the interband and intraband electron-phonon scattering. (c) Time-dependent photocurrent measurements in the mid-infrared region ($\sim 10 \mu\text{m}$). Reproduced from ref. 98.

Photogating effects have been investigated for enhancing the responsivity (to be $> 1 \text{ AW}^{-1}$) of graphene photodetectors at room temperature by either coupling graphene with narrow-bandgap semiconductor nanoparticles,¹⁰⁰ or by introducing a tunneling barrier in a graphene double-layer heterostructure.¹⁰¹ By hybridizing graphene with a

novel narrow-bandgap semiconductor, titanium sesquioxide (Ti_2O_3) with a bandgap of 0.09 eV, room temperature MIR photodetectors with high responsivity were demonstrated (Fig. 1.12(a)).¹⁰⁰ The Ti_2O_3 nanoparticles serve as MIR light absorbers and generate electron-hole pairs upon light illumination. The photo-generated electrons are trapped in the Ti_2O_3 nanoparticles while the holes are transferred into the graphene channel (Fig. 1.12(b)), leading to a change of the channel conductance and thus photodetection. In addition, the photogenerated electrons were trapped in the nanoparticles for a long time ($\sim$ several milliseconds), leading to a photoconductive gain and thus enhanced responsivity. Photocurrents were measured under laser illumination at a wavelength of 10 μm for hybrid graphene/ Ti_2O_3 photodetectors with monolayer-, bilayer- and trilayer-graphene (Fig. 1.12(c)). A maximum responsivity of ~ 300 A/W was obtained under source-drain voltage of 2 mV for hybrid trilayer graphene/ Ti_2O_3 photodetector. Unfortunately, due to the existence of charge trap-states in the graphene-nanoparticle interface, the detector showed a slow time response with measured rise and fall times of 1.2 ms and 2.6 ms respectively. (Fig. 1.12(c)). The photogating effect was also employed in a graphene double-layer heterostructure with a tunneling barrier (Fig. 1.12(d)).¹⁰¹ The detector was a phototransistor consisting of two graphene layers sandwiching a thin tunneling barrier (~ 6 nm thick intrinsic silicon layer), as shown in Fig. 1.12(d). The two graphene layers had different doping levels, with the top graphene layer being more heavily p-doped than the bottom graphene layer. This resulted in an energy band in the tunneling barrier that was tilted toward the bottom graphene layer as a result of the equilibration of the Fermi level (Fig. 1.12(e)). Under optical illumination, photoexcited electrons in the top graphene layer could tunnel through the barrier to the bottom layer. As a result, photoexcited holes were accumulated in the top graphene layer, resulting in a strong photogating effect on the bottom graphene channel layer as this is

very sensitive to external electrostatic perturbation. Figure 1.12(f) shows the measured photocurrent under different illuminating powers with excitation wavelength of 3.2 μm , exhibiting efficient MWIR photodetection at room temperature. The device showed a maximum responsivity of around 1.1 A/W under source-drain bias voltage of 1.5 V in the MWIR at $\lambda = 3.2 \mu\text{m}$, which is comparable to the state-of-the-art MWIR detectors operating at room temperature. However, like other photodetectors that rely on photogating effect, the bandwidth of the detector was limited to 10 – 1000 Hz due to the long carrier trapping time caused by the charge trap states in the tunneling barrier.

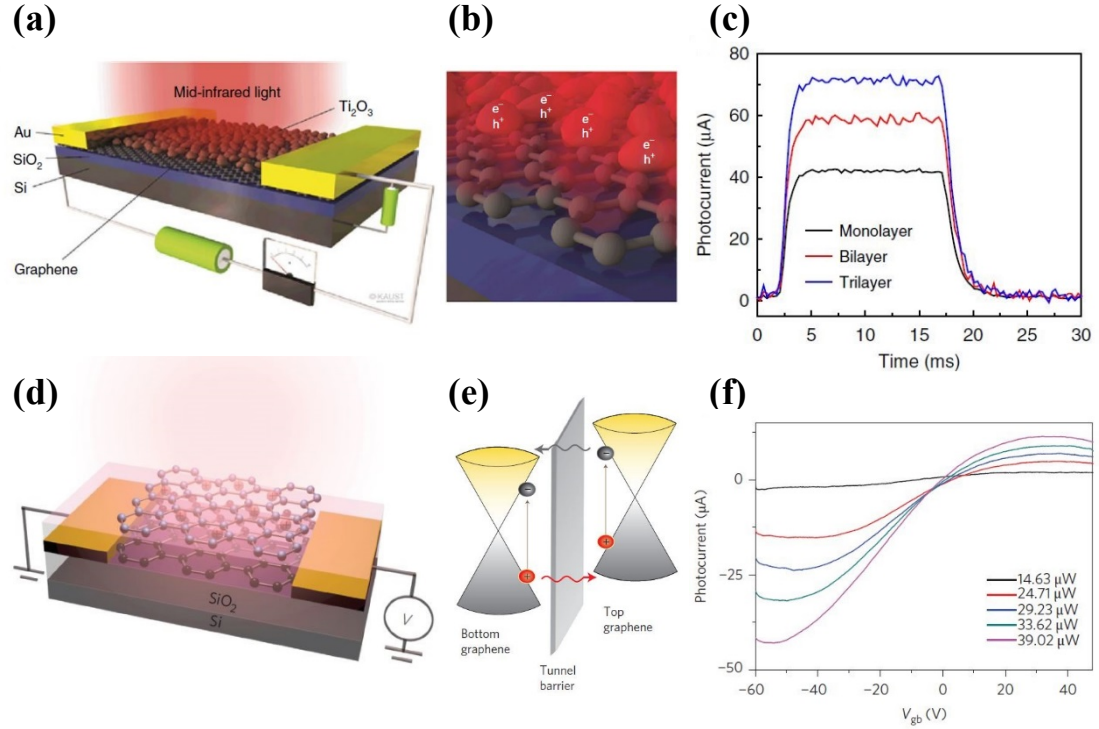


Figure 1.12. Photogating effect for responsivity enhancement in MIR graphene detectors.

(a) Schematic of a hybrid graphene/Ti₂O₃ nanoparticle photodetector. Reproduced from ref. 100.

(b) Illustration of the charge transfer process occurring at the graphene/Ti₂O₃ interface. Reproduced from ref. 100.

(c) Time-dependent photocurrent of the hybrid graphene/TiO₂ photodetector with monolayer, bilayer and trilayer graphene, under light illumination at $\lambda = 10 \mu\text{m}$ with a power density of 2 mW/cm^2 . The source-drain bias voltage and gate voltage are fixed at 2 mV and 80 V respectively. Reproduced from ref. 100.

(d) Schematic of a graphene double-layer heterostructure photodetector. Reproduced from ref. 101.

(e) Schematic of band diagram of the graphene double-layer heterostructure photodetector and photoexcited carrier transport under light illumination. Reproduced from ref. 101.

(f) Gate-dependent photocurrent under different illumination powers with excitation wavelength at $3.2 \mu\text{m}$. Source-drain bias voltage is kept at 1.5 V. Reproduced from ref. 101.

It has been shown that the responsivities of detectors based on the PTE effect assisted by graphene plasmons can be enhanced by engineering an asymmetric electronic

environment of the generated hot carriers on the graphene. For example, Fig. 1.13(a) shows a photodetector in which half of the graphene channel was patterned with an hexagonal array of holes.¹⁰² Upon illumination, graphene plasmons were selectively excited in the patterned section of the graphene, leading to an asymmetric generation of hot-carriers across the channel. This resulted in an enhanced temperature gradient across the channel and thereby yielded an enhanced PTE voltage. Figure 1.13(b) shows the simulated temperature distribution of the graphene channel at a source-drain bias voltage of 0.9 V, for illumination at wavelength of 8.15 μm with an incident power of 153 nW, revealing a temperature gradient of 4.7 K across the channel (upper panel). This temperature gradient yielded a PTE voltage of ~ 0.44 mV (Fig. 1.13, bottom panel). A strong room temperature PTE photoresponse was demonstrated for broadband LWIR illumination (wavelength: 8 – 12 μm), with a measured maximum responsivity of 2900 V/W at a source-drain bias voltage of 0.9 V (Fig. 1.13(c), red curve). Its response to a temporally modulated optical signal was not measured. Instead, its response to a temporally modulated electrical bias signal (under constant LWIR illumination) was measured and a response time of ~ 100 ns was found.

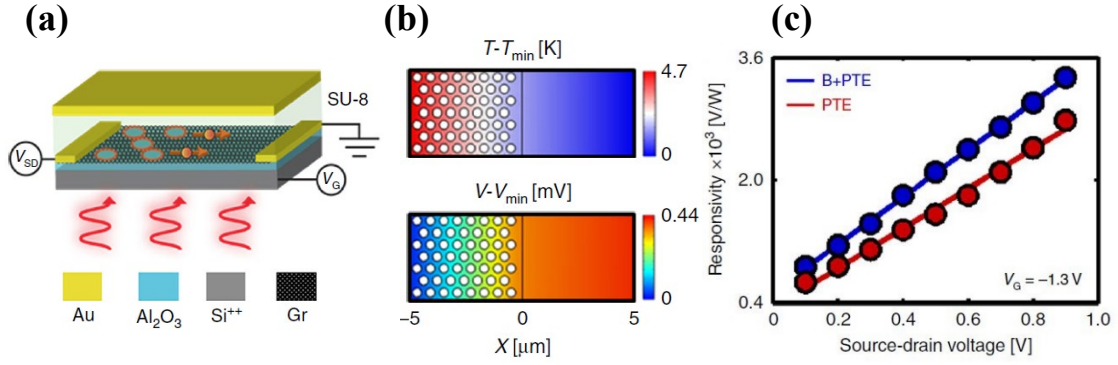


Figure 1.13. Asymmetric plasmon-assisted PTE effect for responsivity enhancement of graphene photodetector. (a) Schematic of the device architecture with an asymmetrically nanopatterned graphene. (b) The simulated temperature (top) and potential (bottom) profiles of the graphene detector at graphene Fermi level $E_F = -0.85$ eV, illumination wavelength $\lambda = 8.15$ μm and source-drain bias $V_{SD} = 0.9$ V. (c) Measured responsivity as a function of source-drain bias voltage for gate voltage, $V_G = -1.3$ V. Blue curve corresponds to the total responsivity. Red curve corresponds to the responsivity due to the PTE contribution from asymmetric hot-carrier generation. Reproduced from ref. 102.

It has also been shown that plasmonic nanoantennas²⁴ and engineered electrodes¹⁰³ improve the detector responsivity while maintaining high operation speed by simultaneously enhancing the optical absorption and carrier collection efficiency in graphene. Figure 1.14(a) shows a device that employs plasmonic end-to-end linear antennas to enhance both the optical absorption and carrier collection efficiency in graphene. The linear antennas collect the incident light and concentrate it within the narrow gaps (~ 100 nm) between adjacent antennas, producing enhanced electric field intensity (Fig. 1.14(b)) and thus enhanced optical absorption by the graphene. The photogenerated carriers are then efficiently collected by the antennas as photocurrent. In

this device, a responsivity of 0.4 V/W was measured at room temperature at $\lambda = 4.45 \mu\text{m}$ under a bias current of 4 mA (Fig. 1.14(c)), which represents an improvement of more than 200 times over devices without the antennas ($< 2 \text{ mV/W}$). One drawback of this detector is that the response was strongly polarization-dependent due to the low symmetry of the employed nanoantennas. In addition, the enhancement of the optical absorption was relatively modest, with the peak value of the absorption being only $\sim 10\%$.

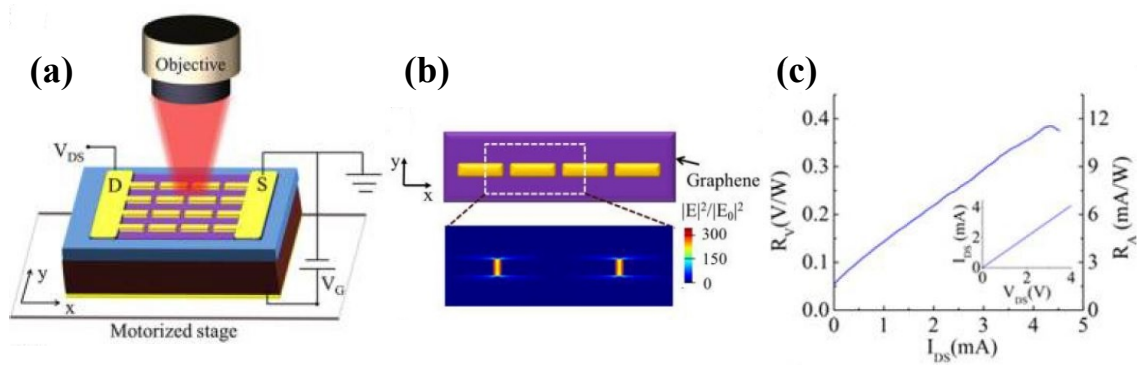


Figure 1.14. Plasmonic antenna-assisted optical absorption and carrier collection enhancement in graphene photodetector. (a) Schematic of a graphene photodetector on a silicon substrate. (b) Normalized electric field intensity enhancement distribution in the xy-plane, calculated at 1 nm above the graphene surface. (c) Measured responsivity as a function of the biased current at room temperature under gate voltage of 4 V. Inset: V_{DS} - I_{DS} plot of the same detector under dark condition. Reproduced from ref. 24.

1.4 Graphene for Mid-infrared Biosensors

The identification of biomolecules and the monitoring of the binding processes they undergo are crucial for understanding the molecular mechanisms of cellular functions (e.g. for fundamental biological studies) and for medical diagnostic applications.

Many techniques have thus been developed for the sensitive detection of biomolecules, including electro-chemical reactions^{104, 105}, field effect transistors¹⁰⁶⁻¹¹⁰, surface plasmon resonances¹¹¹⁻¹¹⁷ and optical fibres¹¹⁸. In general, however, these methods suffer from lack of specificity in terms of what is being measured. On the other hand, infrared (IR) spectroscopy¹¹⁹⁻¹²⁵ is a highly specific sensing modality as it allows direct measurement of the vibrational fingerprints of molecules. It is also non-invasive, label-free, and has been used for a wide variety of biological samples, including proteins¹¹⁹, lipids¹²⁶ and bacteria¹²⁷. Nonetheless, conventional IR spectroscopy faces the challenge of low signal-to-noise for measurements of small quantities of biomolecules (e.g. monolayers), which originates from the large mismatch between the wavelength of light (~micrometres) and the size of biomolecules (<10 nm). This has led to the development of a method that leverages the large optical field enhancement that can occur in the vicinity of metallic nanostructures¹²⁸⁻¹³² that is known as surface-enhanced infrared absorption (SEIRA)¹³³⁻¹³⁵. The detection of small quantities of molecules has been demonstrated using this method^{112, 136-142}. Metallic nanostructures have some drawbacks for SEIRA, however^{131, 143-145}. The spectral bandwidth over which they boost IR absorption is relatively narrow and generally fixed at the time of manufacturing. The field confinement of noble metal plasmons in the mid-infrared molecular fingerprint region is also relatively weak. Recently, graphene has emerged as an attractive candidate for biosensing as it supports mid-infrared plasmons that can be tuned by electrostatic gating^{19, 20}. In addition, graphene plasmons exhibit unprecedented spatial confinement^{17, 18}. Graphene could also be coupled with plasmonic nanostructures to achieve sensitive and/or tuneable detection of biomolecules by leveraging the high sensitivity of its optical conductivity to electrical/molecular doping.^{117, 141, 142} These unique properties of graphene have been exploited for the quantification and identification of biomolecules down to monolayers,

with key improvements over plasmonic sensing devices employing metallic nanostructures.^{21-23, 117, 141, 142}

1.4.1 Biosensing with Tuneable Graphene Plasmons

The electrical tunability and strong spatial confinement of plasmons on graphene make it an attractive platform for the sensitive quantification and identification of biomolecules. For example, Fig. 1.15 shows a graphene-based tuneable MIR biosensor that achieved quantitative detection and chemical specific identification of a bilayer of recombinant protein A/G and goat anti-mouse immunoglobulin G (IgG).²² The sensor consisted of a graphene layer patterned into a nanoribbon array on top of a 280-nm-thick SiO₂ layer over a silicon substrate (Fig. 1.15(a)). On a device with ribbon width $W = 30$ nm and array period $P = 80$ nm (Fig. 1.15(b)), extinction spectra were measured before and after the protein bilayer formation (Fig. 1.15(c)). A prominent resonance associated with localized surface plasmons (LSPs) was observed and was shown to be tuned across the fingerprint region of the protein by changing the gate voltage (Fig. 1.15(c), dotted curves). After the protein formation on the device surface, a resonance red shift exceeding 200 cm^{-1} was observed, due to the modification in refractive index of the medium on top of the sensor surface (Fig. 1.15(c), solid curves). In addition, spectral dips coinciding with the amid I and II bands of the protein were observed and became more intense with increasing overlap between the plasmonic resonance and the protein vibrational modes, providing chemical-specific identification of the protein bilayer.

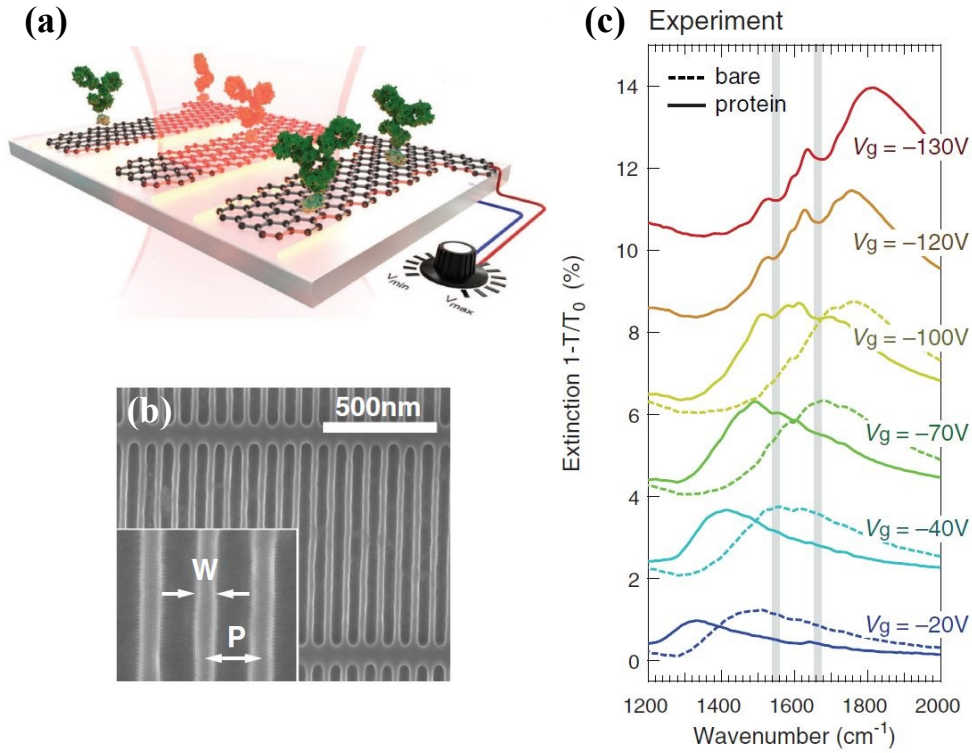


Figure 1.15. Biosensing with tuneable graphene plasmons. (a) Schematic of a tuneable graphene MIR biosensor, consisting a graphene nanoribbon array on top of a SiO₂/Si substrate. (b) SEM image of a graphene nanoribbon array with ribbon width $W = 30$ nm and array period $P = 80$ nm. (c) Measured extinction spectra under gate voltage swept from -20 V to -130 V before (dashed curves) and after (solid curves) the formation of protein bilayer. Extinction is calculated as the relative difference in transmission between regions with and without graphene nanoribbons. Gray shaded areas indicate amide I and II vibrational bands of the protein. Reproduced from ref. 22.

One drawback of this biosensor is the fact that the field enhancement that accompanies graphene plasmon is relatively small (~ 30 times) compared to that occurring with plasmons on noble metals. Field enhancement is important for boosting the light absorption by the protein adsorbed on the device surface. A result is that the reported extinction change caused by the presence of the protein is below 1%, i.e. small.

Thus, one may naturally anticipate that this approach would face challenges related to signal-to-noise ratio, especially for the detection of proteins in sub-monolayers.

1.4.2 Biosensing with Noble Metal Plasmons Coupled with Graphene

Coupling noble metal plasmons with graphene has been demonstrated to enable detection of low-molecular-weight molecules¹⁴² and detection of protein vibrational fingerprints¹⁴¹ via the tuning of graphene optical conductivity by molecular doping¹⁴² and electrostatic doping¹⁴¹ respectively. Figure 1.16(a) shows a biosensor based on a hybrid metasurface that consists of a graphene monolayer on top of an Au nanorod antenna array over an optical cavity substrate. The molecular doping of graphene by the biomolecules adsorbed within the antenna gaps resulted in modification of the graphene optical conductivity and caused a resonance shift of the plasmonic resonance of the antennas. Many conventional optical biosensors employ detection via changes in local or bulk refractive indices and are thus limited by the molecular mass. By contrast, the optical conductivity-based approach is based on the molecular doping effect and thus allows the detection of low-molecular-weight molecules. The measurement of glucose was demonstrated using affinity binding (Fig. 1.16(b)). The graphene was first treated by boronic acid (BAP). Then the binding of glucose converted the BAP from an electron-withdrawing group to an electron-donating group. This resulted in changes in the graphene optical conductivity and allowed for the optical sensing of glucose (Fig. 1.16(c)). A plasmonic resonance shift of $\sim 1.5 \text{ cm}^{-1}$ was observed upon binding of 2 nM (0.36 ng/mL) of glucose. In another example, a metasurface was employed for sensing of proteins, with electrically tunable sensitivity (Fig. 1.16(d)). The metasurface consisted of gold nanorod antenna arrays on graphene on a resonant substrate. The graphene was underneath the antennas to facilitate the electrostatic gating of its optical conductivity. The strong light-molecule interactions in the optical hotspots within the narrow antenna

gaps allowed the quantification of the target molecules through the spectral shifts of the metasurface resonance. The tuning of the graphene optical conductivity via electrostatic gating permitted the metasurface resonance to be tuned across the molecule vibrational bands, allowing for the identification of the molecular fingerprints. The detection of recombinant protein A/G monolayer was demonstrated via the measurement of the reflection spectra upon physisorption of the protein for different gate voltages (Fig. 1.16(e)). Dips in the reflection spectra can be seen to occur at wavenumbers corresponding to the two absorption bands (amide I & II) of the protein. These spectral features could be used to identify the presence of the protein and quantify its amount by the relative absorbance spectra (Fig. 1.16(f)). The relative absorbance is defined as $|\Delta R/R| = |(R - R_p)/R|$, where R_p represents the reflectance spectra of devices with monolayer protein (Fig. 1.16(e)), and R represents polynomial fits to R_p , excluding the two amide bands (i.e., $\omega_I = 1620 - 1680 \text{ cm}^{-1}$ and $\omega_{II} = 1510 - 1580 \text{ cm}^{-1}$). Although both sensors discussed above have shown quantification and/or identification of protein monolayers, their sensitivities are ultimately limited by the relatively weak field confinement of noble metal plasmons.

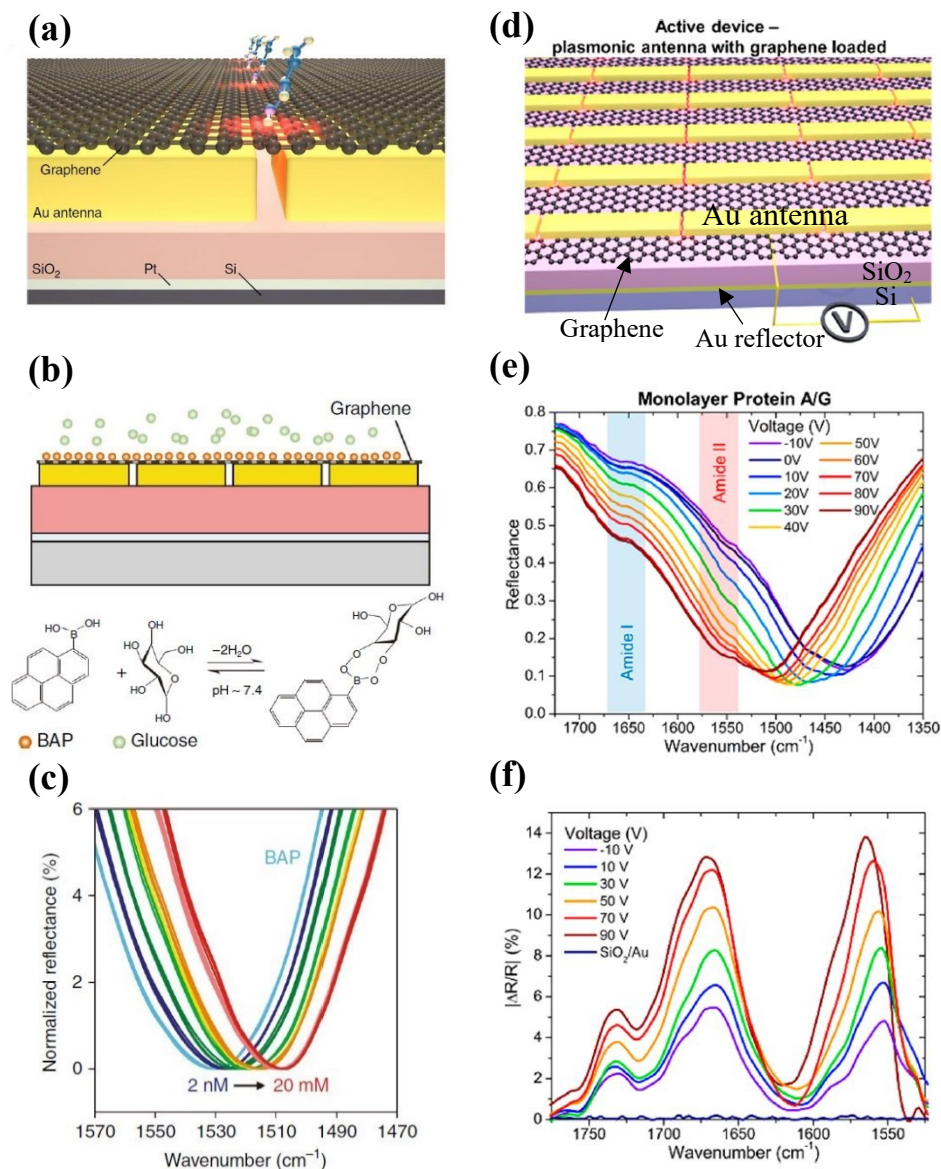


Figure 1.16. Biosensing with Noble Metal Plasmons Coupled with Graphene. (a) Schematic of a hybrid metasurface sensor consisting of gold nanorod antennas covered with graphene. Reproduced from ref. 142. (b) Schematic illustration of the protein binding processes on the hybrid metasurface sensor. Reproduced from ref. 142. (c) Measured normalized reflectance spectra with glucose from 2 nM to 20 mM on the hybrid metasurface sensor. Reproduced from ref. 142. (d) Schematic of an active metasurface sensor consisting of gold nanorod antennas loaded with graphene on a 400 nm SiO₂ spacer on a gold back-reflector. The Fermi level of graphene could be tuned by applying a gate voltage between the graphene and the back gate. Reproduced from ref. 141. (e) Measured reflectance spectra with a protein monolayer (A/G)

adsorbed under different gate voltages. Blue and red shaded regions indicate the amide I band and amide II band of the protein respectively. Reproduced from ref. 141. (f) Relative absorbance spectra of the amide bands at different gate voltages extracted from (e). Reproduced from ref. 141.

1.5 Enhancing Light-Matter Interaction with Magnetic Mirrors

The π -phase shift of light upon reflection from a metal mirror produces a standing wave whose electric field is zero at the mirror surface. This effect suppresses the absorption and/or emission by a material placed at the mirror surface and is undesirable in many optoelectronic devices where metal films are used as both electrical contacts and optical mirrors. In contrast, structures that reflect light with zero phase shift, which are often referred to as magnetic mirrors, have drawn much attention in recent years as they lead to the electric field having an anti-node at the reflective surface, thereby facilitating the light-matter interaction. Early work included radio frequency designs pursued for the goal of suppressing propagating surface waves and for the realization of low-profile antennas.^{146, 147} More recently, much interest has concerned the use of magnetic mirrors for applications that include solar cells,¹⁴⁸ enhanced photoluminescence¹⁴⁹ and electroluminescence¹⁵⁰, surface enhanced Raman scattering¹⁵¹ and tuneable photodetectors¹⁵². In these previous works, it has generally been the case that either the metal or the dielectric material is patterned to realize the magnetic mirror. However, for many optoelectronic devices, it would be advantageous to realize a multi-functional magnetic mirror from hybrid structures containing both metals and dielectrics, with the metal acting as both an electrical conductor and a broadband optical reflector and the dielectric structures providing flexible tunability of the reflected wave-front, e.g. control over phase, amplitude, polarization, and radiation pattern. In this thesis, we demonstrate

a hybrid metal/dielectric magnetic mirror in the LWIR and show that it could be used in a graphene photodetector application to enhance the LWIR light absorption by graphene.

1.5.1 Zero Phase Shift of Reflection

The phase shift of light reflecting from a planar surface is dictated by the Maxwell's boundary conditions and is illustrated in Fig. 1.17(a-c)¹⁵³. For a perfect electric conductor (PEC), for which conventional metal mirror is a good approximation, the tangential electric field is continuous across the conductor surface and is thus zero. This forces a π -phase shift to the electric field when light is reflected from a PEC surface (Fig. 1.17(b)). The surface electric current density $\mathbf{K}_E$ can be regarded as giving rise to the reflected wave, with the tangential magnetic field being non-zero at the conductor surface. On the other hand, for a perfect magnetic conductor (PMC), the tangential magnetic field is continuous across the conductor surface and is thus zero. This forces a π -phase shift to the reflected magnetic field and a zero-phase shift to the electric field (Fig. 1.17(c)). The electric field could be regarded as being generated by the induced surface magnetic current density $\mathbf{K}_M$. Thus, a PMC could be regarded as an ideal magnetic mirror. As a result, when a magnetic mirror is illuminated by a plane wave, the total electric field has an anti-node at the surface. Because of this unusual property, magnetic mirrors can be much more effective than conventional metal mirrors as reflectors in optoelectronic devices for which strong light-matter interaction (e.g. absorption or emission) near the mirror surface is desirable. To illustrate the difference between an electric mirror and a magnetic mirror, we show in Fig. 1.17(d) the simulated phase shift spectra for an Au mirror (100 nm thick) and for a magnetic mirror consisting of a square array of a-Si cuboids on top of an Au mirror (100 nm thick). The Au mirror exhibits a flat spectrum with $\sim\pi$ phase shift across the wavelength spectrum 6-12 μm , i.e. it features electric mirror behaviour (Fig. 1.17(d), red curve). In contrast, the magnetic mirror shows a phase

shift of zero at $\lambda = 8.79 \mu\text{m}$ (Fig. 1.17(d), blue curve) when magnetic dipole resonances are excited in the a-Si cuboids by the incident light. The magnetic dipoles in each cuboid could be conceptually thought of as forming surface magnetic current densities which produce electric fields on top of the cuboids and give rise to the magnetic mirror behaviour. As a result, the standing wave distributions (both at $\lambda = 8.79 \mu\text{m}$) of the normalized electric field feature a node at the Au surface (Fig. 1.17(e)) and an anti-node at the cuboid surface (Fig. 1.17(f)) for the electric mirror and magnetic mirror respectively. The magnetic dipole resonance in the a-Si cuboid can also be verified by the circulating electric field pattern in Fig. 1.17(f).

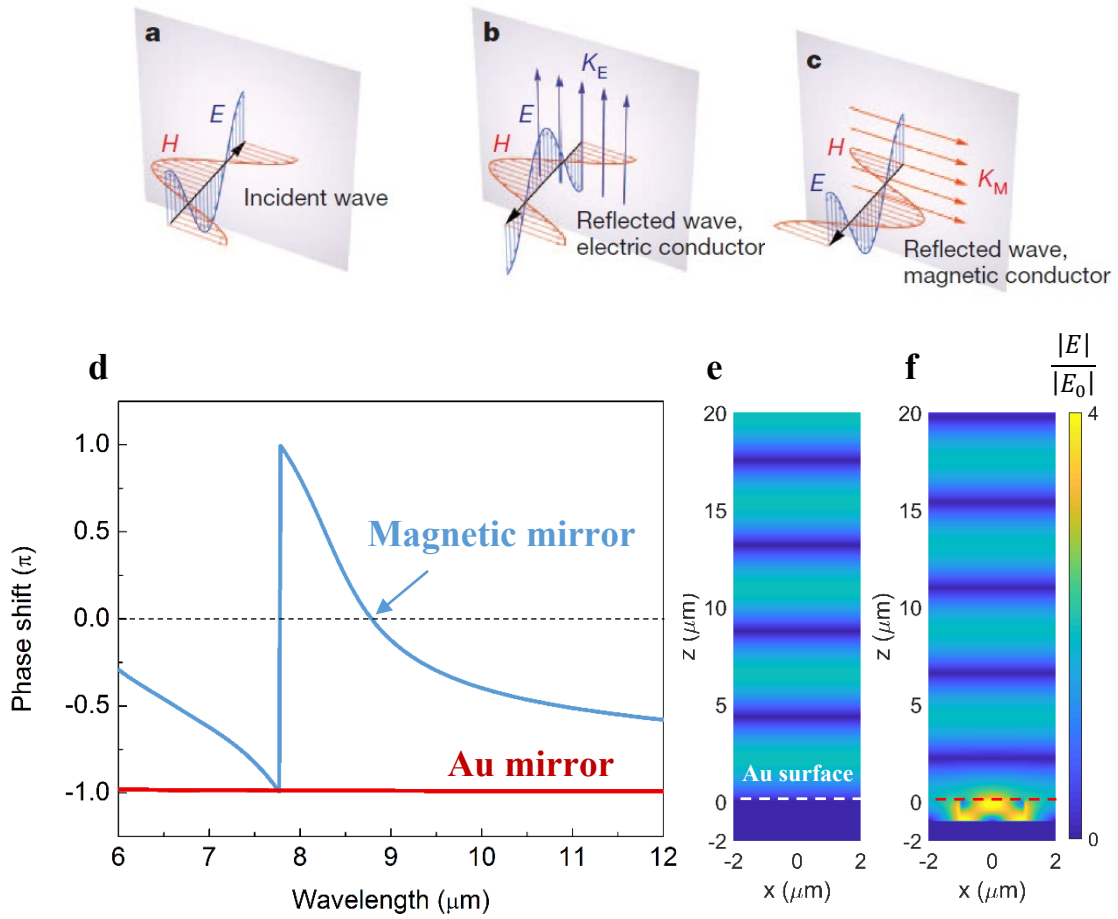


Figure 1.17. Reflection properties for an electric mirror and a magnetic mirror. (a-c) Schematic illustration of a plane wave incident on a conductor (a) and reflects due to the excitation of surface electric current density (b) or surface magnetic current density (c). Reproduced from ref. 153. (d) Simulated phase shift for light reflected from an Au mirror (100 nm thick) and a magnetic mirror consisting of a square array of a-Si cuboids on top of an Au mirror (100 nm thick). Cuboid side length and thickness are 2 μm and 1 μm respectively. Array period is 4 μm . (e-f) Simulated normalized electric field distributions for the Au mirror (e) and magnetic mirror (f) described in (d), both obtained at $\lambda = 8.79$. White and red dashed lines indicate the surface of the Au mirror and cuboids respectively.

1.5.2 Enhancing Light Absorption in Graphene

Because of the zero-phase shift of reflection and the resulting enhanced field intensity near the reflective surface, magnetic mirrors can be much more effective than conventional metal mirrors as reflectors in optoelectronic devices for which strong light-matter interaction (e.g. absorption or emission) near the mirror surface is desirable. An example application is in graphene photodetectors, for which magnetic mirrors could be employed both as back-reflectors to enhance the light absorption in graphene and as electrical contacts for applying gate voltages. Figure 1.18 shows the simulated phase shifts of magnetic mirrors consisting of square arrays of a-Si cuboids on top of Au mirrors. This figure also shows the light absorption spectra for graphene monolayers placed directly on the magnetic mirrors. It can be seen from Fig. 1.18(a) that the phase shift spectrum features a zero-phase shift (dotted line) wavelength that can be tuned by varying the cuboid side length $L = 1.2\text{-}2\text{ }\mu\text{m}$. Correspondingly, the light absorption in graphene is strongly enhanced (to approximately 8%) at the zero-phase shift wavelengths of the magnetic mirrors, due to the enhanced electric field intensity at the cuboid surface (Fig. 1.18(b)). The peak graphene absorption is around four times that of the graphene suspended in air (purple curve in Fig. 1.18(b)) and is around three orders of magnitude larger than the case when graphene is on a gold mirror (brown curve in Fig. 1.18(b)). Figure 1.18(c-d) show 2D maps of the phase shift and graphene absorption with cuboid side length $L = 1\text{-}2.2\text{ }\mu\text{m}$, showing more general trends. Two trends are indicated by the dotted lines. The first trend is that the graphene peak absorption line (red dotted line in Fig. 1.18(d)) coincides with the zero-phase shift line of the magnetic mirrors (red dotted line in Fig. 1.18(c)). The second trend is that the graphene dip absorption line (white dotted line in Fig. 1.18(d)) coincides with the π -phase shift line of the magnetic mirrors (white dotted line in Fig. 1.18(c)). These are direct consequences of the enhanced and

suppressed field intensities that occur at the mirror surface upon zero- and π -phase reflection respectively.

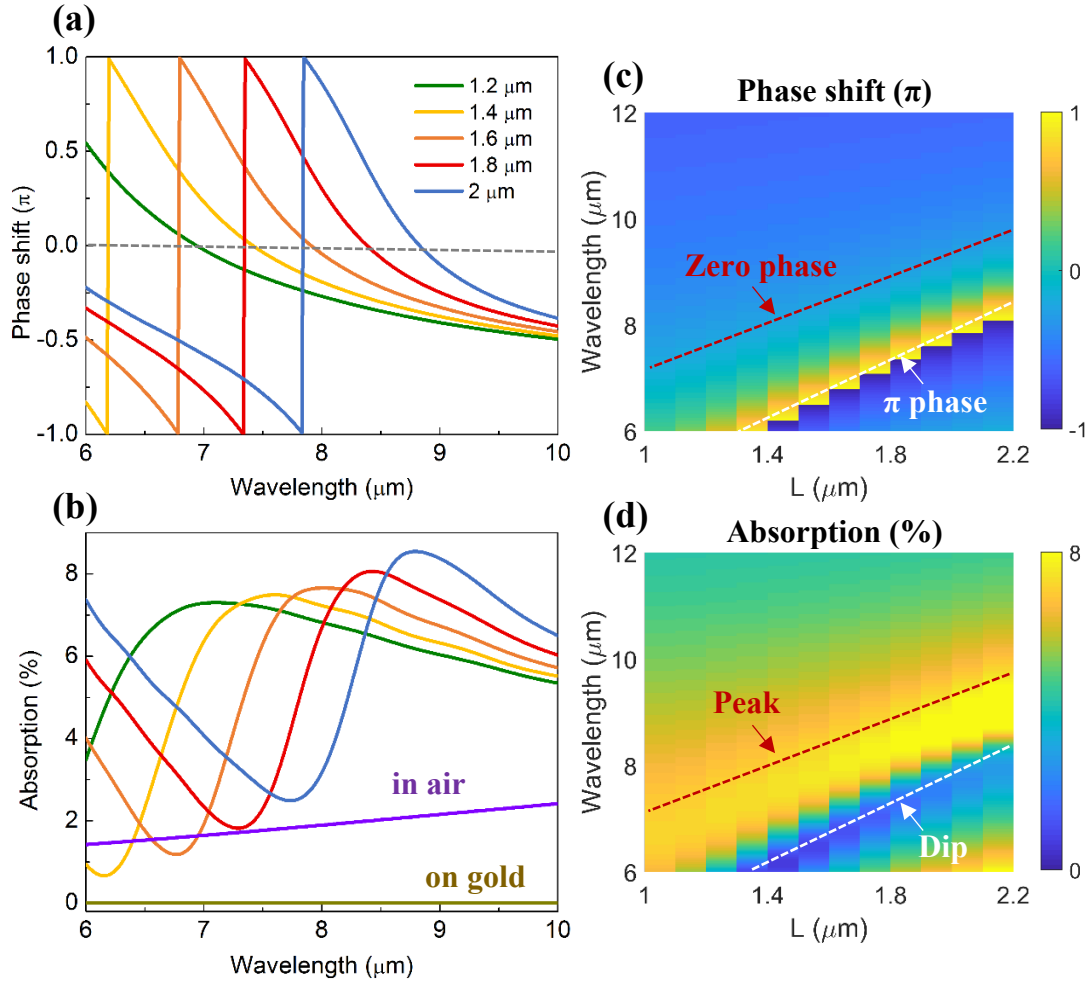


Figure 1.18. Light absorption enhancement in graphene when placed directly on magnetic mirrors consisting of a square array of a-Si cuboids on top of an Au mirror. (a) Simulated phase shift spectra of magnetic mirrors with cuboid side length $L = 1.2\text{--}2\text{ }\mu\text{m}$, in step of $0.2\text{ }\mu\text{m}$. The cuboid thickness is $1\text{ }\mu\text{m}$. Array period is kept as twice of the cuboid side length. (b) Simulated light absorption by graphene placed on the magnetic mirrors described in (a). Purple and brown curves show the graphene absorption when it is suspended in air and placed on a gold mirror respectively. (c-d) 2D maps of the phase shift spectrum of the magnetic mirrors (c) and light absorption by graphene placed on top (d). The cuboid side is $L = 1\text{--}2.2\text{ }\mu\text{m}$ and thickness is $1\text{ }\mu\text{m}$. Array period is kept as twice of the cuboid side length. Red dotted lines depict the zero-phase shift in (c) and peak graphene absorption in (d). White dotted lines depict the π -phase shift in (c) and dip graphene absorption in (d). The scattering rate and chemical potential of graphene are taken as 0.0427 eV and 0.1895 eV respectively.

Chapter 2

Methods

In this chapter, we describe both the simulation and experimental methods employed in this thesis. We will first describe the modelling and simulation details. Then, we will describe the graphene growth, transfer and device fabrication methods. Finally, we will describe the experimental setups used for the device electrical, optical and optoelectronic characterizations.

2.1 Electromagnetic Modelling and Simulation

The electromagnetic modelling and simulations in this thesis are carried out using two methods, both implemented in commercial software packages. One is the finite element method (FEM) implemented in COMSOL Multiphysics, the other is the finite difference time domain method (FDTD) implemented in FDTD Solutions, Lumerical. In this section, we will first describe the electromagnetic modelling of graphene. Then we will describe the optical simulation details for structures that we have studied. These include the multipole expansion of scattering cross section of an a-Si cuboid above a PEC surface (by COMSOL); reflection, absorption and phase shift (by FDTD Solutions, Lumerical) of the magnetic mirror consisting of an a-Si cuboid array on gold film; reflection and absorption (by FDTD Solutions, Lumerical) of the graphene photodetector consisting of a JC-antenna array on graphene on SiO₂/Si substrate; and reflection and absorption (by FDTD Solutions, Lumerical) of the graphene biosensors consisting of linear antennas and/or graphene nanoslits/nanoribbons on Al₂O₃/Al substrates.

2.1.1 Electromagnetic Modelling of Graphene

In the electromagnetic simulations, graphene is modelled as a two-dimensional surface with a surface conductivity. In the local limit of random phase approximation neglecting the spatial dispersion, the surface conductivity is isotropic and is given by the Kubo formula^{154, 155}:

$$\begin{aligned}\sigma(\omega, \mu_c, \Gamma, T) &= \sigma_{intra}(\omega, \mu_c, \Gamma, T) + \sigma_{inter}(\omega, \mu_c, \Gamma, T) \\ &= \frac{ie^2(\omega - i2\Gamma)}{\pi\hbar^2} \left[\frac{1}{(\omega - i2\Gamma)^2} \int_0^\infty \varepsilon \left(\frac{\partial f_d(\varepsilon)}{\partial \varepsilon} - \frac{\partial f_d(-\varepsilon)}{\partial \varepsilon} \right) d\varepsilon \right. \\ &\quad \left. - \int_0^\infty \left(\frac{f_d(-\varepsilon) - f_d(\varepsilon)}{(\omega - i2\Gamma)^2 - 4(\varepsilon/\hbar)^2} \right) d\varepsilon \right]\end{aligned}\quad (2.1)$$

where ω is angular frequency, μ_c is chemical potential, Γ is scattering rate, T is temperature, e is the electron charge, $\hbar = h/2\pi$ is the reduced Planck's constant, $f_d(\varepsilon) = (e^{(\varepsilon - \mu_c)/k_B T} + 1)^{-1}$ is the Fermi-Dirac distribution, and k_B is Boltzmann's constant. The expression consists of two terms that correspond to intraband contributions and interband contributions to the surface conductivity. The intraband term can be evaluated as

$$\sigma_{intra}(\omega, \mu_c, \Gamma, T) = -\frac{ie^2 k_B T}{\pi\hbar^2(\omega - i2\Gamma)} \left(\frac{\mu_c}{k_B T} + 2 \ln(e^{-\mu_c/k_B T} + 1) \right) \quad (2.2)$$

Alternatively, graphene can also be modeled as a very thin layer with frequency dependent uniaxial anisotropic permittivity given by¹⁵⁶⁻¹⁵⁸

$$\varepsilon_1(\omega) = \varepsilon_r + \frac{i\sigma(\omega)}{\varepsilon_0 \omega d}, \quad \varepsilon_2(\omega) = \varepsilon_r \quad (2.3)$$

where ε_1 and ε_2 are the in-plane and out-of-plane permittivities respectively, ε_r is the relative permittivity of the background medium, d is the graphene thickness. For the optical response of graphene in the mid-infrared range, there are negligible differences between the two modelling methods discussed above. In this thesis, we employ the surface conductivity method in our simulations.

2.1.2 COMSOL and FDTD Simulations

Multipole expansion of scattering cross section of an a-Si cuboid above a PEC surface. To provide insights into the physical mechanism of the magnetic mirror presented in this thesis, we study the multipolar scattering properties of an a-Si cuboid above a PEC surface. Due to the presence of the PEC surface, the conventional multipole analysis method - which deals with scatterers in homogeneous environments - is not applicable. We devise a modified multipole analysis method that replaces the PEC surface with image multipole sources based on the method of images. As discussed further below, the corresponding image multipole coefficients can be found directly from the multipole coefficients calculated for multipole sources in the a-Si cuboid by the conventional multipole analysis method via the boundary condition imposed by the presence of the PEC. The scattering of the a-Si cuboid can be decomposed into a set of multipole scatterings with modified multipole coefficients given by (detailed derivation can be seen in the appendix of Chapter 3)

$$\alpha_E^{mod}(l, m) = [1 - (-1)^{l+m}] \alpha_E(l, m) \quad (2.4)$$

$$\alpha_M^{mod}(l, m) = [1 + (-1)^{l+m}] \alpha_M(l, m) \quad (2.5)$$

where $\alpha_{E,M}^{mod}(l, m)$ are the modified electric and magnetic multipole coefficients with order l and degree m . $\alpha_{E,M}(l, m)$ are the conventional multipole coefficients obtained by integrating the current density over the volume of the cuboid and are as follows

$$\begin{aligned} a_E(l, m) &= \frac{(-i)^{l-1} k^2 \eta O_{lm}}{E_0 [\pi(2l+1)]^{1/2}} \int e^{-im\varphi} \left\{ \frac{[\varphi_l(kr) + \varphi_l''(kr)] P_l^m(\cos\theta) \hat{r} \cdot \mathbf{J}_{sca}(\mathbf{r})}{kr} + \frac{\varphi_l'(kr)}{kr} [\tau_{lm}(\theta) \hat{\theta} \cdot \mathbf{J}_{sca}(\mathbf{r}) - i\pi_{lm}(\theta) \hat{\phi} \cdot \mathbf{J}_{sca}(\mathbf{r})] \right\} d^3r \end{aligned} \quad (2.6)$$

$$a_M(l, m) = \frac{(-i)^{l+1} k^2 \eta O_{lm}}{E_0 [\pi(2l+1)]^{1/2}} \int e^{-im\varphi} j_l(kr) [i\pi_{lm}(\theta) \hat{\theta} \cdot \mathbf{J}_{sca}(\mathbf{r}) + \tau_{lm}(\theta) \hat{\phi} \cdot \mathbf{J}_{sca}(\mathbf{r})] d^3r \quad (2.7)$$

$$\mathbf{J}_{sca}(\mathbf{r}) = -i\omega[\varepsilon(\mathbf{r}) - \varepsilon_h] \mathbf{E}(\mathbf{r}) \quad (2.8)$$

where $\mathbf{E}(\mathbf{r})$ is the total electric field, ε_h is the permittivity of the host medium, $\varphi_l(kr) = krj_l(kr)$ are the Riccati-Bessel functions, $P_l^m(\cos\theta)$ are the associated Legendre polynomials, and O_{lm} , τ_{lm} and π_{lm} are defined as follows:

$$O_{lm} = \frac{1}{[l(l+1)]^{1/2}} \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} \quad (2.9)$$

$$\tau_{lm}(\theta) = \frac{d}{d\theta} P_l^m(\cos\theta) \quad (2.10)$$

$$\pi_{lm}(\theta) = \frac{m}{\sin\theta} P_l^m(\cos\theta) \quad (2.11)$$

The scattering cross section of the cuboid could thus be decomposed into multipole contributions by

$$\sigma_{sca} = \frac{\pi}{k^2} \sum_{l=1}^{\infty} \sum_{m=-l}^l (2l+1) [|\alpha_E^{mod}(l, m)|^2 + |\alpha_M^{mod}(l, m)|^2] \quad (2.12)$$

A three-step simulation is carried out in COMSOL. In the first step, we perform a full field simulation of a plane wave incident on an infinitely-extended PEC substrate without the cuboid and obtain the reflected field. Periodic boundary conditions are employed at the x- and y- boundaries of the simulation domain to mimic the infinite extent of the PEC. Perfectly matched layers (PMLs) are used at the z- boundaries. In the second step, we use the reflected field obtained in the first step as the background field and simulate the scattering of the a-Si cuboid above the PEC substrate with PMLs at all boundaries (x, y and z). The obtained scattered field is used to calculate the total scattering cross section of the cuboid by integrating the Poynting vector over the surface of the

cuboid and normalizing it to the illumination intensity. In the last step, we implement the modified multipole analysis model in COMSOL to calculate the multipolar scattering cross sections based on fields calculated in former steps. At the time of writing, a simple multipole expansion model based on the conventional method is also available at the following Internet link: <https://www.comsol.com/model/multipole-analysis-of-electromagnetic-scattering-31901>.

Reflection, absorption and phase shift of the magnetic mirror consisting of an a-Si cuboid array on gold film. The simulations of amplitude and phase of the reflection coefficient of the magnetic mirror are carried out using the FDTD method. Periodic boundaries are applied at the x- and y- boundaries to simulate the square lattice of the cuboids. PMLs are used at the z- boundaries to avoid unwanted backscattering of the electromagnetic field. Illumination is a plane wave at normal incidence. For the phase shift calculation, the top surface of the cuboids is chosen as the reference plane. Simulations of the absorption spectra of monolayer graphene sitting on the magnetic mirror structure are performed using the FDTD method, with the graphene by the surface conductivity method described above. The scattering rate and chemical potential of graphene are taken as 0.0427 eV and 0.1895eV respectively, which are within the range of values one would get from processed graphene.

Reflection and absorption of the graphene photodetector consisting of a JC-antenna array on graphene on SiO₂/Si substrate. The simulations of the reflection spectra, absorption spectra, and electric field distribution of the graphene photodetector are carried out using the FDTD method. Periodic boundary conditions are used at the x- and y- boundaries to simulate the square lattice of the antennas. PMLs are used at the z- boundaries to avoid unwanted backscattering of the electromagnetic field. Illumination is a plane wave polarized along the x-axis at normal incidence (from the air side). Refractive

indexes for all bulk materials are from Palik.¹⁵⁹ The graphene is modelled using the surface conductivity approach described above, with the scattering rate 0.0282 eV and chemical potential 0.1366 eV obtained by fitting a model to the measured gate-dependent electrical conductivity.

Reflection and absorption of the graphene biosensors consisting of linear antennas and/or graphene nanoslits/nanoribbons on Al₂O₃/Al substrate. The simulations of the reflection spectra of the graphene biosensors are conducted using the FDTD method. The computational domain consists of a single unit cell of the structure. Periodic boundaries are used at the x- and y- boundaries. PMLs are used at the z- boundaries to avoid unwanted backscattering of the electromagnetic fields. Illumination is a plane wave linearly polarized along the long axis of the linear antenna at normal incidence. The protein monolayer, which is employed as a target material, is modelled as an 8-nm thick film layer conformally coated on the sensor surface. In the study of the sensing of protein sub-monolayers, each protein is modelled as a cuboid with dimensions of 4 nm (width) $\times$ 14 nm (length) $\times$ 8 nm (height).¹⁶⁰ The protein absorption is obtained by subtracting the absorption in graphene, antennas, and substrates from the total absorption.

2.2 Graphene Growth, Transfer and Device Fabrication

2.2.1 Chemical Vapor Deposition of Graphene and Transfer to Substrate

Graphene was first isolated from graphite by micromechanical exfoliation method which is done by peeling off graphite using adhesive tape.³⁹ Although this is the method of choice for fundamental laboratory research as it produces single layer graphene with high structural and electronic quality, it faces challenges concerning high yield and large

area production. While various approaches have been explored to produce graphene flakes and composites including liquid-phase exfoliation,^{161, 162} carbon segregation¹⁶³⁻¹⁶⁶ and chemical synthesis,¹⁶⁷ chemical vapor deposition (CVD) has emerged as the most promising approach to produce large-scale single layer graphene with low cost and high quality. Roll-to-roll production of 30-inch graphene films grown by CVD has been reported and their use as transparent electrodes in a touch screen panels was demonstrated.⁶⁹ The CVD growth of SLG and FLG can be realized on various substrates by feeding hydrocarbons at suitable temperatures.¹⁶⁸⁻¹⁷² In particular, CVD growth of graphene on copper (Cu) substrate is a very common approach and is used for commercial production of graphene. The graphene that is used in this thesis is prepared by CVD growth on copper (Cu) substrate by the graphene producer Graphenea. The standard CVD processes for growing graphene on a Cu substrate is as follows. Typical Cu substrates consist of Cu foils with thicknesses of tens of micrometres. The Cu foil is first annealed in hydrogen (H₂) in a furnace at 1000 °C to remove the native oxide layer. Then a mixture of H₂/CH₄ gases is flowed into the furnace to initiate the graphene growth. The CH₄ supplies the carbon source for graphene growth and the H₂ serves as a purging gas. The Cu acts as a catalyst to decompose the CH₄ into carbon atoms and H₂ at random locations on the Cu surface. Carbon atoms are trapped by defects on the Cu foil as they wander on the surface and then act as nuclei for graphene growth. As the CH₄ decomposition continues, graphene islands with different crystal orientations are deposited and expand until the whole Cu surface is covered by a continuous polycrystalline graphene layer. The presence of a continuous graphene layer prevents further CH₄ decomposition and multi-layer growth because it acts as an inert blanket. Figure 2.1(a) shows a photograph of the 4-inch diameter Cu foil (thickness: 18 µm, roughness: ~80 nm), on which monolayer graphene had been grown by CVD, that we purchased from Graphenea. The grain size of

the graphene film is up to 20 μm according to the product datasheet provided by the company. To facilitate the graphene transfer onto the target substrate (SiO_2/Si) for device fabrication, a layer of polymethyl methacrylate (PMMA 550K, 4 wt%, Alfa Aesar) is spin-coated on it at 3000 rpm for 90 seconds. Figure 2.1(b) shows the graphene sheet on the Cu foil after this coating step.

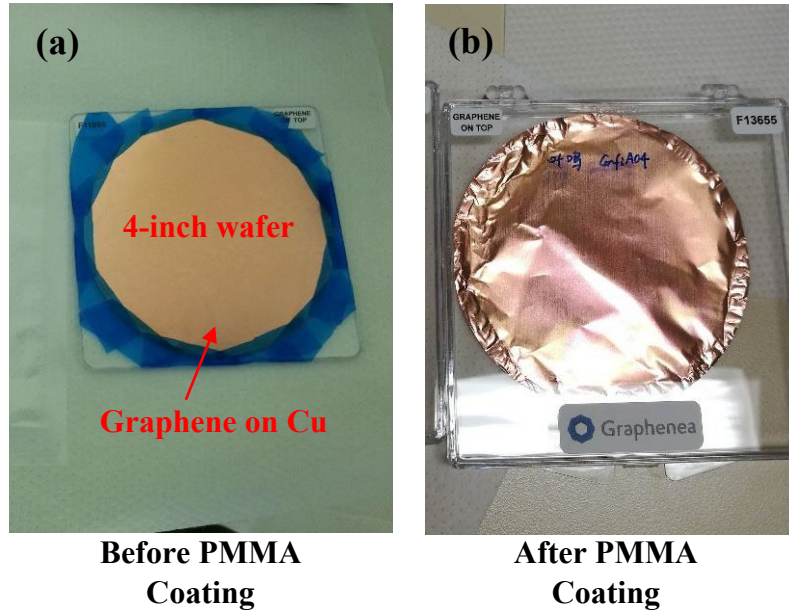


Figure 2.1. Photographs of 4-inch wafer size CVD-grown monolayer graphene on Cu. (a) as purchased from Graphenea. (b) after coating of PMMA (roughness around the edges of the sample is caused by the tape (as shown in (a)) used to fix the sample during spin-coating).

After the coating of PMMA, a wet transfer method is employed to transfer the graphene sheet onto the target SiO_2/Si substrate. The transfer process is schematically illustrated in Fig. 2.2. Before etching of the Cu foil, the backside of the Cu foil is treated in oxygen (O_2) plasma (Diener Electronic) for one minute, with O_2 flow of 30 sccm and a power of 50 W, to remove the graphene grown on the backside of the Cu foil. Then the

Cu foil is etched in Cu etchant (ammonium persulfate, 0.5M, Sigma-Aldrich) for about one and a half hours (Fig. 2.2(a)).

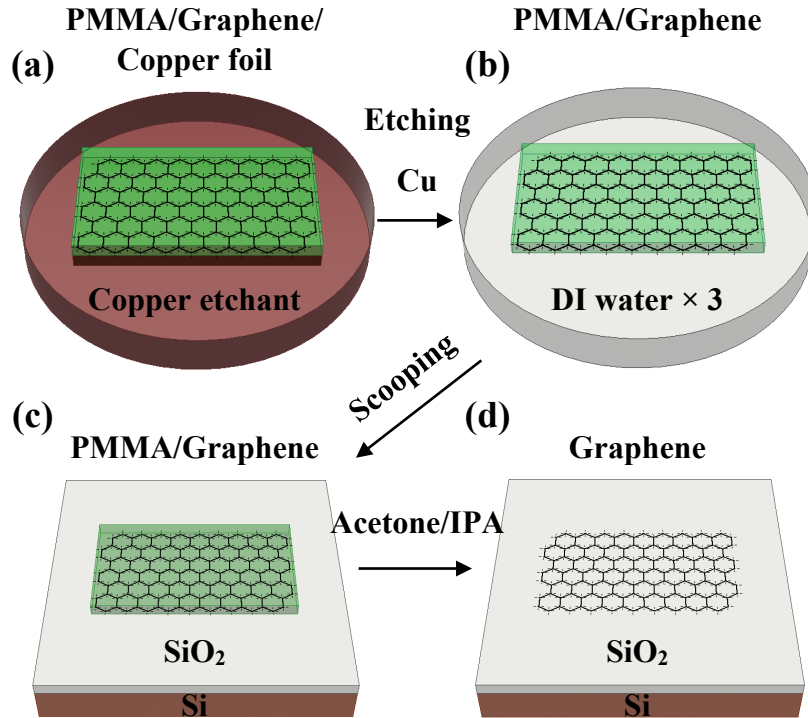


Figure 2.2. Graphene transfer process. (a) Etching copper foil in copper etchant (ammonium persulfate). (b) Rinsing in DI water for three times. (c) Scooping the PMMA/graphene layer onto a substrate (SiO₂/Si). (d) Removing the top PMMA layer in hot acetone and rinsing in isopropyl alcohol (IPA).

The PMMA/graphene stack is then thoroughly rinsed in deionized (DI) water three times, each for five minutes, to remove the solvent and ionic residuals (Fig. 2.2(b)). After the DI water rinsing, the PMMA/graphene stack is carefully scooped onto the O₂ plasma pre-treated SiO₂/Si substrate (Fig. 2.2(c)). The PMMA/graphene stack on SiO₂/Si is left in the ambient environment for one hour to allow it to dry and then heated to 130 °C

for half an hour to improve the adhesion between the graphene and the substrate. Finally, the top PMMA is dissolved in hot acetone (50 °C) twice, each for 20 minutes, and then rinsed in isopropyl alcohol (IPA) twice, each for 10 minutes. Figure 2.3 shows an optical microscope image of a CVD-grown single layer graphene transferred onto a SiO₂/Si substrate. As can be seen from the image, a clean and largely intact graphene sheet is successfully transferred over a large area of several millimetres. The contrast between the single-layer graphene and the substrate is quite visible.

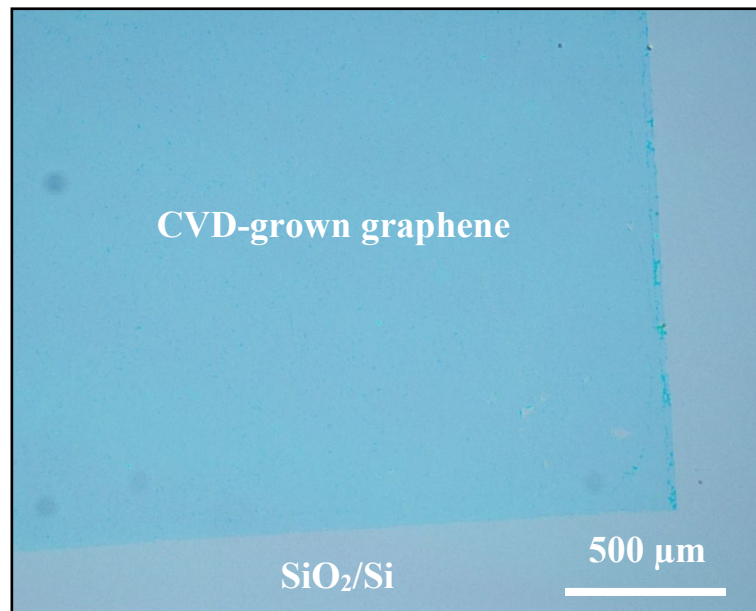


Figure 2.3. Optical microscope image of a CVD-grown single-layer graphene transferred onto a SiO₂/Si substrate.

2.2.2 Device Fabrication

Standard top-down nanofabrication techniques are employed for the fabrication of the devices in this thesis, including both the magnetic mirrors and graphene photodetectors.

The fabrication process for magnetic mirrors consisting of a-Si cuboid arrays on an Au film on a silicon wafer is schematically shown in Fig. 2.4. We first deposit Ti (10 nm) and Au (100 nm) films by electron beam evaporation (Intlvac Nanochrome II Electron Beam and Thermal Evaporation System) and an a-Si (1.1 μm) film by plasma-enhanced chemical vapor deposition (PECVD, Oxford Plasma Lab100) on a silicon wafer. Then the cuboid array pattern is formed in a PMMA layer (A4, 950 K, 200 nm thick) by electron beam lithography (Vistec EBPG5000 Plus EBL) and resist development in 3:1 isopropanol-methyl isobutyl ketone (MIBK, 60 seconds). After that, an etching mask is fabricated by depositing aluminium (Al) to a thickness of 30 nm by electron beam evaporation and lift-off. The sample is then etched by inductively coupled plasma reactive ion etching (Oxford Plasma Lab100 (ICPRIE)-General Etch) for 3 minutes and 25 seconds, with the etch gases consisting of sulfur hexafluoride (SF_6 , at 40 sccm) and perfluorocyclobutane (C_4F_8 , at 90 sccm). The RF and ICP powers are 30 W and 1200 W, respectively. The remaining Al mask is etched away in Al etchant (phosphoric acid & nitric acid, Transene company) for 10 minutes.

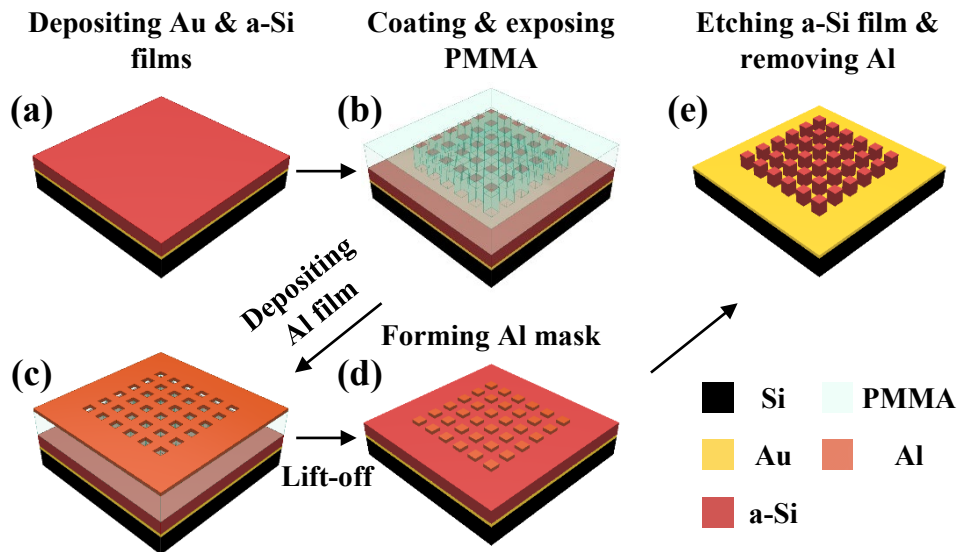


Figure 2.4. Schematic of fabrication process for magnetic mirrors.

For the fabrication of graphene photodetectors, a monolayer of CVD-grown graphene film is first transferred onto a silicon dioxide layer using a PMMA-assisted wet transfer method. Then, a square array ($30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$) of 5-nm Cr/30-nm Au Jerusalem cross antennas (JC-antennas, cross-shaped structures with elongated ends) is fabricated on top of the graphene by electron beam lithography (EBL), electron-beam evaporation and lift-off. Next, the graphene is patterned by EBL and reactive ion etching (O₂ plasma treatment for 30 s at 100 W) to yield a channel ($30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$). Finally, the electrodes and wire-bonding pads are formed by EBL patterning, electron beam evaporation of 10-nm Cr/80-nm Au and lift-off. The fabricated device is wire-bonded in a 28-pin chip carrier (Evergreen Semiconductor) for electrical and optoelectronic characterizations.

2.3 Electrical and Optical/Optoelectronic Characterization

Experimental setup for reflectance spectrum measurement of magnetic mirrors. We measure reflectance spectrum of our magnetic mirrors using a homebuilt microscope attached to a Fourier transform infrared spectrometer (FTIR, PerkinElmer). The optical beam path of the setup is schematically illustrated in Fig. 2.5(a). Figure 2.5(b) shows a photograph of the experimental setup. Light from the FTIR global source, modulated by the internal interferometer, is focused by two parabolic mirrors (PM) and collimated by zinc selenide (ZnSe) lenses L1 (focal length $f = 50\text{ mm}$) and L2 ($f = 50\text{ mm}$), so that the beam that illuminates the sample has a small angular spread. The reflected light is then focused by another two ZnSe lens L3 ($f = 50\text{ mm}$) and L4 ($f = 50\text{ mm}$) onto an MCT detector, whose output is fed back to the FTIR through the external detector interface for retrieving of the spectrum of the reflected light. The reflectance spectrum of a gold film is also measured using the same method. The reflectance spectrum of the magnetic mirror sample is calibrated by dividing it by the reflectance spectrum of the gold film.

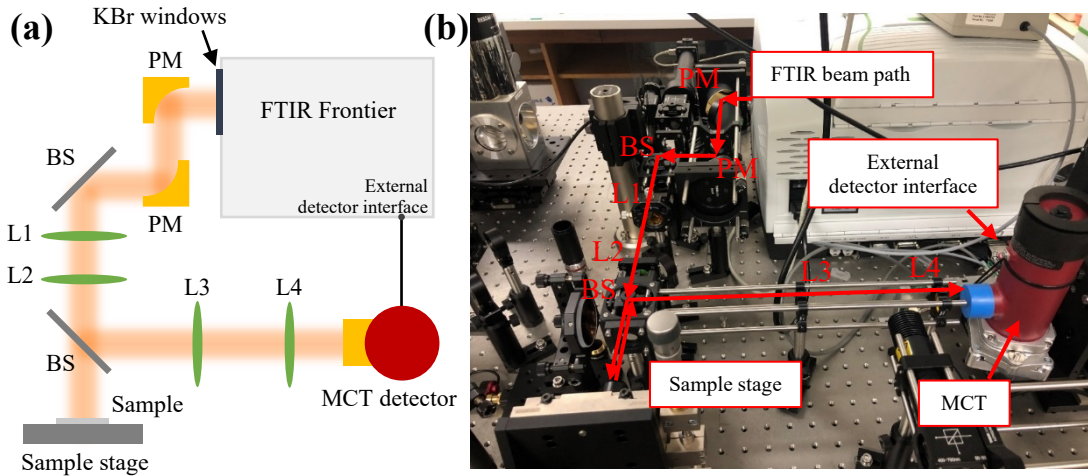


Figure 2.5. Experimental setup for reflectance spectrum measurement of magnetic mirrors.

(a) Schematic illustration of the optical beam path showing a homebuilt microscope attached to a Fourier transform infrared spectrometer (FTIR, PerkinElmer). PM – parabolic mirror; BS – beam splitter; L1, L2, L3, L4 – zinc selenide lens with focal length of 50 mm. (b) Photograph of the experimental setup.

Experimental setup for phase shift measurement of magnetic mirrors. We use a home-built infrared Michelson interferometer as shown in Fig. 2.6 to measure the phase shift of light upon reflection from our magnetic mirror samples. The light source is a continuous-wave Fabry-Perot quantum cascade laser (QCL, ThorLabs) with centre wavelength 8.4 μm . The laser beam is collimated by a ZnSe lens (CL, $f = 100$ mm), attenuated by a neutral density filter (NDF) and then sent to an interferometer system. The two interfering beams are from an Au mirror that is scanned and from the sample under test. The scanning mirror is mounted on a one-axis translation stage (ThorLabs XR25P-K2/M) driven by a Thorlabs PIA50 piezo inertial actuator. According to the manufacturer, this has a typical step size of 20 nm with a variation $\sim 20\%$. The sample is

mounted on another three-axis motorized linear translational stage (Thorlabs LNR50S). The bidirectional repeatability of the stage is $0.3\ \mu\text{m}$ and the backlash is less than $6\ \mu\text{m}$, which are sufficient for our sample positioning. A liquid nitrogen cooled MCT detector from Infrared Associates is used to detect the light from the interferometer. A source meter unit (Keithley 2450) is used to provide bias voltage to the MCT detector and to measure the photocurrent. Control over the translation stages, source supply and current readout is achieved using a Matlab control script. Detailed information on how the measurements are done is provided in a later chapter of the thesis.

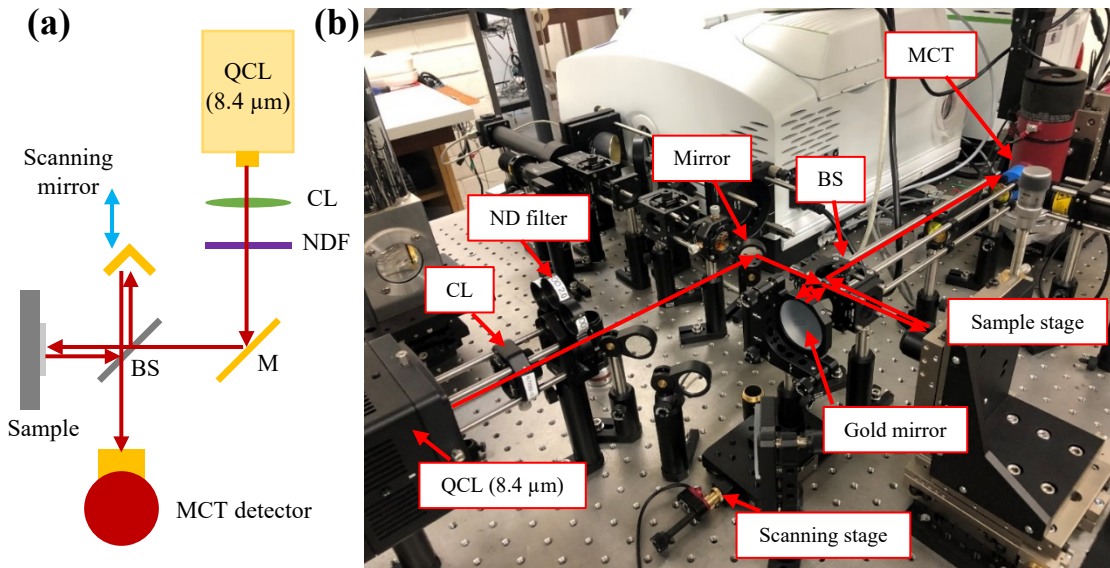


Figure 2.6. Infrared Michelson interferometer setup for the phase measurement of magnetic mirrors. (a-b) Schematic illustration and photograph of the interferometer used for phase shift measurement, respectively. CL – collimation lens; NDF – neutral density filter; M – mirror; BS – beam splitter.

Experimental setup and voltage supply for electrical and optoelectronic characterization of graphene photodetectors. The experimental setup we used for the

photoresponse characterization of the graphene photodetectors shown in Fig. 2.7 (a). The infrared (IR) light is from the FTIR globar. The power density spectrum (Fig. 2.8) peaks in the MWIR. The IR beam exiting from the FTIR external port is focused by a parabolic mirror (PM) and a reflective objective onto the device. A home-built optical microscope is used to locate the detector active area. For low temperature measurements, the device is mounted on a cryostat (Janis Research), with a 28-pin chip carrier socket as shown in Fig. 2.7(b). The electrical characteristics of the device are measured using two source measure units (SMUs, Keithley 2450). One SMU provides the gate voltage, while the other SMU provides the source-drain voltage and is used to measure the current. For temporal response characterization, a chopper is used to modulate the IR beam. The device bias and current amplification is provided by a transimpedance low-noise current preamplifier (SR570, Stanford Research Systems). The output of the preamplifier is sent to an oscilloscope (Tektronix, TDS3034B) and is then sampled by a computer. Photographs of the SMUs, preamplifier and oscilloscope are shown in Fig. 2.7(c). All the measurements are performed on devices wire-bonded on 28-pin chip carriers (Evergreen Semiconductor). Figure 2.7(d) shows a photograph of a representative wire-bonded device. More detailed information on the measurements are provided in a later chapter of the thesis.

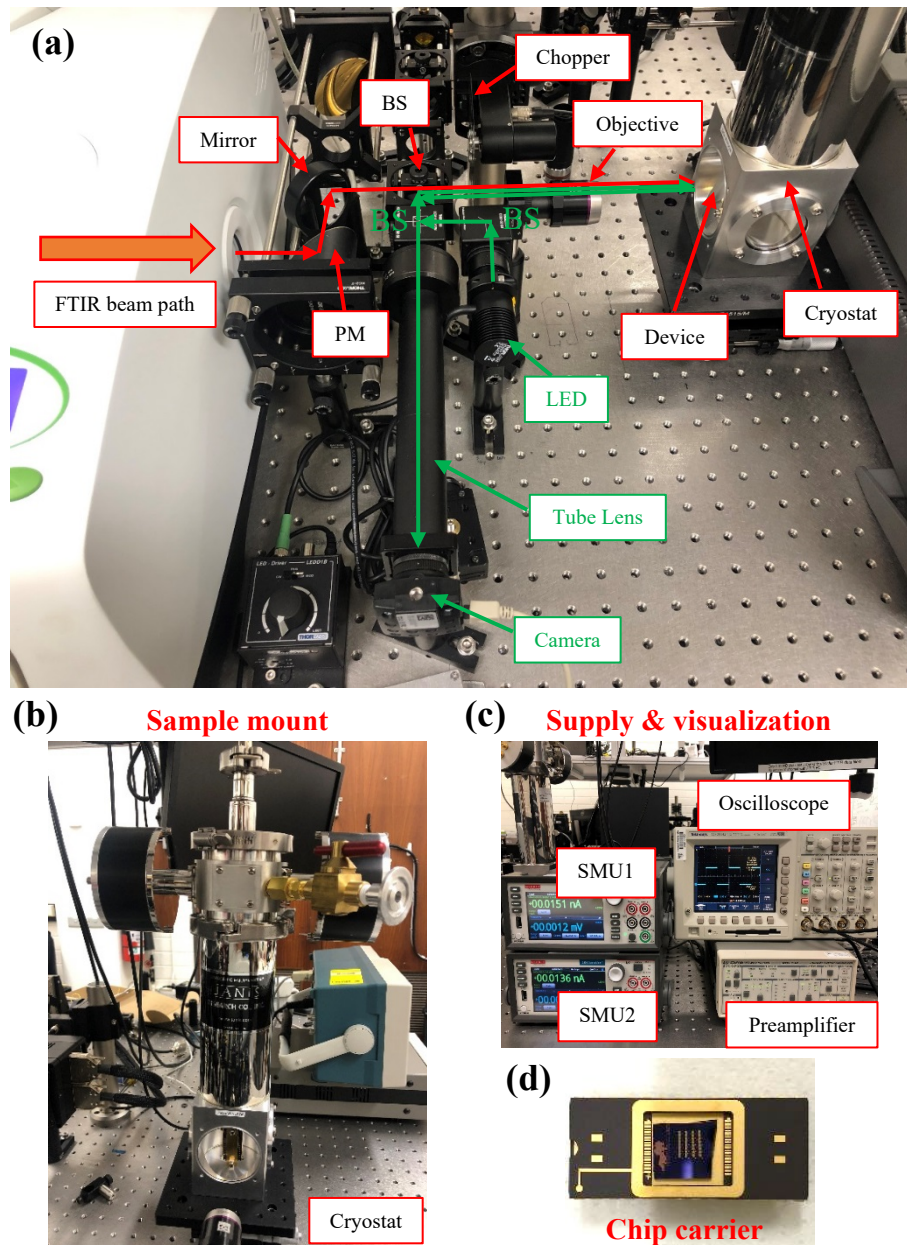


Figure 2.7. Photographs of the experimental setup and instruments for the electrical and optoelectronic characterization of graphene photodetectors. (a) Experimental setup for mid-infrared photoresponse characterizations. (b)

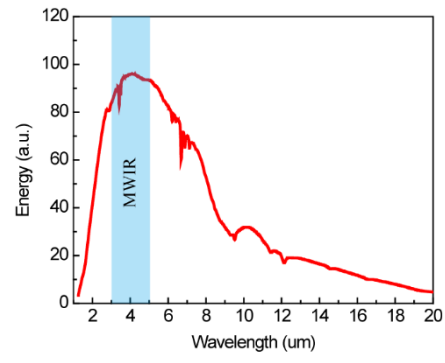


Figure 2.8. Energy spectrum of the globar source measured by a DTGS detector.

Chapter 3

Long-wave Infrared Magnetic Mirror Based on Mie Resonators on Conductive Substrate

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Long-wave infrared magnetic mirror based on Mie resonators on conductive substrate

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Abstract: Metal films are often used in optoelectronic devices as mirrors and/or electrical contacts. In many such devices, however, the π -phase shift of the electric field that occurs upon reflection from a perfect electric conductor (for which a metal mirror is a reasonable approximation) is undesirable. This is because it results in the total electric field being zero at the mirror surface, which is unfavorable if one wishes for example to enhance absorption by a material placed there. This has motivated the development of structures that reflect light with zero phase shift, as these lead to the electric field having an anti-node (rather than node) at the surface. These structures have been denoted by a variety of terms, including magnetic mirrors, magnetic conductors, and high impedance surfaces. In this work, we experimentally demonstrate a long-wave infrared device that we term a magnetic mirror. It comprises an array of amorphous silicon cuboids on a gold film. Our measurements demonstrate a phase shift of zero and a high reflectance (of $\sim 90\%$) at a wavelength of $8.4\ \mu\text{m}$. We present the results of a multipole analysis that provides insight into the physical mechanism. Lastly, we investigate the use of our structure in a photodetector application by performing simulations of the optical absorption by monolayer graphene placed on the cuboids.

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1. Introduction

Structures that reflect light with zero phase shift of the electric field have drawn much attention in recent years. These are often referred to as magnetic mirrors, but also as magnetic conductors and high impedance surfaces. Early work included radio frequency designs pursued for the goal of suppressing propagating surface waves and for the realization of low profile antennas [1, 2]. More recent investigations [3-15] have explored other structures and other applications, and have included experimental studies in the visible, infrared, and terahertz portions of the electromagnetic spectrum. These previous works have generally fallen into two categories. In the first, metals are employed [4-9]. By introducing corrugations into the metal, it becomes possible for the incident light to be coupled into surface plasmon polariton modes, and for these to be subsequently coupled back out to free-space propagating modes. By choosing the geometric parameters of the corrugations appropriately, the reflected beam can be made to have the desired phase shift (of zero) at the target wavelength. In the second, high index dielectric nanoparticles supporting resonances (akin to Mie resonances of spheres) are used [10-15]. The reflected wave can be then thought of as the envelope comprising the sum of the scattered waves generated by these resonances. Judicious choice of nanoparticle geometry and material permits these resonances to be tuned, allowing control over the phase of the scattered light and thereby achieving the desired functionality. This approach benefits from recent work on nano-optical devices based on nanoparticles with high refractive indices [16-23]. The theoretical foundations for this approach have a long history, e.g. with Lewin showing in 1946 that non-unity

permeability could be achieved with an array of non-magnetic, sub-wavelength dielectric resonators [24]. Phase modulators operating in reflection mode based on nano-optics have also been demonstrated [25, 26]. These [25, 26] and related previous works can achieve the desired zero phase shift, but often reflect light poorly as they operate near the perfect absorption regime.

For conventional metal mirrors, electromagnetic boundary conditions force a π -phase shift of the electric field upon reflection (in the ideal case that the metal can be considered as a perfect electric conductor). For the magnetic mirror, boundary conditions lead to a π -phase shift of the magnetic field, rather than electric field. As a result, when a magnetic mirror is illuminated by a plane wave, the total electric field has an anti-node at the surface. Because of this unusual property, magnetic mirrors can be much more effective than conventional metal mirrors as reflectors in optoelectronic devices for which strong light-matter interaction (e.g. absorption or emission) near the mirror surface is desirable. These structures have been thus pursued for applications that include solar cells [5], enhanced photoluminescence [7], surface-enhanced Raman scattering [8] and tunable photodetectors [9]. In previous works [3-15], it has generally been the case that either the metal or the dielectric material is patterned to realize the magnetic mirror. However, for many optoelectronic devices, it would be advantageous to realize a multi-functional magnetic mirror from hybrid structures containing both metals and dielectrics, with the metal acting as both an electrical conductor and a broadband optical reflector and the dielectric structures providing flexible tunability of the reflected wave-front, e.g. control over phase, amplitude, polarization, and radiation pattern. This approach would also be timely, given the recent trend toward optoelectronic devices that employ ultra-thin active regions, e.g. comprising two dimensional materials. These have included photodetectors [27-34] for the mid-wave and long-wave infrared (MWIR and LWIR). The use of very thin materials is partly motivated by the principle, well-established for MWIR and LWIR detectors [35], that reducing the volume of the active material in turn reduces the noise associated with thermal generation of charge carriers. Such materials, however, face the challenge of inherently weak optical absorption, which is exacerbated by the fact that it is generally desirable for them to be placed close to an electrical conductor (e.g. metal) for electrostatic gating. This motivates the development of an LWIR magnetic mirror that incorporates both high index semiconductor resonators and a metal film. This is the topic of this paper.

In this work, we harness the high reflectance of a conductive substrate (gold film) and the versatile scattering properties of high index Mie resonators (a-Si, i.e. amorphous silicon, cuboids) to achieve a thin LWIR magnetic mirror with high reflectance. A modified multipole analysis method is employed to provide insights into the resonances supported by the resonator when it is brought close to a perfect electric conductor (PEC) substrate. We experimentally demonstrate a LWIR magnetic mirror comprising an array of thin a-Si cuboids ($\sim 1.1 \mu\text{m}$ thick) on gold substrate that shows zero phase shift and high reflectance of $\sim 90\%$ at a wavelength of $8.4 \mu\text{m}$. We further show by simulation that the optical absorption in monolayer graphene placed on our structure is more than three orders of magnitude greater than the absorption that would result were the graphene instead placed on a gold mirror.

The organization of our paper is as follows. In the next section (Section 2), we describe the design of our LWIR magnetic mirror. The magnetic mirror functionality is based on the a-Si cuboids supporting magnetic dipole resonances. Excitation of these result in a boundary condition in which the electric field does not change sign upon reflection. In Section 2 we thus elucidate the physics of the scattering by our dielectric resonator (a-Si cuboid) when it is placed above a PEC substrate. We then present magnetic mirror designs that span the wavelength range

~ 6.6 to $12\ \mu\text{m}$. Results are shown as Figs 1-3. In Section 3, we describe the experimental realization of our magnetic mirror, including its fabrication and optical characterization. We measure the reflection spectrum of the fabricated device using a homebuilt infrared microscope interfaced to a Fourier transform infrared (FTIR) spectrometer. We measure the phase of the reflected beam using a homebuilt Michelson interferometer, with a quantum cascade laser as the light source. In Section 3, we also explore the potential application of using the magnetic mirror to enhance the light absorption in monolayer graphene via simulations. Results are shown as Figs 4-6. The conclusions of this study are provided as Section 4. We provide additional details on the multipole expansion method, sample fabrication, and optical characterization in the Appendix. These details may be of interest to specialists working in the field. Results are shown as Figs 7-10.

2. Design of LWIR magnetic mirror

It is well known that the tangential electric field on the surface of a perfect electric conductor (PEC) is zero [36]. There is thus a π -phase shift of the electric field upon reflection and an induced electric current on the PEC surface [36]. An analogous situation occurs for perfect magnetic conductors (PMCs). Regular materials do not function as PMCs, unlike the situation for PECs for which metals are a reasonable approximation. Nonetheless, PMCs are a useful conceptual tool for electromagnetics problems. The tangential magnetic field is zero on the surface of a PMC [36]. This leads to a π -phase shift of the magnetic field upon reflection and an induced magnetic current on the PMC surface [36]. The phase shift of the electric field upon reflection is zero. It has been previously shown that an array of dielectric resonators supporting magnetic dipole resonances could provide this functionality (e.g. [12]). One may think of the magnetic dipoles as serving the role of the magnetic current in the PMC case. In [12] and similar studies, the dielectric resonators were on substrates with relatively low refractive indices. As discussed, in this work our dielectric resonators are on conductive substrates. This modifies the multipole resonances of the particles [37-44]. In this Section, we describe the design of our LWIR magnetic mirror. To elucidate the physics on how the multipolar resonances are modified by the conductive substrate, we begin this Section by studying the scattering properties of our resonator as a function of its distance from a PEC. We next consider in greater detail the situation in which the resonator is on the PEC and contrast its scattering properties with the case of a resonator that is twice as thick and in a homogeneous medium. This Section concludes with the presentation of designs in which the conductive substrate is gold, i.e. a realistic metal rather than a PEC.

We begin by studying the scattering properties of an a-Si cuboid (thickness $D = 1\ \mu\text{m}$, side length $L = 3\ \mu\text{m}$) separated from a PEC surface by different distances. Figure 1(a) shows the four configurations we study where the a-Si cuboid is at distances $H = 0, \lambda/12, \lambda/6, \lambda/2$ ($\lambda = 10.5\ \mu\text{m}$) above the PEC surface. The origins of coordinate system, denoted as O1, O2, O3, O4, are chosen to be the points at which the perpendicular bisector of the cuboid crosses the PEC surface. Illumination is from a normally-incident plane wave linearly polarized along the x axis. In our calculation, the background field is taken as the standing wave distribution produced by the PEC upon plane wave illumination, i.e. without the a-Si cuboid. The total field is that occurring with both the PEC and the a-Si cuboid under plane wave illumination. The scattered field is the difference between the total field and the background field. Due to the presence of the PEC surface, conventional multipole analysis method - which deals with scatterers in homogeneous environments - cannot be directly applied. To apply multipole analysis in our case, we replace the PEC surface with image multipole sources based on the method of images. The

corresponding image multipole coefficients can be found and related to the original multipole coefficients (calculated for a-Si cuboid by conventional method) using the PEC boundary condition.

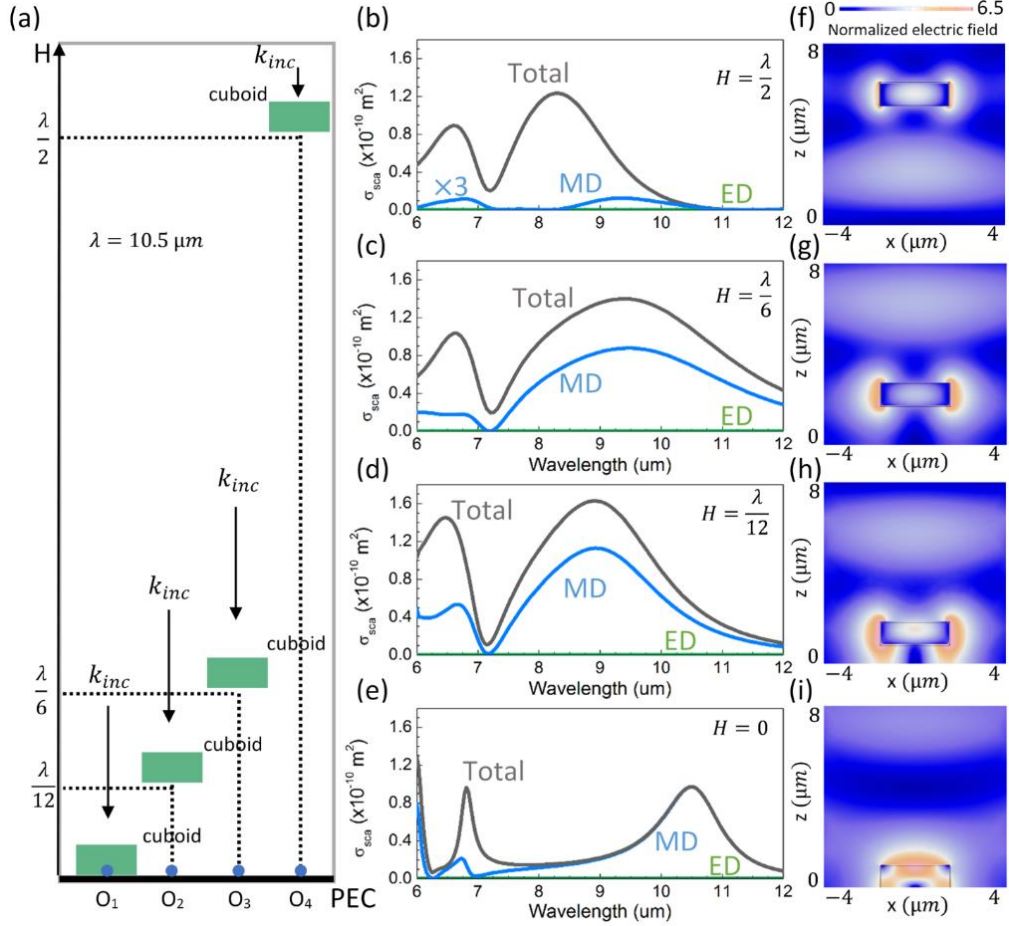


Fig. 1. Multipole analysis of scattering from a-Si cuboid ($D = 1 \mu\text{m}$, $L = 3 \mu\text{m}$) above PEC surface. (a) Schematic of scattering configurations with a-Si cuboid above PEC surface at different height $H = 0, \lambda/12, \lambda/6, \lambda/2$ ($\lambda = 10.5 \mu\text{m}$). O_1, O_2, O_3, O_4 are coordinate origins of the four configurations. (b-e) Total scattering cross section σ_{sca} (black curve) calculated by integrating Poynting vector over the surface of cuboid and partial scattering cross sections of electric dipole (ED, green curve) and magnetic dipole (MD, blue curve) components, calculated using the modified multipole expansion method for the four configurations of panel a. In panel b, a factor of 3 is applied to MD contribution for better visualization. (f-i) Normalized electric field distribution on cross section ($8 \mu\text{m} \times 8 \mu\text{m}$) through a-Si cuboid, calculated at wavelength corresponding to those of the longer-wavelength peak in MD scattering spectra of panels (b-e).

The scattering of the a-Si cuboid can thus be decomposed into a new set of multipole scatterings with modified multipole coefficients (see Appendix A1 for derivation) that are given as follows

$$\alpha_E^{\text{mod}}(l, m) = [1 - (-1)^{l+m}] \alpha_E(l, m) \quad (1)$$

$$\alpha_M^{\text{mod}}(l, m) = [1 + (-1)^{l+m}] \alpha_M(l, m) \quad (2)$$

where, $\alpha_{E,M}^{\text{mod}}(l, m)$ are the modified electric and magnetic multipole coefficients with order l and degree m . $\alpha_{E,M}(l, m)$ are the conventional multipole coefficients [45]. We note that we previously developed a related multipole expansion method for dielectric resonators on PECs and employed it in the visible wavelength range for structural color applications [43]. Details on the differences between the two methods are given in Appendix A1.

The calculated total scattering cross sections σ_{sca} and multipolar scattering cross section components are shown as Fig. 1(b-e). For clarity, only electric dipole (ED) and magnetic dipole (MD) are shown here, with the results for higher order multipole contributions provided in the Appendix (see Fig. 9). It can be seen that for all the cases, ED scattering contributions are negligible as the original electric dipole and its image cancel each other. Large MD scattering contributions can be seen and become more dominant as the cuboid is brought closer to the PEC surface. When the cuboid is on the PEC surface ($H = 0 \mu\text{m}$), the MD contribution accounts for almost the entirety of the scattering of the cuboid at the wavelength of the spectral peak ($\lambda = 10.5 \mu\text{m}$, Fig. 1(e)), which is important for the design of magnetic mirror. Figure 1(f-i) show the electric field profile at wavelengths corresponding to those of the longer-wavelength peak in the MD scattering spectra of Fig. 1(b-e). The characteristic field pattern of an MD resonance is visible and becomes stronger as the cuboid is brought closer to the PEC, which is consistent with the scattering cross section calculation.

The advantages of placing the cuboid directly onto a PEC surface can be further seen by comparing its multipolar scattering behavior to that of a cuboid in air. Figure 2(a,b) show the calculated total scattering cross section and multipolar contributions (up to octupolar order) for two cases: an a-Si cuboid ($D = 2 \mu\text{m}$, $L = 3 \mu\text{m}$) in air (Fig. 2(a)) and an a-Si cuboid (half as thick $D = 1 \mu\text{m}$, $L = 3 \mu\text{m}$) on a PEC surface (Fig. 2(b)). For both cases, the multipole calculation of the total scattering cross section matches perfectly with that calculated using the Poynting method, in which we integrate the Poynting vector over a closed surface surrounding the cuboid. This verifies the validity of our modified multipole analysis method. Note that for the case of the cuboid in air, the coordinate origin is chosen to be the cuboid center. Some interesting facts can be seen from the results. It can be seen that, due to their distinct mirror symmetry properties, the interaction of different multipoles with their corresponding images (resulting from the PEC) leads to either cancellation or enhancement of the overall scattering. More specifically, for the case of the cuboid on PEC, the scattering strengths of the ED, magnetic quadrupole (MQ) and electric octupole (EO) are strongly diminished, while the scattering strengths of the MD, electric quadrupole (EQ) and magnetic octupole (MO) are retained and approximately doubled. Of particular interest is the retention and enhancement of the MD when the cuboid is on the PEC. This can be understood conceptually by the schematic illustration of Fig. 2(d), i.e. the PEC can be thought of as supporting image electric fields that mirror the electric fields of the cuboid on the PEC, resulting in the formation of a circulating electric field pattern, i.e. an MD configuration. These resemble the MD that occurs when the cuboid is in air. These observations are consistent with our previous study [43] at shorter wavelengths that was motivated by

structural color applications. Figure 2(c,d) show the electric field profiles at MD resonance wavelength for the two cases corresponding to Fig. 2(a,b) respectively. The suppression/enhancement of the electric dipole/magnetic dipole contribution and reduction (50%) of structure thickness for the cuboid on PEC are beneficial for the realization of the magnetic mirror functionality.

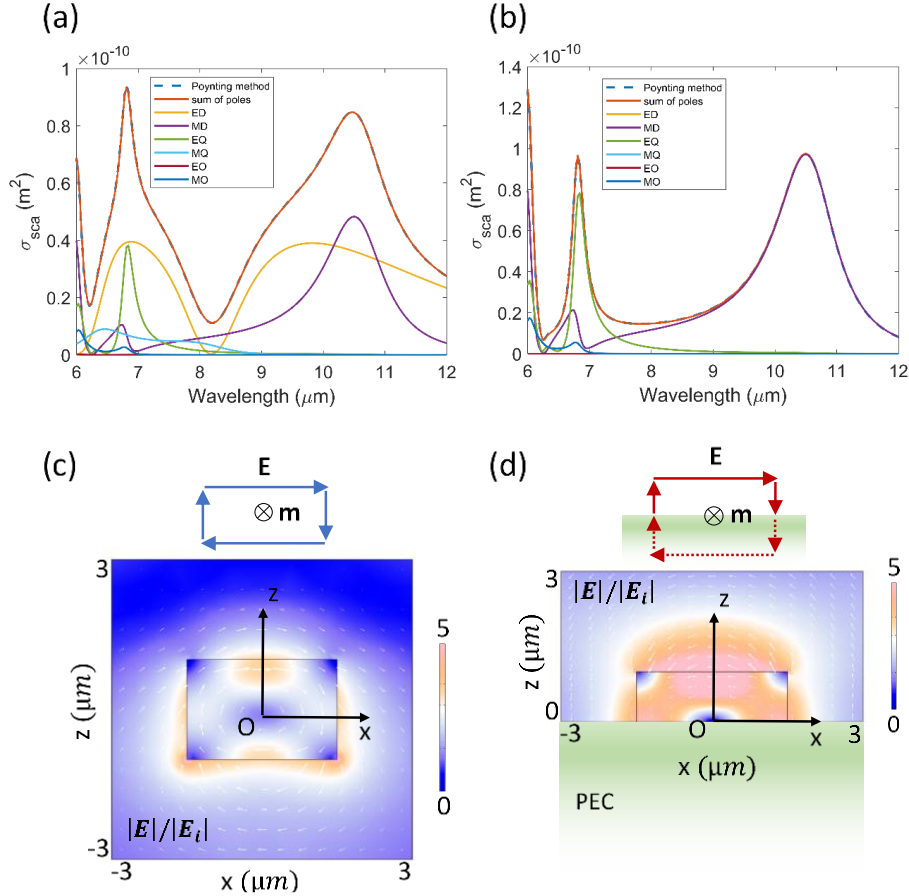


Fig. 2. Multipole analysis of scattering from (a) an a-Si cuboid ($D = 2 \mu\text{m}$, $L = 3 \mu\text{m}$) in air and (b) an a-Si cuboid ($D = 1 \mu\text{m}$, $L = 3 \mu\text{m}$) on PEC surface. (c,d) Normalized electric field magnitude profiles on cross section ($6 \mu\text{m} \times 6 \mu\text{m}$ in (c), $6 \mu\text{m} \times 3 \mu\text{m}$ in (d)) through the cuboid center in XZ plane are shown at $\lambda = 10.5 \mu\text{m}$ for scenarios in (a,b) respectively.

The magnetic mirror structure we propose thus consists of a square array of a-Si cuboids on an Au film (100 nm thick) on a silicon wafer (Fig. 3(a)). We choose gold film to play the role of the PEC because of its high conductivity in the LWIR. We begin by simulating the reflectance and phase shift using the finite difference time domain method implemented in a commercial software package (FDTD Solutions, Lumerical). Figure 3 (b,c) show the simulated reflectance and phase shift spectra for structures consisting of cuboids with $D = 1 \mu\text{m}$ and $L = 1 \mu\text{m} - 4 \mu\text{m}$. The period of the (square) array is taken to be $2L$. For the phase calculation, the reference plane is taken to be the top surface of the cuboids. It can be seen that as we increase the cuboid side

length, the reflection dip caused by the MD resonance (green colored diagonal Fig. 3(b)) as well as the wavelength at which the reflection phase shift is zero (see Fig. 3(c)) red shift. Multipole resonances of order higher than the MD can also be seen at shorter wavelengths. The wavelength at which the phase shift is zero and its corresponding reflectance are plotted as a function of cuboid side length as Fig. 3(d). It can be seen that magnetic mirrors (i.e. zero phase shift) with high reflectance (e.g. 96% at $\lambda = 6.6 \mu\text{m}$) can be achieved over a range of wavelengths that span the LWIR by properly choosing the structure parameters. Interestingly, the reflectance in (Fig. 3(d)) increases as the cuboid side length decreases, which is due to the reduction of MD strength as a result of the mismatch between the cuboid dimension and the excitation wavelength.

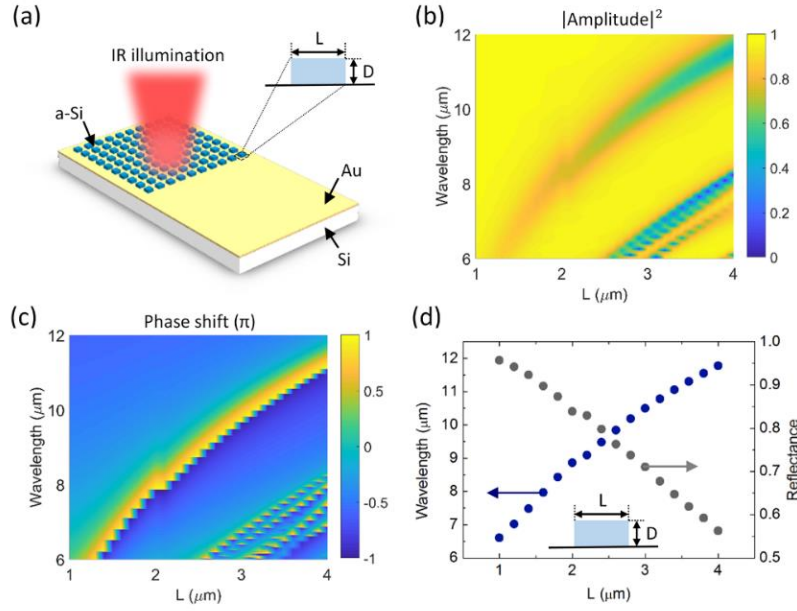


Fig. 3. (a) Schematic of proposed LWIR magnetic mirror. Simulated reflectance (b) and phase shift (c) of magnetic mirror structures with cuboid thickness $D = 1 \mu\text{m}$ and side length $L = 1\text{--}4 \mu\text{m}$. Period of the structure is $2L$. Top surface of the cuboid is selected as the reference plane for the phase shift calculation. (d) Extracted zero phase shift wavelengths and corresponding reflectance from panels b and c.

3. Experimental demonstration of LWIR magnetic mirror

To demonstrate the magnetic mirror experimentally, we fabricate a series of samples with cuboid thickness $D = 1.1 \mu\text{m}$, and side lengths $L = \{1.4 \mu\text{m}, 1.5 \mu\text{m}, 1.6 \mu\text{m}, 1.7 \mu\text{m}, 1.85 \mu\text{m}, 2 \mu\text{m}\}$. Fabrication starts with deposition of Au (100 nm thick) and a-Si (1.1 μm thick) films onto a silicon wafer by electron beam evaporation and plasma-enhanced chemical vapor deposition, respectively. An Al (30 nm thick) etch mask is then added by electron beam lithography, evaporation and lift off. The a-Si film is then etched down to the Au surface by inductively coupled reactive ion etching. Wet etching is then used to remove the Al mask. Figure 4(a) shows the scanning electron microscope (SEM) images of a completed magnetic mirror sample. A well-defined cuboid array is fabricated uniformly over a large area. We measure reflection spectra using a homebuilt microscope attached to a Fourier transform

infrared (FTIR) spectrometer (Fig. 4(b)). For comparison, we simulate the reflection spectra of structures with the same cuboid thickness and side length as that fabricated. The reflectance in both the simulation and measurement are obtained by using the reflectance from a gold film as the reference. It can be seen that the simulated reflection spectra (Fig. 4(c)) match well with the measured spectra in terms of the reflection dip position. The dips of the measured spectra are slightly deeper than those of simulations, however. This might be caused by fabrication imperfections. The small dips that appear at shorter wavelengths in the measurement might be a consequence of the illumination in our set-up not being purely at normal incidence [46].

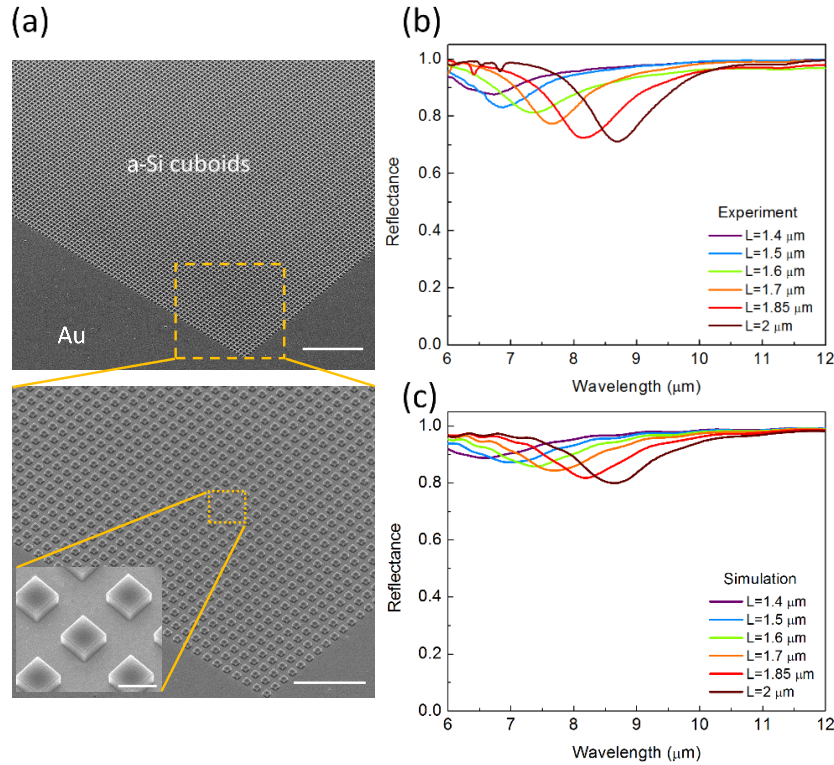


Fig. 4. (a) SEM images (tilted view) of fabricated magnetic mirror sample containing cuboids with side length $L = 1.7 \mu\text{m}$ and thickness $D = 1.1 \mu\text{m}$. Scale bars: 50 μm , 20 μm and 2 μm respectively. (b,c) Measured and simulated reflection spectra of magnetic mirrors containing cuboids with cuboid dimensions $D = 1.1 \mu\text{m}$ and $L = \{1.4 \mu\text{m}, 1.5 \mu\text{m}, 1.6 \mu\text{m}, 1.7 \mu\text{m}, 1.85 \mu\text{m}, 2 \mu\text{m}\}$.

To determine the phase shift of our magnetic mirror samples, we employ an interferometric method based on a homebuilt infrared Michelson interferometer system that employs a quantum cascade laser (QCL) operating at $\lambda = 8.4 \mu\text{m}$. The two interfering beams are from a gold mirror (whose position is scanned) and from the sample under test. Using this setup, we measure interferograms from the magnetic mirror samples and from a gold reference sample. These interferograms consist of the photodetector signals measured as a function of position of the scanning gold mirror. The relative phase of the reflection between a magnetic mirror sample and the gold reference sample is retrieved by comparing the interferograms. Two of the

measured interferograms are shown in the inset of Fig. 5(a). The top interferogram (blue dots) is from a magnetic mirror sample (with $D = 1.1 \mu\text{m}$ and $L = 1.7 \mu\text{m}$). The bottom interferogram (green dots) is from the gold reference sample. We fit the measured interferograms to sinusoidal functions, from which we extract the relative phase of reflection from different samples. Note that the height difference (of $1.1 \mu\text{m}$) between the gold reference sample and the magnetic mirror samples is taken into account in the phase determination. This height difference arises from the fact that the gold reference sample comprises a region of the magnetic mirror chip in which there are no a-Si cuboids (i.e. beam reflects from gold film). The results for our phase shift measurements are shown as Fig. 5(a). It should be noted that these results take the phase shift of reflection from the gold reference sample to be $-\pi$. The measured phase shifts of the fabricated samples vary from -0.12π to 0.69π as the cuboid side length increase from $1.4 \mu\text{m}$ to $2 \mu\text{m}$, which is in reasonable agreement with the simulation. It can be seen that the desired zero phase shift, i.e. magnetic mirror functionality, is realized for the sample with cuboid side length $L = 1.7 \mu\text{m}$. Figure 5(b) shows simulated and measured reflectance at the operating wavelength ($8.4 \mu\text{m}$). The measurements (of Fig. 5(b)) are extracted from the spectra of Fig. 4(c). It can be seen that the measured reflectance for the sample with the magnetic mirror behavior ($L = 1.7 \mu\text{m}$) is as high as 90%. Possible reasons for the small optical losses include absorption in a-Si cuboids and the ohmic loss in the metal caused by the near field coupling between cuboids and the gold substrate on magnetic dipole resonance.

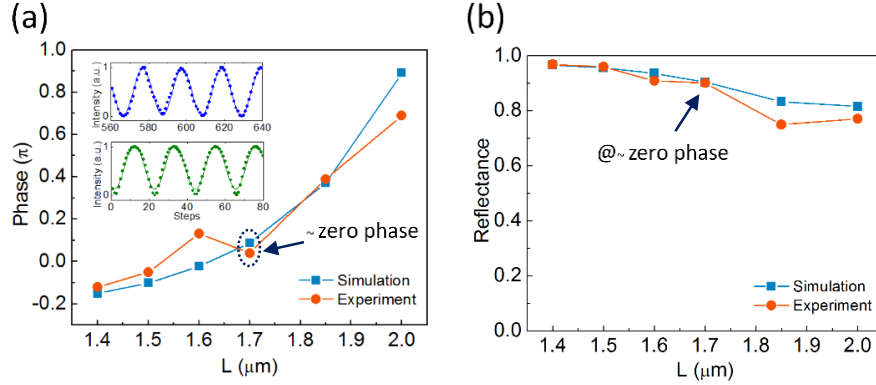


Fig. 5. Measured and simulated phase shift (a) and reflectance (b) at $8.4 \mu\text{m}$ for samples with $D = 1.1 \mu\text{m}$, and $L = 1.4 - 2 \mu\text{m}$. Inset of (a) shows the interferograms from a magnetic mirror sample with $D = 1.1 \mu\text{m}$, and $L = 1.7 \mu\text{m}$ (top) and a gold reference sample (bottom).

To investigate a potential application of our magnetic mirror, we study its use to increase the optical absorption in monolayer graphene placed directly on it via simulations. For comparison, we consider two other cases, in which the graphene monolayer is situated in free space and in which it is placed on a gold mirror. The results are shown as Fig. 6(a) and consist of the absorption spectra simulated for monolayer graphene placed on the magnetic mirror designs we consider in this paper (a-Si cuboids on gold). The cuboids have $D = 1 \mu\text{m}$, and $L = 1 - 2.2 \mu\text{m}$ in steps of $0.2 \mu\text{m}$ (solid curves). It can be seen that the absorption in graphene is strongly enhanced at wavelengths corresponding to zero phase shift wavelengths of the magnetic mirrors (Fig. 6(b)). Further details on the simulation method are provided in Appendix A3.2. The peak

absorption of each device is around four times greater than that of the graphene suspended in air (grey dashed curve in Fig. 6(a)). The peak absorption is around three orders of magnitude larger than the case when graphene is on a gold mirror (grey dotted curve in Fig. 6(a)). This is a direct result of the enhancement of the electric field intensity (roughly four times of incident field intensity) at the surface of the magnetic mirror when it reflects light with zero phase shift. Likewise, due to the electric field intensity being very small on the gold surface, absorption in graphene is strongly suppressed when it is placed on a gold mirror. In a photodetector application, the use of our magnetic mirror would allow the graphene to be electrostatically gated (by applying a voltage to the metal) while allowing optical absorption to be substantial. We furthermore note that while in each device of Fig. 6, cuboids have the same design, this does not have to be the case. One could for example have a device in which the cuboid side length is varied to produce a phase shift distribution akin to that of a concave mirror, i.e. so that the reflected wave is focused to a small spot in the device center, at which a photodetector could be located. In this way, magnetic mirrors could perform the function normally performed by microlenses in optically-immersed photodetector devices [35].

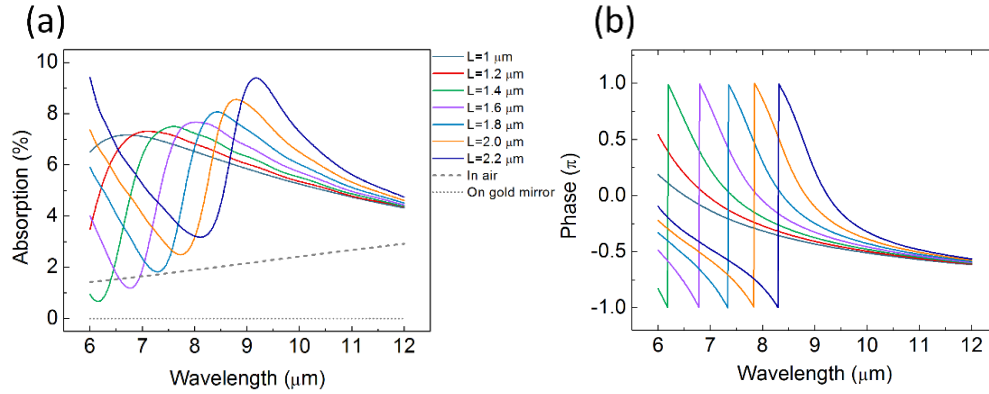


Fig. 6. (a) Absorption spectra for monolayer graphene placed on magnetic mirrors with cuboid parameters $D = 1 \mu\text{m}$, and $L = 1 - 2.2 \mu\text{m}$ in steps of $0.2 \mu\text{m}$ (solid curves), suspended in air (grey dashed curve) and on gold mirror (grey dotted curve). (b) Phase shift from magnetic mirrors considered in panel a.

4. Conclusions

In summary, in this work we describe a LWIR magnetic mirror that consists of an array of a-Si cuboids on a gold substrate. A modified multipole analysis method is employed to reveal the physical mechanism of the magnetic mirror functionality of the structure, showing efficient excitation of the magnetic dipole resonance of the cuboid on the PEC surface. The image effect (due to the presence of conductive substrate) allows us to use resonators that are half the thickness of dielectric resonators in a homogeneous environment. We fabricate magnetic mirror samples and demonstrate the magnetic mirror functionality at wavelength $\lambda = 8.4 \mu\text{m}$ from one of the samples (cuboid side length $L = 1.7 \mu\text{m}$, thickness $D = 1.1 \mu\text{m}$) by measuring the phase shift using a homebuilt Michelson interferometer. The magnetic mirror shows a measured phase shift of zero and reflectance of 90% at $\lambda = 8.4 \mu\text{m}$. The proposed magnetic mirror is also shown to offer significantly stronger light absorption for monolayer graphene placed on it than were

the graphene to be suspended in air or placed on a gold surface. Our findings provide important information for the development of thin and low-loss magnetic mirrors, especially in the long wave infrared (LWIR) spectral range.

Appendix

A1. Multipole analysis of scatterer above a perfect electric conductor (PEC) substrate

Multipole analysis is a well-established method and has proven successful for many scattering problems [40-42, 44, 45, 47, 48]. Nonetheless, most conventional multipole analysis methods have the constraint of requiring the scatterer to be situated in a homogeneous environment. In case of the scatterer being situated in an inhomogeneous environment, such as being above a perfect electric conductor (PEC) substrate, conventional methods cannot be directly applied. For this reason, various approaches have been developed to study light scattering by scatterers in the presence of a substrate. Early efforts include studies of simple geometries such as a circular cylinder parallel to a reflecting flat surface illuminated by a plane wave [38,39]. In these works, a cylindrical-wave approach is employed to decompose the fields. This takes into account the fields reflected from the surface. But multipole contributions to the scattering are not investigated in this approach, and the method imposes restrictions on the geometry and orientation of the scatterer, i.e. an infinite cylinder parallel to the reflective surface. Multipole analysis of light scattering by arbitrary-shaped nanoparticles located near or on a plane surface is studied up to the orders of magnetic quadrupole and electric octupole based on the decomposed discrete dipole approximation method, where the induced polarization is decomposed into multipole moments around a point at the center of mass of the scatterer [40]. The multipole decomposition of the scattered field in the far-field zone is then obtained using the far-field approximation of Green's tensors for reflection from the surface. A method termed the generalized point-dipole approximation was devised to study substrate-induced resonant magnetoelectric effects for a dielectric sphere on a substrate [41]. In this method, the dielectric particle is replaced by a pair of point electric and magnetic dipoles located at the center of the particle with the substrate-modified polarizabilities that contain cross-coupling terms between electric and magnetic dipoles. The applicability of the method is limited for particles with certain geometries such as sphere or cylinder since the effective polarizabilities are expressed through Mie's dipole scattering coefficients. More recently, an analytical model based on a modified Mie theory is used to study the fields generated by plane-wave illumination of a dielectric cylinder above a reflective mirror [42]. The method neglects the near-field interaction between the cylinder and the mirror, thus requires the cylinder to be sufficiently away from the mirror. It also imposes restrictions on the shape of the scatterer as it is based on Mie's theory. Here we present a set of modified multipole coefficients that describe the scattering from a scatterer above a PEC substrate. These modified multipole coefficients are found by introducing a set of image multipole coefficients based on the method of images. The method we present is applicable for arbitrarily-shaped particles above a PEC surface with any direction of the incident wave. While we have employed it to study the scattering of a single particle on a PEC surface, it also can be applied for particles in an array on PEC surface in a manner similar to [45]. We note that in another paper we published [43], related work was shown, but with some differences. In that work, we studied the case of a scatterer on the PEC substrate (situated in the YZ plane). In this work, the presented method is employed to study the case of a scatterer above (with separation) the PEC substrate (situated in the XY plane). In addition, in this work, we derive the result in a different way. We hope that the derivation we present in this paper will provide additional physical insight. The conventional multipole analysis method states that for a

monochromatic plane wave with electric field amplitude E_0 , angular frequency ω and wavevector $\mathbf{k}$, incident on a particle in an otherwise homogeneous lossless dielectric medium, the scattered electric field can be written in spherical coordinates in the form of multipole expansion [45]:

$$\mathbf{E}_s(\mathbf{r}) = E_0 \sum_{l=1}^{\infty} \sum_{m=-l}^l i^l [\pi(2l+1)]^{1/2} \left\{ \begin{aligned} & \frac{1}{k} \alpha_E(l, m) \nabla \times [h_l^{(1)}(kr) \mathbf{X}_{lm}(\theta, \varphi)] \\ & + \alpha_M(l, m) h_l^{(1)}(kr) \mathbf{X}_{lm}(\theta, \varphi) \end{aligned} \right\} \quad (3)$$

where $h_l^{(1)}(kr)$ is the spherical Hankel function of the first kind, $\mathbf{X}_{lm}(\theta, \varphi)$ is the normalized vector spherical harmonics, $\alpha_E(l, m)$ and $\alpha_M(l, m)$ are electric and magnetic multipole coefficients of order l and degree m respectively. The vector functions in the multipole expansion form a complete basis for representing the electromagnetic field outside an arbitrary localized source. Using the orthogonality of the basis, the multipole coefficients can be calculated as:

$$\alpha_E(l, m) = \frac{(-i)^{l-1} k^2 \eta O_{lm}}{E_0 [\pi(2l+1)]^{1/2}} \int e^{-im\varphi} \left\{ \begin{aligned} & [\varphi_l(kr) + \varphi_l''(kr)] P_l^m(\cos \theta) \hat{r} \cdot \mathbf{J}_{sca}(\mathbf{r}) \\ & + \frac{\varphi_l'(kr)}{kr} [\tau_{lm}(\theta) \theta \cdot \mathbf{J}_{sca}(\mathbf{r}) - i\pi_{lm}(\theta) \varphi \cdot \mathbf{J}_{sca}(\mathbf{r})] \end{aligned} \right\} d^3r \quad (4a)$$

$$\alpha_M(l, m) = \frac{(-i)^{l+1} k^2 \eta O_{lm}}{E_0 [\pi(2l+1)]^{1/2}} \int e^{-im\varphi} j_l(kr) [i\pi_{lm}(\theta) \theta \cdot \mathbf{J}_{sca}(\mathbf{r}) + \tau_{lm}(\theta) \varphi \cdot \mathbf{J}_{sca}(\mathbf{r})] d^3r \quad (4b)$$

$$\mathbf{J}_{sca}(\mathbf{r}) = -i\omega[\varepsilon(\mathbf{r}) - \varepsilon_h] \mathbf{E}(\mathbf{r}) \quad (4c)$$

where $\mathbf{E}(\mathbf{r})$ is the total electric field, ε_h is the permittivity of the host medium, $\varphi_l(kr) = kr j_l(kr)$ are the Riccati-Bessel functions, $P_l^m(\cos \theta)$ are the associated Legendre polynomials, and O_{lm} , τ_{lm} and π_{lm} are defined as follows:

$$O_{lm} = \frac{1}{[l(l+1)]^{1/2}} \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} \quad (5a)$$

$$\tau_{lm}(\theta) = \frac{d}{d\theta} P_l^m(\cos \theta) \quad (5b)$$

$$\pi_{lm}(\theta) = \frac{m}{\sin(\theta)} P_l^m(\cos \theta) \quad (5c)$$

The scattering cross section of the particle can thus be decomposed into multipole contributions by $\sigma_{sca} = \frac{\pi}{k^2} \sum_{l=1}^{\infty} \sum_{m=-l}^l (2l+1) [|\alpha_E(l, m)|^2 + |\alpha_M(l, m)|^2]$.

Consider the configuration of a particle with arbitrary size and shape in a homegeous medium above a PEC substrate that extends infinitely in the XY plane (Fig. 7(a)). The $z=0$ plane is

assumed to be the surface of the PEC substrate. A plane wave linearly polarized along the x direction ($\mathbf{E}_{ia} = E_0 \exp(-ikz)\hat{\mathbf{x}}$) is normally incident on the PEC substrate and is scattered by the particle. Here, a time dependence of $\exp(-i\omega t)$ is assumed. This scattering problem is fully specified by the electromagnetic field above the PEC (which satisfies the time harmonic form of Maxwell's equations) and the boundary condition at $z = 0$. These are given as follows:

$$\begin{cases} \nabla \times \mathbf{H} + i\omega(\epsilon + i\frac{\sigma}{\omega})\mathbf{E} = 0 \\ \nabla \times \mathbf{E} - i\omega\mu\mathbf{H} = 0 \\ \nabla \cdot (\epsilon\mathbf{E}) = 0 \\ \nabla \cdot (\mu\mathbf{H}) = 0 \end{cases} \quad (6)$$

$$\begin{cases} n \times \mathbf{E} = 0 \\ n \cdot \mathbf{H} = 0 \end{cases}, z = 0 \quad (7)$$

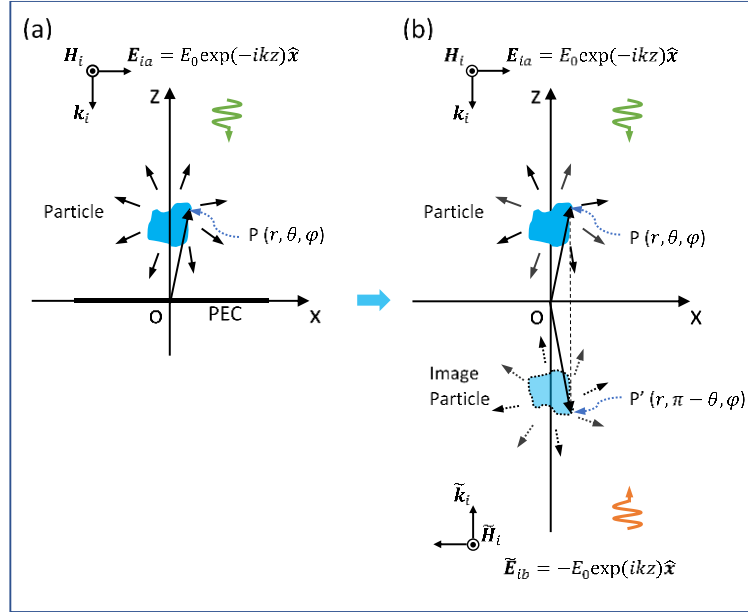


Fig. 7. Schematic illustration of two equivalent scattering problems. (a) Particle is above PEC ($z = 0$ plane) with x -polarized plane wave excitation. (b) Equivalent scattering problem, in which PEC is replaced by an image particle and image plane wave.

We first prove that this scattering problem is equivalent to the scattering problem described in Fig. 7(b), for which the PEC substrate is replaced by an image particle that mirrors the original particle with respect to $z = 0$, and an image source comprising a plane wave described by $\mathbf{E}_{ib} = -E_0 \exp(ikz)\hat{\mathbf{x}}$. The image source can be thought of as the wave reflected by the PEC, i.e. $\mathbf{E}_{ib} = \mathbf{E}_r$.

To prove this claim, we have to verify that in the new configuration, the field in the upper half space ($z \geq 0$) also satisfies Eqs. (6) and (7). By the principle of linear superposition, the scattered fields caused by the incident waves $\mathbf{E}_{ia}$, and $\mathbf{E}_{ib}$ can be considered separately. Suppose the solution of the scattering problem with incident wave $\mathbf{E}_{ia}$ is:

$$\begin{cases} \mathbf{E}_a(x, y, z) = E_x(x, y, z)\mathbf{x} + E_y(x, y, z)\mathbf{y} + E_z(x, y, z)\hat{\mathbf{z}} \\ \mathbf{H}_a(x, y, z) = H_x(x, y, z)\mathbf{x} + H_y(x, y, z)\mathbf{y} + H_z(x, y, z)\hat{\mathbf{z}} \end{cases} \quad (8)$$

By definition, this solution must satisfy Maxwell's equation (6). For the scattering problem with incident wave $\mathbf{E}_{ib}$, due to mirror symmetry of the problem, its solution can be related to the solution in Eq. (8) as follows:

$$\begin{cases} \mathbf{E}_b(x, y, z) = -E_x(x, y, -z)\mathbf{x} - E_y(x, y, -z)\mathbf{y} + E_z(x, y, -z)\hat{\mathbf{z}} \\ \mathbf{H}_b(x, y, z) = H_x(x, y, -z)\mathbf{x} + H_y(x, y, -z)\mathbf{y} - H_z(x, y, -z)\hat{\mathbf{z}} \end{cases} \quad (9)$$

Since one can substitute the expressions for $\mathbf{E}_b$ and $\mathbf{H}_b$ (Eq. (9)) into Eq. (6) and quickly find that they also satisfy Maxwell's equations. Furthermore, $\mathbf{E}_{ib}$ and $\mathbf{E}_{ia}$ are also related to each other by Eqs. (8-9) because by definition $\mathbf{E}_{ib} = \mathbf{E}_r$. The total electric and magnetic field for the scattering problem in Fig. 7(b) are thus linear superpositions of the fields described in Eqs. (8-9)

$$\begin{cases} \mathbf{E}_{total} = \mathbf{E}_a + \mathbf{E}_b \\ \mathbf{H}_{total} = \mathbf{H}_a + \mathbf{H}_b \end{cases} \quad (10)$$

By substituting Eqs. (8) and (9) into Eq. (10), we can easily prove that the total field satisfy both Maxwell's equations (6) and boundary condition (7) at $z=0$. According to the uniqueness theorem, the solution described by Eq. (10) must be the same as the solution solved for configuration in Fig. 7(a). Thus, we have proven the two scattering problems illustrated in Fig. 7(a) and 7(b) are equivalent.

Since the new configuration (Fig. 7(b)) only consists particles in a homogeneous environment, we can apply conventional multipole analysis method directly. In this case, the multipole coefficients can be calculated from the electric fields in both the original particle and the image particle, with the incident field being the superposition of two counter propagating plane waves $\mathbf{E}_{ia}$ and $\mathbf{E}_{ib}$. Furthermore, since the fields above $z=0$ is the same for Fig. 7(a) and Fig. 7(b), the multipole coefficients calculated from fields in the original particle is also the same for the two configurations. We next find the relation between the multipole coefficients calculated from fields in the original particle and fields in the image particle, namely the relation between the original multipole coefficients and the image multipole coefficients.

Let us consider the equivalent configuration in Fig. 7(b). From the mirror symmetry relation in Eqs. (8-9), it can be understood that the total electric field described in Eq. (10) also satisfies mirror symmetry with respect to $z=0$,

$$\begin{cases} E_x(x, y, z) = -E_x(x, y, -z) \\ E_y(x, y, z) = -E_y(x, y, -z) \\ E_z(x, y, z) = E_z(x, y, -z) \end{cases} \quad (11)$$

The spherical components of the total electric field can be related to their Cartesian components as,

$$\begin{cases} E_r = \sin \theta \cos \varphi E_x + \sin \theta \sin \varphi E_y + \cos \theta E_z \\ E_\theta = \cos \theta \cos \varphi E_x + \cos \theta \sin \varphi E_y - \sin \theta E_z \\ E_\varphi = -\sin \varphi E_x + \cos \varphi E_y \end{cases} \quad (12)$$

With Eqs. (11-12), we can obtain the following relation in spherical coordinate,

$$\begin{cases} E_r(r, \theta, \varphi) = -E_r(r, \pi - \theta, \varphi) \\ E_\theta(r, \theta, \varphi) = E_\theta(r, \pi - \theta, \varphi) \\ E_\varphi(r, \theta, \varphi) = -E_\varphi(r, \pi - \theta, \varphi) \end{cases} \quad (13)$$

Let us denote the original multipole coefficients as $\alpha_E(l, m)$, $\alpha_M(l, m)$, and the image multipole coefficients as $\alpha'_E(l, m)$, $\alpha'_M(l, m)$. These can be calculated in the same way as Eqs. (4a-c),

$$\alpha_E^{(l)}(l, m) = \frac{(-i)^{l-1} k^2 \eta O_{lm}}{E_0 [\pi(2l+1)]^{1/2}} \int e^{-im\varphi} \left\{ [\varphi_l(kr) + \varphi_l''(kr)] P_l^m(\cos \theta) \hat{r} \cdot \mathbf{J}_{sca}(\mathbf{r}) + \frac{\varphi_l'(kr)}{kr} [\tau_{lm}(\theta) \theta \cdot \mathbf{J}_{sca}(\mathbf{r}) - i\pi_{lm}(\theta) \varphi \cdot \mathbf{J}_{sca}(\mathbf{r})] \right\} d^3r \quad (14a)$$

$$\alpha_M^{(l)}(l, m) = \frac{(-i)^{l+1} k^2 \eta O_{lm}}{E_0 [\pi(2l+1)]^{1/2}} \int e^{-im\varphi} j_l(kr) [i\pi_{lm}(\theta) \theta \cdot \mathbf{J}_{sca}(\mathbf{r}) + \tau_{lm}(\theta) \varphi \cdot \mathbf{J}_{sca}(\mathbf{r})] d^3r \quad (14b)$$

$$\mathbf{J}_{sca}(\mathbf{r}) = -i\omega[\varepsilon(\mathbf{r}) - \varepsilon_h] \mathbf{E}(\mathbf{r}) \quad (14c)$$

Note that in Eqs. (14a-b), the integration for the original multipole coefficients is over the volume of the original particle, while the integration for the image multipole coefficients is over the volume of the image particle. By substituting Eq. (14c) into Eqs. (14a-b), we have

$$\alpha_E^{(l)}(l, m) = \frac{(-i)^l \omega k^2 \eta O_{lm}}{E_0 [\pi(2l+1)]^{1/2}} \int e^{-im\varphi} [\varepsilon(\mathbf{r}) - \varepsilon_h] \left\{ [\varphi_l(kr) + \varphi_l''(kr)] P_l^m(\cos \theta) E_r(\mathbf{r}) + \frac{\varphi_l'(kr)}{kr} [\tau_{lm}(\theta) E_\theta(\mathbf{r}) - i\pi_{lm}(\theta) E_\varphi(\mathbf{r})] \right\} d^3r \quad (15a)$$

$$\alpha_M^{(l)}(l, m) = \frac{-(-i)^l \omega k^2 \eta O_{lm}}{E_0 [\pi(2l+1)]^{1/2}} \int e^{-im\varphi} j_l(kr) [\varepsilon(\mathbf{r}) - \varepsilon_h] [i\pi_{lm}(\theta) E_\theta(\mathbf{r}) + \tau_{lm}(\theta) E_\varphi(\mathbf{r})] d^3r \quad (15b)$$

Since the integration spaces for the original and image multipole coefficients possess a one-to-one correspondence, each integration point $P(r, \theta, \varphi)$ in the original particle corresponds to an image integration point $P'(r, \pi - \theta, \varphi)$ in the image particle. With Eq. (13) and the following symmetry properties for $P_l^m(\cos \theta)$, τ_{lm} , and π_{lm}

$$\begin{cases} P_l^m(\cos(\pi - \theta)) = (-1)^{l+m} P_l^m(\cos(\theta)) \\ \tau_{lm}(\pi - \theta) = -(-1)^{l+m} \tau_{lm}(\theta) \\ \pi_{lm}(\pi - \theta) = (-1)^{l+m} \pi_{lm}(\theta) \end{cases} \quad (16)$$

It can be easily shown that the image multipole coefficients and original multipole coefficients satisfy the following relation

$$\begin{cases} \alpha_E'(l, m) = -(-1)^{l+m} \alpha_E(l, m) \\ \alpha_M'(l, m) = (-1)^{l+m} \alpha_M(l, m) \end{cases} \quad (17)$$

Thus, we can define a new set of multipole coefficients as follows:

$$\begin{cases} \alpha_E^{\text{mod}}(l, m) = [1 - (-1)^{l+m}] \alpha_E(l, m) \\ \alpha_M^{\text{mod}}(l, m) = [1 + (-1)^{l+m}] \alpha_M(l, m) \end{cases} \quad (18)$$

with $\alpha_E(l, m)$ and $\alpha_M(l, m)$ being the original multipole coefficients that can be calculated from the field distribution in the original particle in Fig. 7(a).

The scattering cross section is then given:

$$\sigma_{\text{sca}} = \frac{\pi}{2k^2} \sum_{l=1}^{\infty} \sum_{m=-l}^l (2l+1) [|\alpha_E^{\text{mod}}(l, m)|^2 + |\alpha_M^{\text{mod}}(l, m)|^2] \quad (19)$$

where a factor of 2 is added in the denominator to account for the fact that only the scattering into the upper half space is relevant.

A2. Multipole expansion of scattering cross section for an amorphous silicon (a-Si) cuboid above PEC at different heights

Using the modified multipole coefficients derived in A1, we study the scattering properties of an a-Si cuboid with thickness $D = 1 \mu\text{m}$ and side length $L = 3 \mu\text{m}$ that is placed at different distances (H) from a PEC. This is also considered in Fig. 1 of the main manuscript, but only the dipole contributions are plotted there. Figure 8(a-d) show the multipole contributions to the scattering cross section when the cuboid is at distances of $H = \{0 \text{ nm}, 875 \text{ nm}, 1750 \text{ nm}, 5250 \text{ nm}\}$ above the PEC. The total scattering cross section is also calculated by the integral of the Poynting vector associated with scattered field over the surface of the cuboid, divided by the illumination intensity ("Poynting method"). Note that we only calculate the multipolar scattering cross section up to octupolar order. It can be seen that, for all cases considered, the contributions to the scattering cross section from the ED, MQ, and EO are strongly suppressed. On the other hand, scatterings from the MD, EQ and MO together account for nearly the entire scattering cross section. For the case $H = 5250 \text{ nm}$, the sum of the multipolar scattering cross sections (up to octupolar order, orange solid line of Fig. 8(d)) is less than the total scattering

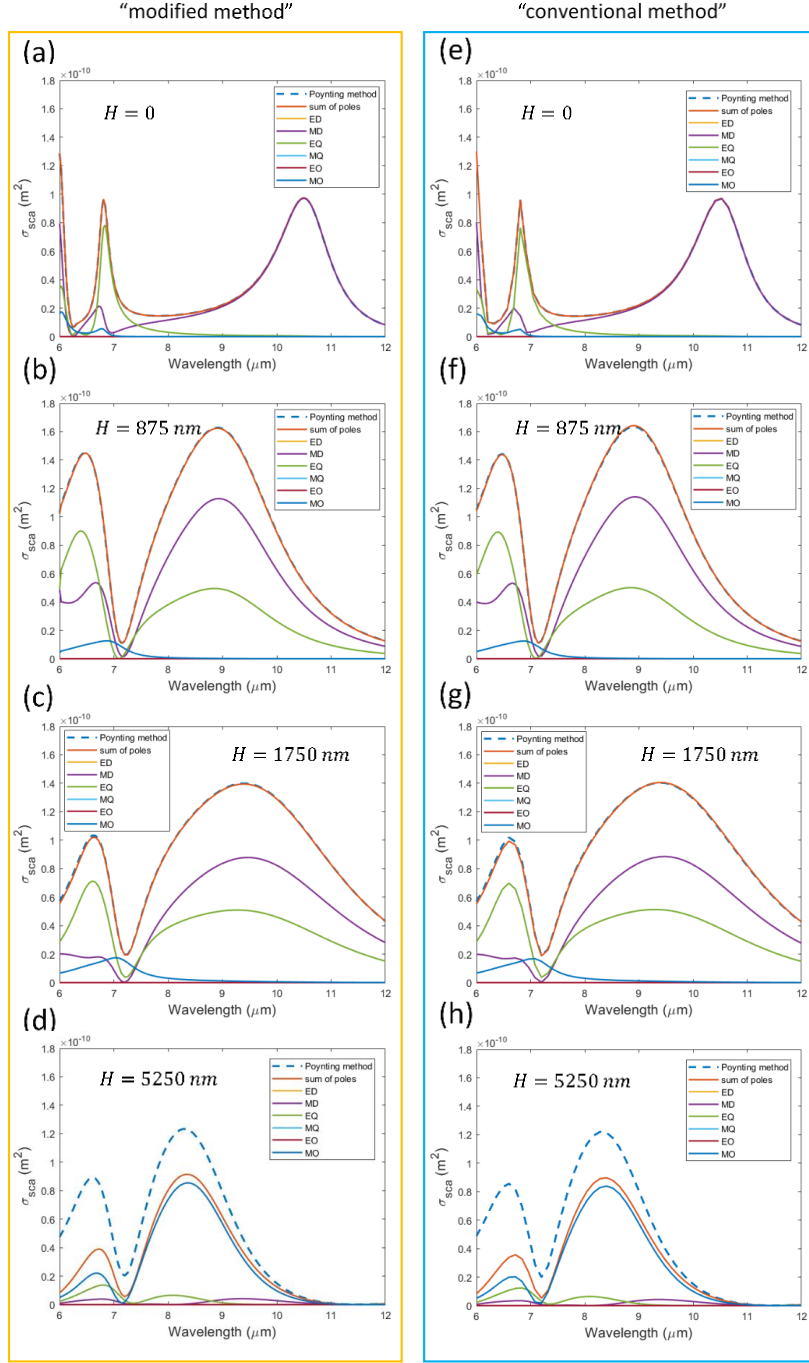


Fig. 8. Multipole expansion of scattering cross section for an a-Si cuboid ($D = 1 \mu\text{m}$, $L = 3 \mu\text{m}$) above PEC calculated using modified multipole coefficients at different heights (a) $H = 0 \text{ nm}$, (b) $H = 875 \text{ nm}$, (c) $H = 1750 \text{ nm}$, (d) $H = 5250 \text{ nm}$, and calculated using conventional method under the equivalent configuration as described in Fig. 7(b) for (e) $H = 0 \text{ nm}$, (f) $H = 875 \text{ nm}$, (g) $H = 1750 \text{ nm}$, (h) $H = 5250 \text{ nm}$. Total scattering cross section denoted “Poynting method” is calculated by integrating the Poynting vector over the surface of the cuboid and dividing the result by the illumination intensity. The curve labeled “sum of poles” is the summation of scattering cross sections from all multipoles considered (i.e. up to octupolar).

cross section (blue dashed line, Fig. 8(d)). This is because higher order multipoles (i.e. beyond octupolar) are non-negligible for $H = 5250 \text{ nm}$. The contribution to the scattering cross section from the MD becomes larger as the cuboid is brought closer to the PEC. Indeed, when the cuboid is on the PEC, the scattering cross section for wavelengths longer than $9 \mu\text{m}$ is dominated by the MD. In Fig. 8(e-h), we plot the result of performing the multipole expansion by applying the conventional method to two cuboids (original and image) illuminated with counter-propagating plane waves, i.e. the equivalent configuration described in Fig. 7. We can see the results agree with those calculated using our modified multipole coefficients (Fig. 8(a-d)).

A3. Electromagnetic simulations

A3.1. Scattering cross section of an a-Si cuboid above PEC

The calculation of scattering cross section of an a-Si cuboid above a PEC and its multipole expansion is done using a commercial finite element method software package (COMSOL). A three-step simulation is carried out in COMSOL. In the first step, we perform a full field simulation of a plane wave incident on an infinitely-extended PEC substrate without the cuboid and obtain the reflected field. Periodic boundary conditions are employed at the x - and y -boundaries of the simulation domain to mimic the infinite extent of the PEC. Perfectly matched layers (PMLs) are used at the z -boundaries. In the second step, we use the reflected field obtained in the first step as the background field and simulate the scattering of the a-Si cuboid above the PEC substrate with PMLs at all boundaries (x , y and z). The obtained scattered field is used to calculate the total scattering cross section of the cuboid by integrating the Poynting vector over the surface of the cuboid and normalizing it to the illumination intensity. In the last step, we implement the multipole analysis model in COMSOL with our modified multipole coefficients to calculate the multipolar scattering cross sections based on fields calculated in former steps. At the time of writing, a simple multipole expansion model based on the conventional method is also available at the following Internet link:

<https://www.comsol.com/model/multipole-analysis-of-electromagnetic-scattering-31901>

A3.2. Reflection, absorption and phase shift simulation

The simulations of amplitude and phase of the reflection coefficient in the main manuscript are carried out using the finite difference time domain method with a commercial package (FDTD Solutions, Lumerical). Periodic boundaries are applied at the x - and y -boundaries to simulate the square lattice of the cuboids. PMLs are used at the z -boundaries to avoid unwanted backscattering of the electromagnetic field. Illumination is from a plane wave at normal incidence. For the phase shift calculation, the top surface of the cuboids is chosen as the reference plane. The simulations of absorption spectra for monolayer graphene placed on magnetic mirrors are performed in FDTD, where the graphene is modelled based on a surface conductivity approach. The scattering rate and chemical potential of graphene are taken as 0.0427 eV and 0.1895 eV respectively in the simulation.

A4. Fabrication of long-wave infrared magnetic mirror

Figure 9 shows the fabrication process for the magnetic mirror. The fabrication starts with deposition of Ti (10 nm), Au (100 nm) films by electron beam evaporation (Intlvac Nanochrome II Electron Beam and Thermal Evaporation System) and deposition of a-Si (1.1 μm) film by Plasma-enhanced chemical vapor deposition (PECVD, Oxford Plasma Lab100) on a silicon

wafer. The cuboid arrays are then patterned in a PMMA layer (A4, 950K, 200 nm thick) layer by electron beam lithography (Vistec EBP5000 Plus EBL) and developed in 3:1 isopropanol–methyl isobutyl ketone (MIBK, 60 seconds). After that, Al is deposited to a thickness of 30 nm by evaporation and lift-off is performed, resulting in the etching mask. The sample is then etched by inductively coupled plasma reactive ion etching (Oxford Plasma Lab100 (ICPRIE)-General Etch) for 3 minutes and 25 seconds. The following gases are used: sulfur hexafluoride (SF₆, 40 sccm) and perfluorocyclobutane (C₄F₈, 90 sccm). The RF and ICP powers are 30 W and 1200 W, respectively. The remaining Al mask is etched away in Al etchant for 10 minutes.

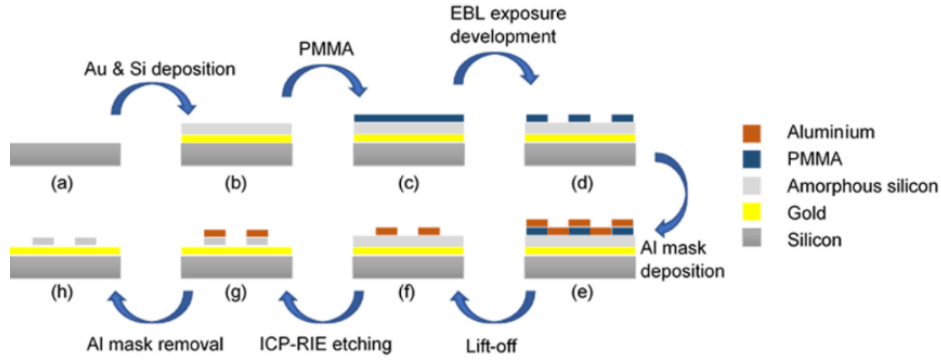


Fig. 9. Schematic of the fabrication process for magnetic mirror structures.

A5. Interferometry measurements

We use a home-built infrared Michelson interferometer as shown in Fig. 10(a) to measure the phase shift of light upon reflection from our magnetic mirror samples. A continuous-wave Fabry-Perot quantum cascade laser (QCL, ThorLabs) with center wavelength 8.4 μm is used as the light source. A ZnSe lens with a focal length of 100 mm is used to focus the laser beam through a ZnSe beam splitter (1 inch) onto the sample. The scanning Au mirror is mounted on a one-axis translation stage (ThorLabs XR25P-K2/M) driven by a Thorlabs PIA50 piezo inertial actuator. According to the manufacturer, this has a typical step size of 20 nm with a variation ~20%. The sample is mounted on another 3-axis motorized linear translational stage (Thorlabs LNR50S) with bidirectional repeatability of 0.3 μm and backlash less than 6 μm , which is sufficient for sample positioning. A liquid nitrogen cooled MCT detector from Infrared Associates is used to detect the light from the interferometer. A source meter unit (Keithley 2450) is used to provide bias voltage to the MCT detector and to measure the photocurrent. Control over the translation stages, source supply and current readout is achieved using a Matlab control script. Figure 10(b-d) show the interferograms measured for a gold reference sample and six magnetic mirror samples with cuboid thickness $D = 1.1 \mu\text{m}$, and cuboid side length L ranging from 1.4 μm to 2 μm . To avoid hysteresis of the piezo inertial actuator, the scanning mirror is scanned in one direction for all measurements. A height difference of 1.1 μm between the gold reference sample and the magnetic mirror samples is taken into account in the phase determination.

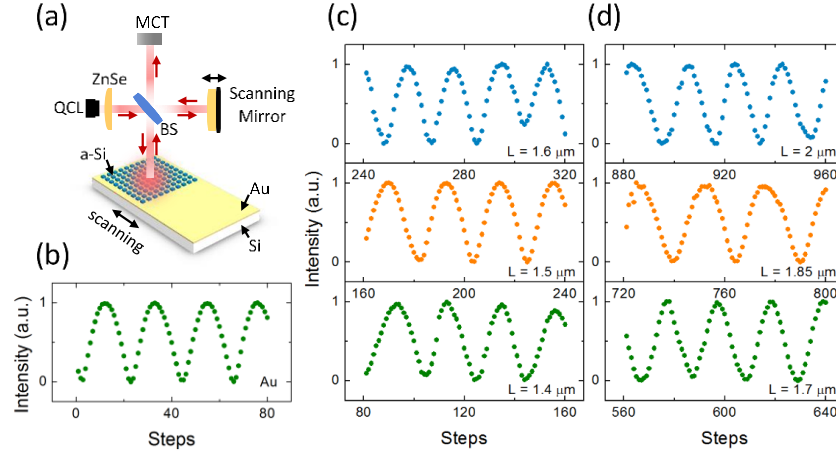


Fig. 10. (a) Schematic of the infrared Michelson interferometer setup for the phase measurement. (b-d) Measured interferogram for a gold reference sample (b) and magnetic mirror samples with cuboids ($D = 1.1 \mu\text{m}$, $L = 1.4 \mu\text{m}$, $1.5 \mu\text{m}$, $1.6 \mu\text{m}$) in (c) and cuboids ($D = 1.1 \mu\text{m}$, $L = 1.7 \mu\text{m}$, $1.85 \mu\text{m}$, $2 \mu\text{m}$) in (d).

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Appendix of Chapter 3

A3.1. Discussion on how the structure dimensions, shape and filling factor are chosen.

The basic guidance for choosing the dimensions of the a-Si cuboids is to demonstrate both magnetic mirror behaviour (zero-phase shift of reflection) and high reflectance in the long wave infrared (LWIR: $\lambda = 8\text{-}12\ \mu\text{m}$) spectral region. The general trend for the zero-phase shift condition is that the wavelength redshifts as the cuboid side length and thickness increases. We also find through simulation that the reflectance at the zero-phase shift wavelength reduces as the cuboid thickness decreases, perhaps due to the larger optical losses in the gold mirror due to stronger near field coupling from the magnetic dipole resonances in the cuboids to the gold mirror. Therefore, the thickness of the cuboids was chosen to be $\sim 1\ \mu\text{m}$ throughout the paper to permit a high reflectance (90% realized in experiment). In our multipolar scattering study in Fig. 1&2, the cuboid side length was chosen to be $3\ \mu\text{m}$ to demonstrate magnetic dipole resonance in approximately the middle of the LWIR region ($\lambda = 10.5\ \mu\text{m}$). Note that in our simulation in Fig. 3, we have studied more general cases with cuboid side length ranging from $1\text{-}4\ \mu\text{m}$. In our experiment, cuboid side lengths were chosen from $1.4\ \mu\text{m}$ to $2\ \mu\text{m}$ so that their magnetic dipole resonances span across a spectral region that includes the operating wavelength ($\lambda = 8.4\ \mu\text{m}$) of our QCL source. It was found that magnetic mirror device with cuboid side length of $1.7\ \mu\text{m}$ shows zero phase shift at the operating wavelength. The filling factor (50%) and square shape were simply chosen for the ease of structure fabrication.

A3.2. Discussion on the portions of the enhanced graphene absorption due to local field enhancement and due to graphene being at the anti-node of the reflected electric field.

The absorption for a graphene sheet placed at $\lambda/2$ above a regular mirror will be enhanced by 4 times because the field intensity is 4 times of the incident field intensity. Therefore, in our case, the absorption enhancement due to the graphene sheet being at the anti-node of the reflected electric field is 4 times. Our simulation (Fig. 6) shows a peak absorption enhancement factor of slightly larger than 4, e.g. 4.27 times for magnetic mirror device with cuboid side length of $2.2 \mu\text{m}$. Therefore, the absorption enhancement due to local field enhancement is very small in our case, e.g. $4.27/4 \approx 1.07$ times.

Chapter 4

Mid-wave infrared Polarization-Independent Graphene Photoconductor with Integrated Plasmonic Nanoantennas Operating at Room Temperature

Graphene photodetectors operating in the mid-wave infrared (MWIR, 3-5 μm) face challenges that include the optical absorption of monolayer graphene being intrinsically low and the carrier lifetime in graphene being very short. Previous reports of graphene photoconductors in the MWIR have sought to overcome these challenges using approaches that include the integration of plasmonic nanoantennas and/or engineered electrodes. However, this has led to the photoresponse of these detectors being strongly polarization dependent. Here, we report a graphene photoconductor that achieves polarization-independent response via the integration of plasmonic nanoantennas that we term Jerusalem-cross antennas (JC-antennas). These serve to concentrate the incident light onto graphene for polarization-independent optical absorption, as well as to collect the photocarriers. We demonstrate MWIR detection, both at room temperature and at cryogenic temperatures. In addition to the MWIR response, our device also shows a broadband photoresponse that extends to visible and near-infrared wavelengths, thanks to the carrier collection by the JC-antennas. We demonstrate a temporal response that would be sufficient for many applications (e.g. imaging), with a measured rise time of 11.4 μs .

4.1 Introduction

Graphene is an attractive material for developing high-speed photodetectors operating in the MWIR because of its gapless band structure and ultrafast carrier dynamics.¹¹⁻¹⁴ However, due to the intrinsically-low optical absorption (less than 2.3% in the MWIR)¹⁷³ and the short (sub-picosecond) lifetime of photocarriers in graphene, graphene detectors generally suffer from low responsivity.^{15, 16} This hinders the operation of graphene detectors in the MWIR due to the low signal-to-noise ratio at room temperature. Previous efforts have explored the benefits of charge trapping centres and photogating effects to improve the responsivity of graphene detectors operating in the MWIR regime.^{100, 101} However, this often comes at the expense of slow responses ($\sim$ ms) of the detectors due to the long carrier trapping time. Plasmonic nanoantennas²⁴ and engineered electrodes¹⁰³ have been demonstrated to improve the responsivities of graphene detectors while maintaining high operating speed by simultaneously enhancing the optical absorption and carrier collection efficiency in graphene. While this approach is promising, there is still much room for improvement. For instance, the detector response in these previous works was strongly polarization-dependent, due to the low symmetry of the employed nanoantennas and electrodes. In addition, the enhancement of the optical absorption was relatively modest, with the peak value of the absorption being only $\sim 10\%$.²⁴

Here, we demonstrate a polarization-independent graphene photoconductor with integrated Jerusalem-cross nanoantennas (JC-antennas). Our device shows significant MWIR photoresponse at room temperature, with further enhancement at cryogenic temperatures. Responsivities of 4.6 mA/W (14.5 V/W) and 1.9 A/W (4.4×10^3 V/W) are measured at room temperature and 78 K respectively. Unlike previous methods that relied on charge trapping centres or photogating effects, our approach, in which JC-antennas are

used to increase optical absorption and improve photocarrier collection, does not hinder the detector speed. We measure a rise time of 11.4 μs from our graphene photodetector. Compared to the low symmetric end-to-end rod antennas (two-fold symmetry) which were employed in previously reported detector,²⁴ our JC-antennas, with their elongated ends and narrower gaps (~ 40 nm) between adjacent antennas, render stronger optical absorption enhancement in the graphene. The simulated graphene absorption in our photodetector shows a peak absorption of 16.4% in the MWIR at $\lambda = 4.12$ μm , which is 64% and 167% larger than that occurring in the rod-antenna configuration of the previous study²⁴ for polarized and unpolarized light, respectively. Moreover, this absorption is polarization-independent due to the highly symmetric shape (four-fold symmetry) of the JC-antennas.¹⁷⁴ Thanks to the carrier collection by the JC-antennas, our device also shows strong and broadband photoresponse at visible and near-infrared wavelengths, with measured responsivities of ~ 28 AW^{-1} , 74 AW^{-1} and 118 AW^{-1} at wavelengths of 532 nm, 650 nm and 850 nm, respectively.

4.2 Device Geometry and Light Detection Mechanism

Figure 4.1a shows the architecture of our graphene photoconductor with integrated JC-antennas. The photoconductor consists of a graphene monolayer on a 285-nm thick silicon dioxide layer thermally grown on a highly doped silicon substrate (p-type, <0.005 $\Omega\cdot\text{cm}$). The graphene layer serves as both the charge transport channel and the light absorber. A square array of JC-antennas is formed on top of the graphene channel. Figure 4.1b shows a scanning electron microscope (SEM) image of a fabricated device (Dev#1), showing JC-antennas with well-defined shapes and ~ 40 nm gaps. The measured geometric parameters of the antennas are $P = 606$ nm, $W = 88$ nm, $E = 273$ nm, $G = 44$ nm. The working principle of the photodetector is as follows. Illumination of the device results in excitation of the plasmon resonance of the antennas, leading to enhanced fields

in the narrow gaps between the two long edges of adjacent antennas. This results in light absorption by the graphene and generation of electron-hole pairs, which are collected as photocurrent (with photoconductive gain) by the antennas/electrodes under the external voltage bias. We believe that thermal effects such as bolometric effect play negligible roles in contributing to the photocurrent generation in our device as the temperature coefficient of resistance (TCR) of single layer graphene is very small, i.e. below $0.147\%K^{-1}$ at room temperature.⁹⁶ Compared to previous works that employed end-to-end rod antennas,²⁴ our JC-antennas permit a polarization-independent absorption enhancement in graphene. Our design, with narrower and longer gaps between antennas, also enables a much larger absorption in graphene.

The reflectance spectrum (Fig. 4.1c, black curve) is measured by a Fourier transform infrared (FTIR) spectrometer coupled to a microscope and shows reasonable agreement with the simulated (finite difference time domain, FDTD) reflectance spectrum (Fig. 4.1c, red curve). The simulated graphene absorption spectrum (Fig. 4.1c, light blue curve) shows a peak absorption of 16.4% in the MWIR at $\lambda=4.12\ \mu m$, which is 64% and 167% larger than that occurring in the rod-antenna configuration of a previous study²⁴ for polarized and unpolarized light, respectively. The strong graphene absorption arises from the enhancement of the electric field intensity by the antennas (Fig. 4.1d-f). Due to the highly symmetric shape of our JC-antenna, strong field intensity can be generated for any incident polarization. Figure 4.1d-f show the normalized electric field intensity distributions for incident polarizations of 0° (Fig. 4.1d), 45° (Fig. 4.1e), and 90° (Fig. 4.1f) with respect to the x-axis. It can be seen that as the polarization changes from 0° through 45° to 90° , the region for strong field enhancement changes from the gaps along the y-axis to the gaps along the x-axis, maintaining strong light-graphene interaction and

thus total absorption. A maximum field intensity enhancement factor of $\sim 2 \times 10^3$ is achieved in Fig. 4.1d,f.

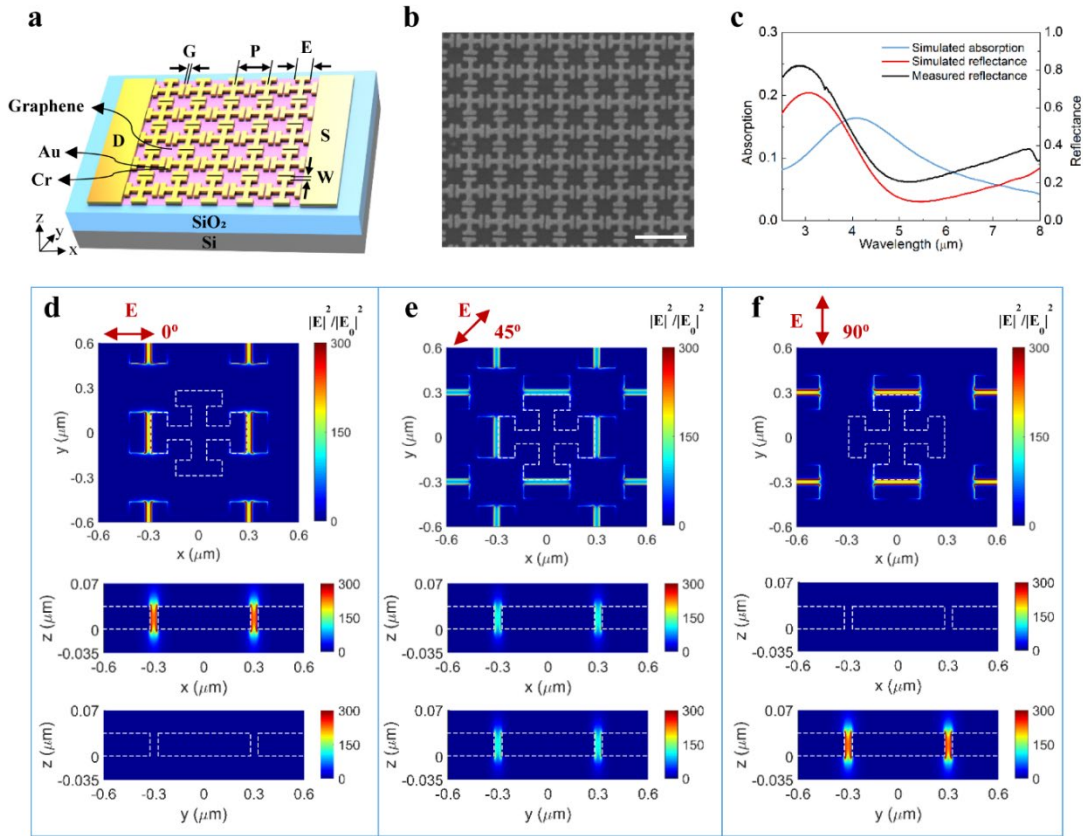


Figure 4.1. Design, characterization, and optical simulation of graphene photodetectors. a

Schematic of graphene photodetector with integrated JC-antennas. Graphene is on SiO₂ layer (285 nm thick) on highly doped Si substrate. **b** Scanning electron microscopy (SEM) image of fabricated graphene detector (Dev#1) with design values of $P = 600$ nm, width $W = 90$ nm, length $E = 270$ nm, gap $G = 40$ nm. Scale bar is 1 μ m. **c** Simulated device reflectance spectrum, simulated graphene absorption spectrum and measured device reflectance spectrum for the device described in **b**. In the simulation, scattering rate of 0.0282 eV and chemical potential of 0.1366 eV are used, which are obtained by fitting a model to the measured gate-dependent electrical conductivity (**d-f**) Normalized electric field intensity distributions for incident polarization of 0° (**d**), 45° (**e**) and 90° (**f**), with respect to x-axis. Graphene is located at $z = 0$ μ m. Top panel: field in graphene plane.

Middle & bottom panels: field in xz- & yz- plane, respectively, through middle of antenna. Fields are obtained at wavelength of peak absorption ($\lambda = 4.12 \mu\text{m}$) for structure with same parameters as that of (b). White dashed lines show contour of JC-antennas.

4.3 Polarization Independent Enhancement of Graphene Absorption

Figure 4.2 shows the simulated graphene absorption for the device described in Fig. 4.1b for incident polarizations of 0° (Fig. 4.2a), 45° (Fig. 4.2b), and 90° (Fig. 4.2c) with respect to x-axis. Due to the four-fold symmetry of our JC-antennas, the graphene absorption is polarization-independent, showing peak absorption of 16.4% for all three polarizations, as is clear in Fig. 4.2d. The polarization-independent absorption enhancement in graphene by the JC-antennas gives rise to the polarization-independent MWIR photoresponse of our detectors.

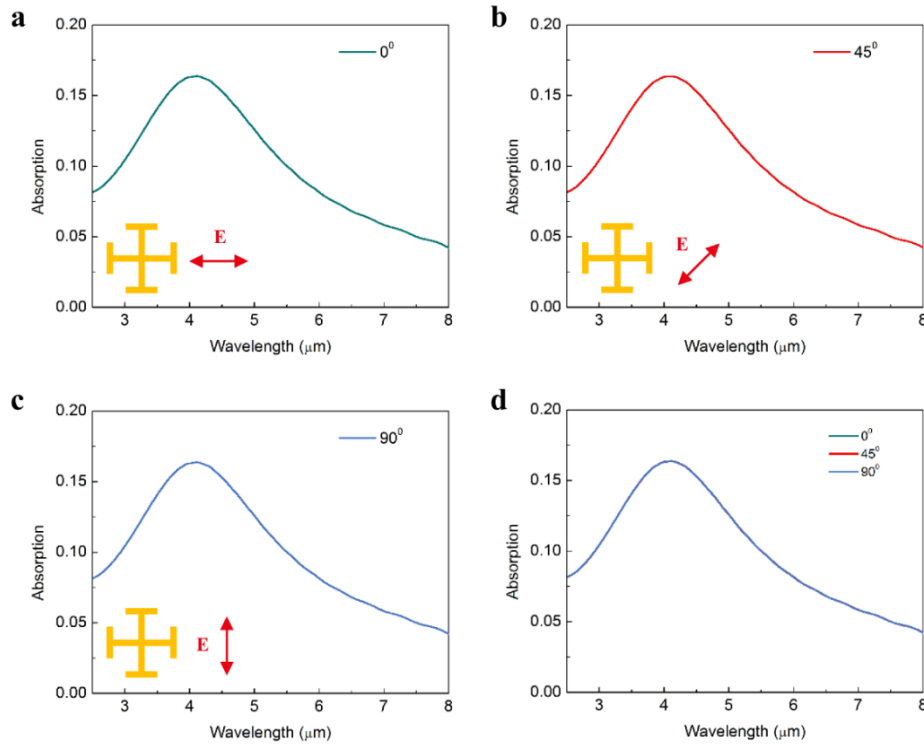


Figure 4.2. Simulated graphene absorption. For incident polarizations of 0° (a), 45° (b), and 90° (c) with respect to the x-axis. Panel d plots all three curves of panels (a-c) in one plot, confirming polarization-independent absorption. Simulations are performed for device described in Fig. 4.1b (Dev#1).

4.4 Experimental Measurements

4.4.1 Microscopy and Raman Characterizations

We fabricate the graphene photodetectors following the process described in the Method chapter. Figure 4.3a shows an optical microscope image of a completed device (Dev#1). The patterned graphene channel is denoted by the white dashed box. The JC-antenna arrays are fabricated on top of the graphene and are connected by electrodes and bonding pads. Each array is $30\ \mu\text{m} \times 30\ \mu\text{m}$. The device has three arrays that are arranged in a linear fashion. Figure 4.3b is a scanning microscope image of the same device shown in Fig. 4.3a. Figure 4.3c shows the Raman spectrum of the graphene in the completed device. The measurement is performed at room temperature with a commercial Raman spectrometer (Renishaw) equipped with a green laser ($\lambda = 532\ \text{nm}$). The Raman spectrum exhibits two main peaks, comprising the 2D peak at $2680\ \text{cm}^{-1}$ and the G peak at $1586\ \text{cm}^{-1}$. The 2D peak exhibits a symmetric shape and an intensity that is around 3 times of the G peak, indicating that the graphene is monolayer. The weak D peak at around $1341\ \text{cm}^{-1}$ and G^* peak at around $2457\ \text{cm}^{-1}$ indicate a low level of defects in the processed graphene. Note that defects including cracks and residuals would generally reduce the graphene conductivity.

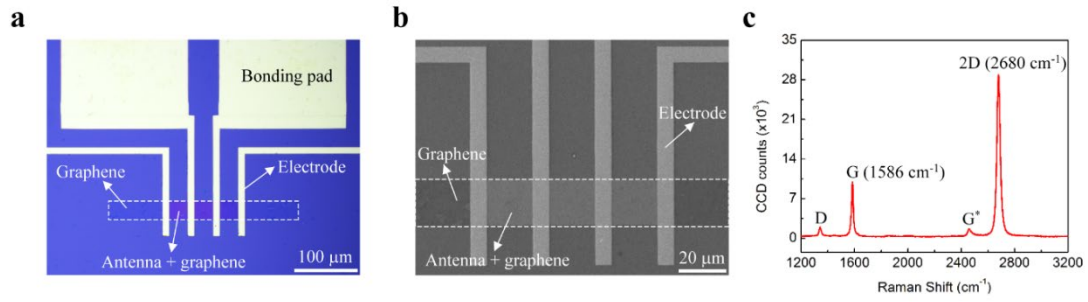


Figure 4.3. Microscopy and Raman Characterizations. **a-b** Optical **(a)** and scanning electron **(b)** microscope image of fabricated graphene device (Dev#1). **c** Raman spectrum of graphene in the device in **(a-b)**.

4.4.2 Transfer Characteristics of Graphene Device

The transfer characteristics of the fabricated device (Dev#1) is then obtained by biasing the source and drain with $V_{DS} = 0.1$ V and measuring the current (I_{DS}), while sweeping the gate voltage (V_G) both positively from -50 V to 50 V and negatively from 50 V to -50 V. The measurement is performed at room temperature and in low pressure condition. Figure 4.4(a) shows the measured transfer characteristics for both positive (red curve) and negative (blue curve) sweeping of the gate voltage. Both curves show typical ambipolar characteristics with charge neutrality point (CNP) at $V_G = 16$ V, indicating that the graphene is intrinsically p-type doped after all fabrication processes. The p-type doping of graphene could be caused by the metal doping effect by Cr contacts and the doping effect by residual molecules from the processing chemicals. An on/off ratio greater than 3:1 is achieved within the range of gate voltage applied, which means that the carrier density in graphene is strongly modulated. Notably, no obvious hysteresis effect is observed in our device, which could be seen more clearly in the zoom-in figure

Fig. 4.4(b). The negligible hysteresis is important for the successful measurement of the photoresponse at room temperature as will be shown later.

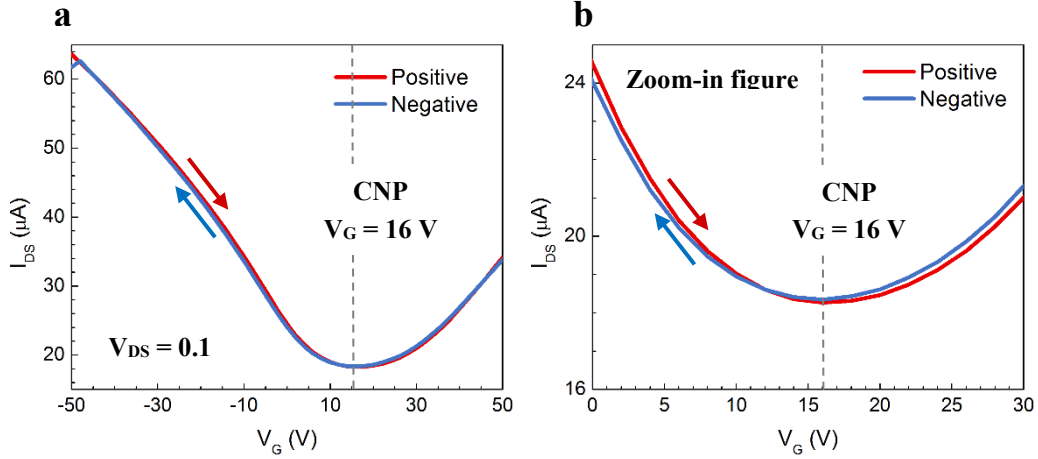


Figure 4.4. Transfer characteristics. **a** Measured transfer characteristic of the graphene device (Dev#1) at room temperature in low pressure with gate voltage swept between -50 V and 50 V in both positive and negative directions. Source-drain bias voltage $V_{DS} = 0.1$ V. The charge neutrality point (CNP) occurs at $V_G = 16$ V. Arrows indicate the sweeping direction of the gate voltage. **b** Zoom-in figure of **(a)** showing region close to CNP.

Figure 4.5 shows the parameter fitting of contact resistance R_c , residual carrier density n_0 and maximum carrier mobility μ in graphene using the measured gate-dependent total resistance R_{tot} :

$$R_{tot} = R_c + \frac{L/D}{q\mu\sqrt{n_0^2 + \Delta n^2}} \quad (4.1^{175})$$

where, Δn is the gate induced carrier density, L ($= 30 \mu\text{m}$) and D ($= 30 \mu\text{m}$) are the length and width of the graphene channel respectively. The gate-dependent carrier density Δn is estimated using a capacitance model:¹⁷⁶

$$|V_G - V_{Dirac}| = \frac{\hbar|V_f|\sqrt{\pi\Delta n}}{q} + \frac{\Delta nq}{C_G} \quad (4.2)$$

where $\hbar$ is the reduced Planck constant, $V_f=1\times 10^8$ cm/s is the Fermi velocity, q is the electron charge, $C_G = \epsilon_r \epsilon_0 / d_G$ is the geometrical capacitance of the gate dielectric (SiO₂) with dielectric constant $\epsilon_r = 4$ and thickness $d_G = 285$ nm. ϵ_0 is the permittivity of free space.

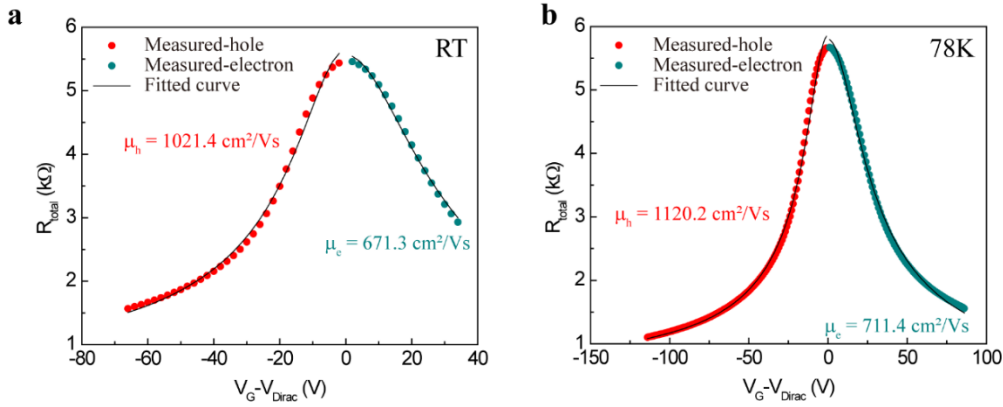


Figure 4.5. Fitting of the measured gate-dependent total resistance (on Dev#1). a-b Fitting results for both hole-doped and electron-doped regions at room temperature (a) and 78 K (b).

The fitting is performed separately for the hole-doped region ($V_G - V_{Dirac} < 0$) and the electron-doped region ($V_G - V_{Dirac} > 0$). The curve fitting results at room temperature and 78 K are shown in Fig. 4.5a and Fig. 4.5b respectively. The fitted parameters are as follows: (1) Room temperature, hole-doped region, $R_c=338.3 \Omega$, $n_0=1.15 \times 10^{12} \text{ cm}^{-2}$, maximum hole mobility $\mu_h=1021.4 \text{ cm}^2/\text{Vs}$. (2) Room temperature, electron-doped region, $R_c=10 \Omega$, $n_0=1.67 \times 10^{12} \text{ cm}^{-2}$, maximum electron mobility $\mu_e= 671.3 \text{ cm}^2/\text{Vs}$. (3) 78 K, hole-doped region, $R_c=455.9 \Omega$, $n_0=1.03 \times 10^{12} \text{ cm}^{-2}$, maximum hole mobility $\mu_h=1120.2 \text{ cm}^2/\text{Vs}$. (4) 78 K, electron-doped region, $R_c=203 \Omega$, $n_0=1.57 \times 10^{12} \text{ cm}^{-2}$, maximum electron mobility $\mu_e= 711.4 \text{ cm}^2/\text{Vs}$. It should be noted that the carrier mobility

values extracted here are slightly different from that shown in later part of the chapter which are obtained based on a different model.

4.4.3 MWIR Photoresponse at Room Temperature

We next measure the photoresponse of the graphene detector at room temperature. An infrared beam from a broadband globar source exiting from the FTIR is focused by two parabolic mirrors and a reflecting objective (Edmund Optics, magnification 10 ×, NA=0.23) onto the detector. The energy spectrum of the light source is centred at the interested MWIR region. The beam diameter, which is defined as the full width half maximum of the intensity, is measured to be around 3.8 mm by mechanically translating a commercial MCT detector and obtaining the beam intensity profile. The total power of the beam is measured to be 6.735 mW using a thermal power meter (Thorlabs, Model S401C), from which the power incident on the active area of the detector is calculated to be 64.6 μ W.

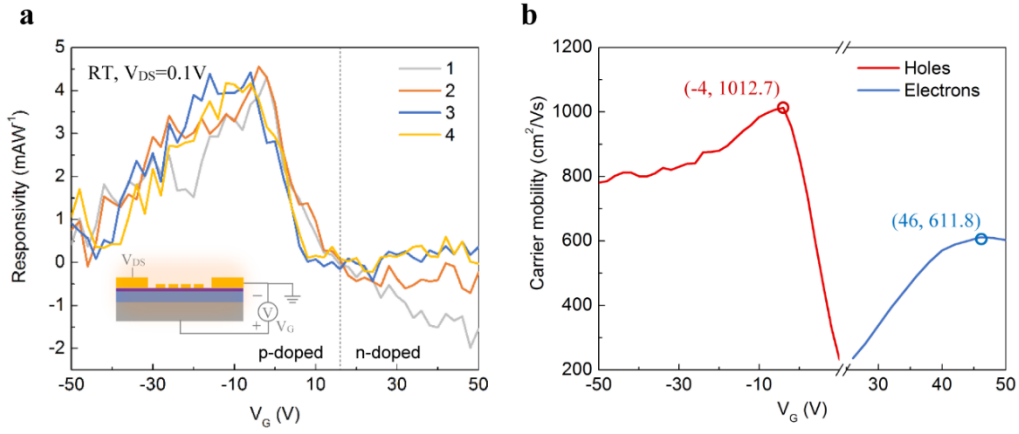


Figure 4.6. Photoresponse characterization and analysis of graphene photodetector with integrated JC antennas (Dev#1) at room temperature (RT). **a** Measured responsivity of detector as a function of gate voltage (V_G) under MWIR illumination from a global source (illuminating power $64.6 \mu\text{W}$). Source-drain bias voltage $V_{DS} = 0.1\text{V}$. Curves correspond to consecutive measurements. Inset: schematic of detector under test. **b** Extracted electron (light blue) and hole (dark red) mobilities as a function of gate voltage based on measured electrical properties.

Figure 4.6a shows the measured gate-dependent responsivity based on the measured photocurrent and the power incident onto the detector. The photocurrent is obtained by measuring the drain current at each gate voltage (I_D - V_G) with and without IR illumination, and then taking the difference. The source-drain bias voltage is kept at $V_{DS} = 0.1\text{ V}$. Four responsivity vs gate voltage curves are measured consecutively in this way and show consistent photoresponse (Fig. 4.6a). The detector shows a maximum responsivity of 4.6 mA/W for $V_G \approx -4\text{ V}$ at room temperature. This corresponds to a voltage responsivity of 14.5 V/W based on the relation between the photovoltage (V_p) and photocurrent (I_p) $V_p = I_p \times R_G$, where R_G is the graphene channel resistance.¹⁰² Unlike previous works on graphene photoconductors,^{77, 177} a distinct “gate-switchable”

characteristic of the photoresponse is observed in our case, where the detector shows clear photoresponse (“working state” of the detector) when the graphene channel is p-type doped ($V_G < V_{\text{Dirac}} = 16 \text{ V}$), but negligible photoresponse (“silent state” of the detector) when graphene channel is n-type doped ($V_G > V_{\text{Dirac}} = 16 \text{ V}$). We attribute the strong suppression of the photoresponse in the n-type doped regime of graphene to the existence of p-type impurities such as absorbed hydrocarbon molecules or from humidity,¹⁰⁰ which could significantly increase the electron recombination rate. To further understand the gate-dependent photoresponse, we extract the gate-dependent carrier mobility from the measured gate-dependent electrical conductivity as follows:²⁴

$$\mu = \frac{1}{q} \frac{\partial \sigma_G}{\partial \Delta n} = \frac{1}{q} \frac{\partial \sigma_G}{\partial V_G} \left(\frac{\partial \Delta n}{\partial V_G} \right)^{-1} \quad (4.3)$$

where the graphene effective conductivity is $\sigma_G = L / ((R_{\text{tot}} - R_c)D)$. Here, L ($= 30 \text{ }\mu\text{m}$) is the channel length, D ($= 30 \text{ }\mu\text{m}$) is the channel width, and R_c is the contact resistance obtained by fitting the measured gate-dependent total resistance.

The extracted gate-dependent carrier mobility is shown in Fig. 4.6b. We can see that as the gate voltage decreases in the p-type doped regime of graphene, the hole mobility (Fig. 4.6b, red curve) first increases to a maximum value of $1013 \text{ cm}^2/\text{Vs}$ at $V_G = -4 \text{ V}$, then decreases to $781 \text{ cm}^2/\text{Vs}$ at $V_G = -50 \text{ V}$, showing a similar trend to the gate-dependent photoresponse (Fig. 4.6a). This is understandable because higher mobility permits shorter carrier transit time, which would consequently result in greater photoresponse. The initial increase and subsequent decrease of the hole mobility could be attributed to it being limited by substrate surface polar phonon scattering and short-range scattering by defects, respectively, a trend that has been reported previously using Hall measurements.¹⁷⁸ It is notable that hole mobility and responsivity take their maximum values at a similar gate voltage ($\sim -4 \text{ V}$). In addition, it can be seen that the electrons show

smaller mobility (maximum $612 \text{ cm}^2/\text{Vs}$, blue curve in Fig. 4.6b) than holes in the part of the p-type doped regime of graphene that shows significant photoresponse, which could also contribute to the suppression of the detector response in the n-type doped regime.

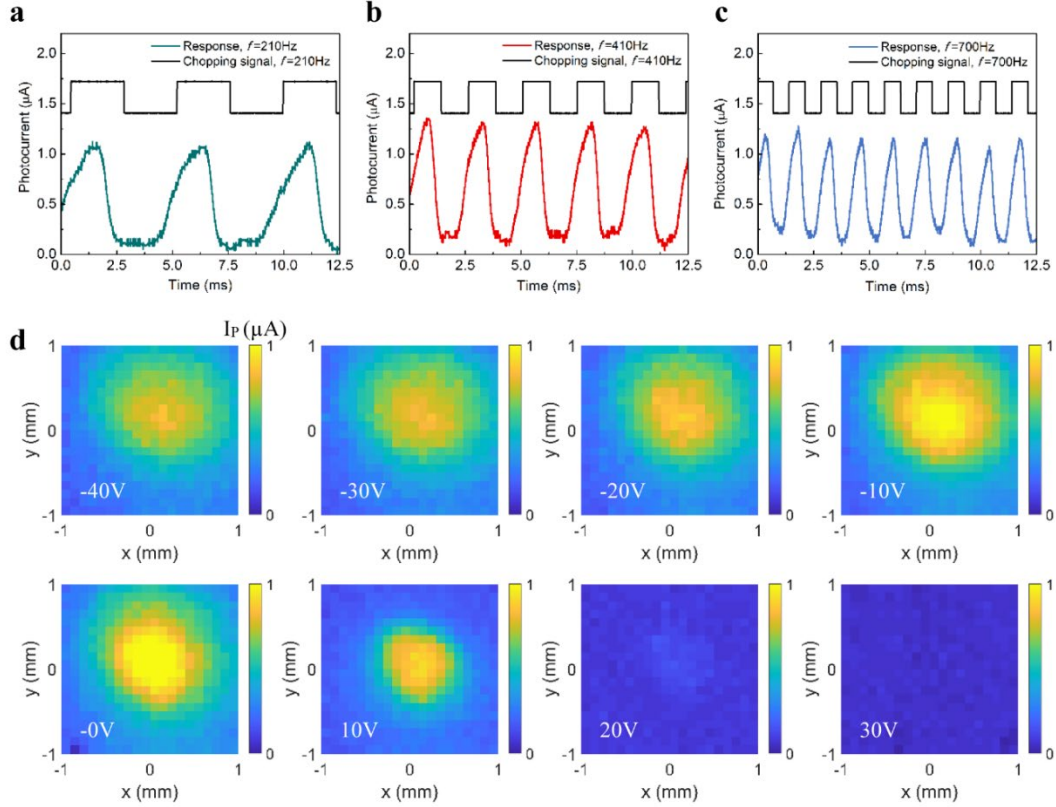


Figure 4.7. Modulated photoresponse and mapping of an IR beam. **a-c** Photoresponse to MWIR illumination chopped at frequencies of 210 Hz **(a)**, 410 Hz **(b)** and 700 Hz **(c)**, with the source-drain voltage of 2.952 V **(a)**, 2.951 V **(b)** and 2.943 V **(c)**. Gate voltage $V_G = 0 \text{ V}$ for all measurements. **d** Photocurrent maps of an IR beam measured under different gate voltages ranging from -40 V to 30 V, in steps of 10 V. Source-drain bias voltage is kept at 0.92 V. All measurements are performed at room temperature on another device (Dev#2).

We also test the detector response to modulated IR illumination. We modulate the output from the FTIR globar source with a chopper and measure the detector signal with

a low-noise current preamplifier (SR570, Stanford Research Systems). The output of the preamplifier is sent to an oscilloscope (Tektronix, TDS3034B) and is then sampled by a computer. Figure 4.7a-c demonstrate the modulation of the photocurrent at chopping frequencies of 210 Hz (Fig. 4.7a), 410 Hz (Fig. 4.7b), and 700 Hz (Fig. 4.7c). It should be noted that the gradual rise and fall of the photocurrent are caused by the relatively large spot size of the beam that is being chopped. Hence, the results of Fig. 4.7a-c do not represent the intrinsic response time of our detector. This is consistent with the fact that the rise/fall times become shorter as the chopping frequency increases.

For a simple application, we use our detector to map the intensity profile of the IR beam that is used as the light source in our experiments. Note that in the measurement, the 10X objective is replaced by a 40X objective (Thorlabs, LMM-40X-P01-160), and the beam is chopped at a frequency of 700 Hz. The photocurrent is measured by the low-noise preamplifier, while the detector is scanned over the beam area by a motorized stage (Thorlabs LNR50S). The source-drain bias voltage is provided by the preamplifier, and the gate voltage is provided by an SMU. Control over the motorized stage and control over the acquisition of the data are achieved using a MATLAB script. Figure 4.7d shows the mapping results under different gate voltages of the detector, ranging from -40 V to 30 V. The source-drain bias is kept at $V_{DS} = 0.92$ V for all mapping experiments. It can be seen that the mapped beam photocurrent strongly depends on the applied gate voltage, which is consistent the gate dependence of the detector photoresponse discussed above. The intensity profile with the greatest photocurrent is obtained for gate voltage $V_G = 0$ V. Further increase or decrease of the gate voltage leads to a weaker intensity profile due to the reduced responsivity of the detector. In particular, the beam intensity profile is barely observable when the detector is biased at $V_G = 20$ V and 30 V, as for these voltages, the detector is in “silent state” as the graphene channel is n-type doped. The full width half

maximum (FWHM) beam diameter is estimated to be around 1.4 mm, based on the profile obtained under $V_G = 0$ V.

4.4.4 MWIR Photoresponse at Low Temperature

We next measure the photoresponse at 78 K and low pressure by mounting the device on a cryostat. A temperature controller (Lake Shore Cryotronics, Model 325) is used to control the temperature of the cryogenic stage. Figure 4.8a shows the transfer characteristic curves measured under dark and light conditions ($V_{DS} = 0.1$ V). At low temperature, the dark current is strongly reduced due to the suppression of thermal generation. Due to the improved carrier mobility at low temperature and reduced Pauli blocking, the measured responsivity (Fig. 4.8b) is substantially larger than that measured at room temperature, with a peak value of 0.34 A/W (corresponds to 920 V/W) at $V_G = -42$ V. Similar to what we observed at room temperature, the detector shows a gate-switchable photoresponse, featuring a large photoresponse in the p-type doped regime of graphene and a photoresponse close to zero in the n-type doped regime of graphene. The extracted hole mobility (Fig. 4.8c, red curve) shows a similar trend as the responsivity curve under different gate voltages and is larger than the electron mobility (Fig. 4.8c, blue curve). Furthermore, both holes and electrons show increased mobility compared to that at room temperature, probably due to the suppression of lattice scattering from the substrate.¹⁷⁹ The fact that the gate voltage for maximum responsivity ($V_G = -42$ V) is different to that for maximum hole mobility ($V_G = -7$ V) might be due to the larger mismatch between the predicted and actual gate-induced carrier density at 78K, since there is a larger number of vacant trapping centres to be filled by the gate-induced carriers.

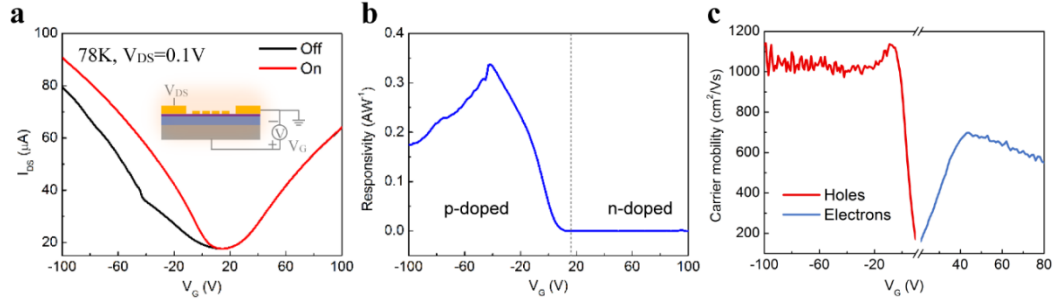


Figure 4.8. Photoresponse characterization and analysis of graphene photodetector with integrated JC antennas (Dev#1) at 78 K. **a** Transfer characteristic measured under dark and light conditions (global source, illuminating power $64.6 \mu\text{W}$) with gate voltage V_G swept from -100 V to 100 V , and source-drain bias voltage $V_{DS} = 0.1 \text{ V}$. Inset: Schematic of the detector under test. **b** Gate-dependent responsivity calculated from photocurrent and illumination power. Photocurrent is obtained by taking difference between source-drain current with and without IR illumination from **(a)**. **c** Extracted electron (light blue) and hole (dark red) mobilities as a function of gate voltage based on measured electrical properties.

4.4.5 Zero-Bias Photoresponse to MWIR Light

Our device also exhibits zero-bias photoresponse at both room temperature and 78 K as shown in Fig. 4.9, providing opportunity toward applications requiring low power consumption. We use the same method as that employed in Fig. 4.7a-c. The photocurrent measured is in the nanoampere range, with 2-3 times improvement at 78 K (Fig. 4.9d-f) over that at room temperature (Fig. 4.9a-c). Nonetheless, it is much smaller than that measured with source-drain bias (Fig. 4.7a-c). This is due to the fact that under zero source-drain bias, the photocurrent collected by the device is that generated in a smaller region near the electrodes and separated by the built-in potential between the electrodes and graphene.

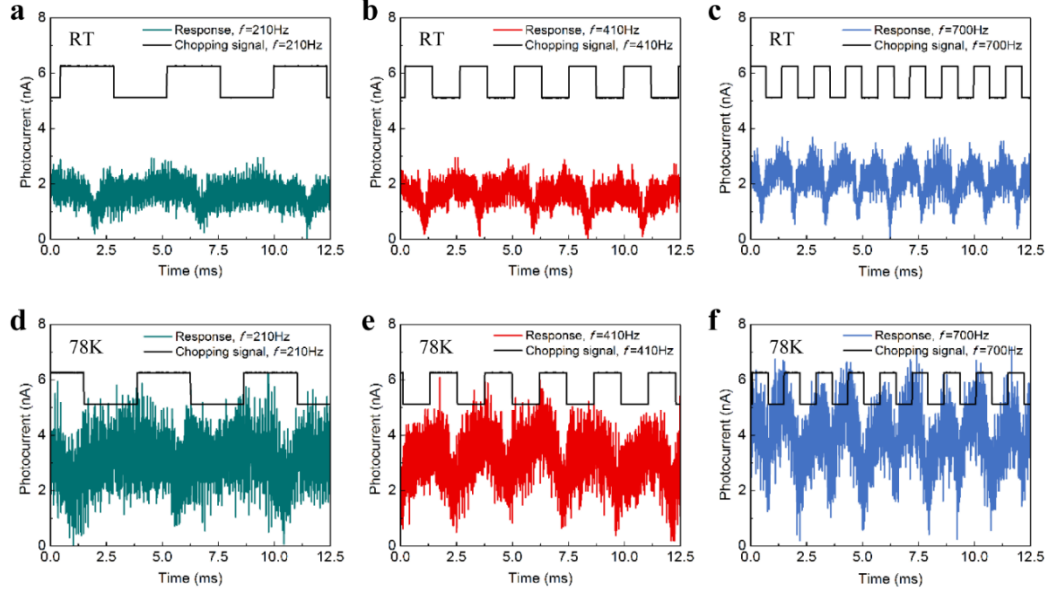


Figure 4.9. Modulated photoresponse to MWIR illumination under zero source-drain bias. Measured photocurrent with MWIR illumination being chopped at frequencies of 210 Hz **(a,d)**, 410 Hz **(b,e)** and 700 Hz **(c,f)**, under zero source-drain bias voltage $V_{DS} = 0$ V and gate voltage $V_G = 0$ V at both room temperature **(a-c)** and 78K **(d-f)**. Measurements are performed on Dev#1.

4.4.6 Effects of Polarization, Source-Drain Bias and Temperature on Photoresponse

We further characterize the polarization dependence of our detector response. Polarized light is produced by a linear polarizer placed before the 10 $\times$ objective and rotated to change the polarization angle. Figure 4.10a shows the photocurrent measured as the incident polarization is varied from 0 $^\circ$ to 90 $^\circ$ (with respect to the x-axis) under different source-drain bias voltages. The photocurrent is normalized by the measured illumination power as the polarization is varied. Due to the polarization-independent

absorption enhancement in graphene that arises from the symmetric shape of the JC antennas, the detector exhibits a largely polarization-insensitive photoresponse. The effect of source-drain bias on the detector photoresponse is also investigated in Fig. 4.10b-c. Figure 4.10b shows the gate-dependent photocurrents under different source-drain bias voltages, demonstrating a consistent increase of photocurrent as source-drain bias voltage increases from 0.1 V to 0.9 V. This is due to the increased carrier drift velocity and collection efficiency as a result of the increased electric field between source and drain electrodes. The linear relationship between the source-drain bias and the detector responsivity is evident in Fig. 4.10c, where the responsivity is measured at V_{DS} swept from 0 V to 3 V for $V_G = 0$ V, -4 V and -8 V. Notably, a maximum responsivity of 1.9 A/W (corresponds to $\sim 4.4 \times 10^3$ V/W) is obtained at $V_G = -8$ V and $V_{DS} = 3$ V. The photocurrent is also characterized at different temperatures (Fig. 4.10d). It can be seen that the photocurrent decreases as the temperature increases from 100 K to 220 K, which could be due to the stronger carrier scattering at higher temperatures.¹⁷⁸

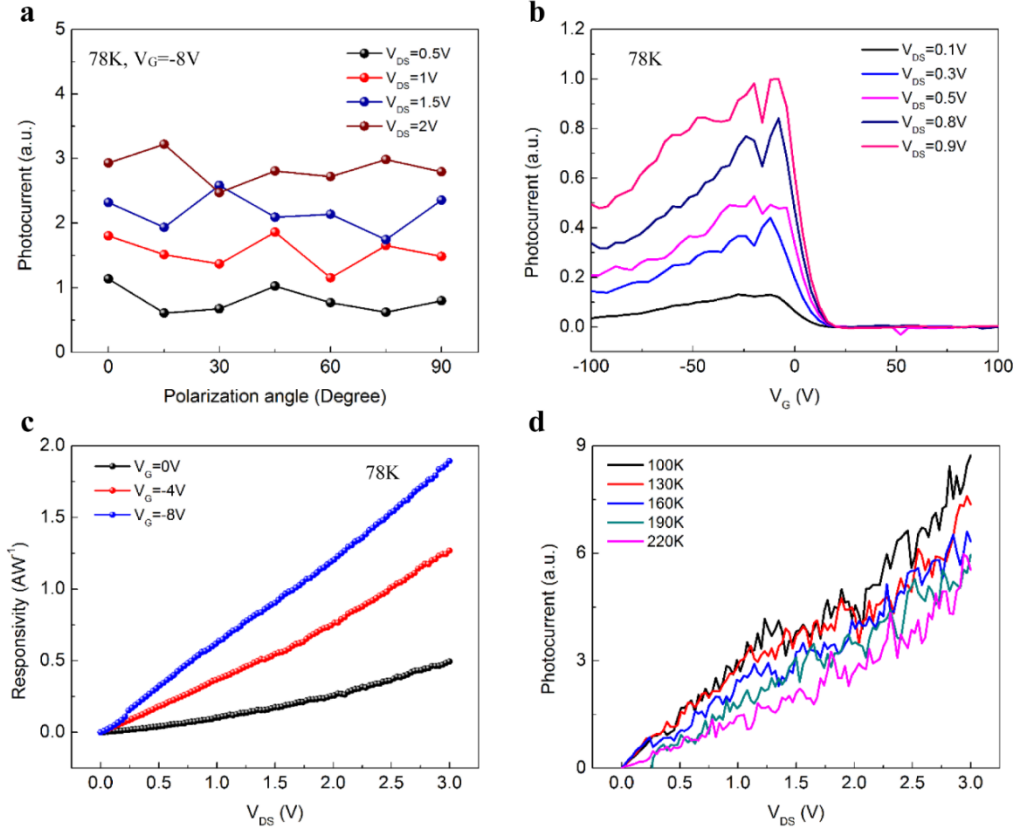


Figure 4.10. Effects of polarization, source-drain bias, and temperature on the photoresponse of graphene detector. **a** Photocurrent measured at 78 K as a function of polarization of incident light (global source) under different source-drain bias voltages, with fixed gate voltage $V_G = -8$ V. **b** Gate-dependent photocurrent measured at 78 K under different source-drain bias from 0.1 V to 0.9 V. **c** Photoresponsivity as a function of source-drain bias voltage measured at 78 K under different gate voltages ($V_G = 0$ V, -4 V, -8 V). **d** Photocurrent measured as a function of source-drain bias voltage from 0 V to 3 V at different temperatures (100 K, 130 K, 160 K, 190 K, 220 K), with gate voltage $V_G = -8$ V. Note that measurements in **(a, c-d)** are performed on another device (Dev#3) fabricated on the same chip as Dev#1.

4.4.7 Photoresponse in the Visible to Near-Infrared Region

To measure the response time of our detector, we use a monochromatic light (centre wavelength $\lambda = 532$ nm, power 250 nW) from a laser-driven light source filtered

by a monochromator. The light is chopped at a frequency of 1 kHz. The current output from the detector is amplified with a current preamplifier, whose output is monitored with an oscilloscope. The measured temporal photocurrent signal (Fig. 4.11a, cyan curve) shows sharp rise and fall edges, with zoomed-in versions of these shown in the left and right panel of Fig. 4.11b. From these results, we obtain the rise (τ_1) and fall (τ_2) times as the 10% to 90% intervals and find them to be $\tau_1 = 11.4 \pm 0.4 \mu\text{s}$ and $\tau_2 = 66.4 \pm 0.4 \mu\text{s}$, respectively. Our detector thus shows fast response with a response time in the range of tens of microseconds, which is much shorter than previous works that employ carrier trapping centres ($\sim 100 \text{ s}$)⁹⁸ or photogating effects ($\sim 1\text{-}3 \text{ ms}$)^{100, 101}. It is also possible that the intrinsic response time of the device is even shorter than that measured, as there are limitations on the latter that arise from the bandwidth of our preamplifier ($<1 \text{ MHz}$) and the finite size of the beam that is chopped. Although the antennas are designed to enhance the graphene absorption in the MWIR region, our detector exhibits a strong and broadband photoresponse across the visible and near-infrared regime. Specifically, we measured the temporal response of our detector under monochromatic illumination at wavelengths of 650 nm (power 85 nW, Fig. 4.11a, red curve) and 850 nm (power 30 nW, Fig. 4.11a, blue curve). The rise (fall) time is found to be $16.2 \pm 0.4 \mu\text{s}$ ($67 \pm 0.4 \mu\text{s}$) and $38 \pm 0.4 \mu\text{s}$ ($78 \pm 0.4 \mu\text{s}$) for 650 nm (Fig. 4.11c) and 850 nm (Fig. 4.11d) illumination, respectively. The responsivity is calculated to be $\sim 28 \text{ AW}^{-1}$, 74 AW^{-1} and 118 AW^{-1} at wavelengths of 532 nm, 650 nm and 850 nm, respectively. We attribute the large responsivity in the visible and near-infrared region to the increased carrier collection efficiency by our JC antennas.

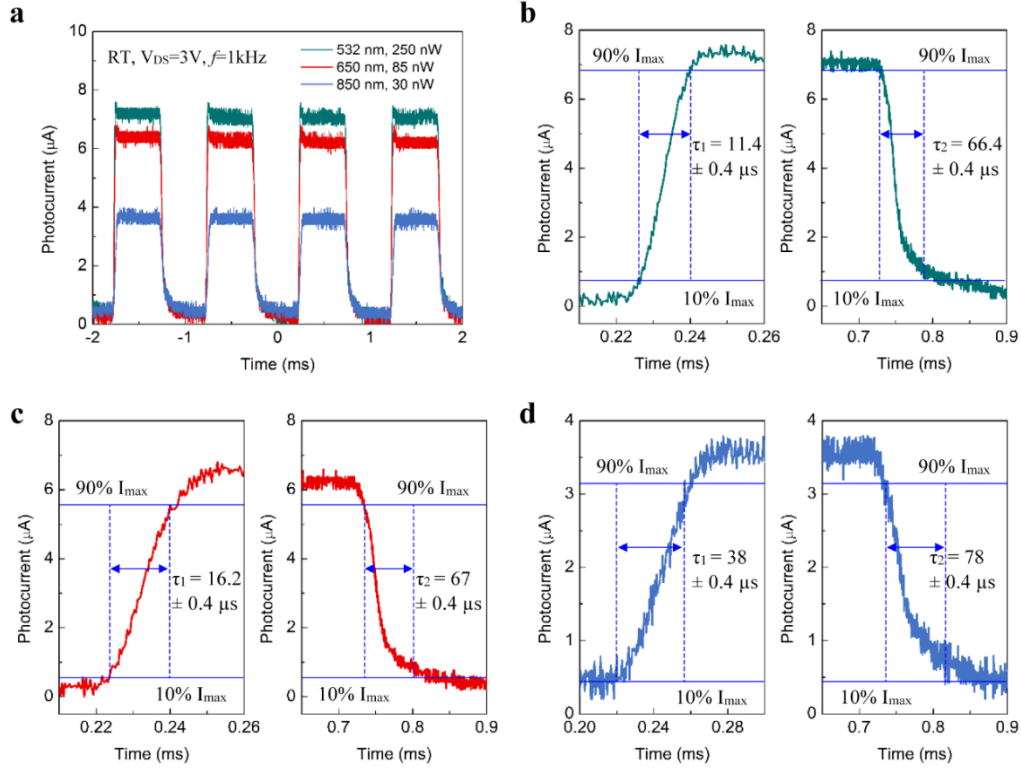


Figure 4.11. Temporal response of graphene photodetector with integrated JC antennas (Dev#2) in the visible to near-infrared region. (a) Measured photocurrent in response to chopped monochromatic illumination ($\lambda = 532$ nm, 650 nm, and 850 nm, chopping frequency $f = 1$ kHz) from a laser-driven light source filtered by a monochromator. Device is biased with $V_{DS} = 3$ V, $V_G = 0$ V. (b-d) Zoomed-in figures showing rise and fall regions of measured photocurrent in panel (a) under illumination at 532 nm (b), 650 nm (c) and 850 nm (d), respectively. Measurements are performed at room temperature.

4.4.8 Graphene Absorption Enhancement with Bottom Optical Cavity

Finally, we show through simulation that the optical absorption in graphene could be further enhanced by adding an optical cavity to the graphene photoconductor with integrated JC antennas, as shown in Fig. 4.12a. The device structure is similar to what we have experimentally demonstrated in this chapter, except that the original SiO_2 layer is

replaced by layers of alumina (30 nm), germanium (100 nm) and aluminum (100 nm) from top to bottom. This approach has also been employed for other applications of enhanced light-matter interactions.^{180, 181} In Fig. 4.12b, we show the simulated graphene absorption as we scale up the sizes of the JC-antennas, with the period P increasing from 350 nm to 500 nm, in steps of 50 nm. Other parameters are kept as $E = 9P/20$, $W = 3P/20$, $G = 40$ nm. It can be seen from Fig. 4.12b that the graphene absorption is greatly enhanced in the mid-wave infrared region, with the peak absorption as high as 47% (Fig. 4.12b, black curve) for graphene Fermi level of 0.1366 eV (same as what we extracted for the graphene fabricated in this chapter), representing an improvement of more than one order of magnitude than the intrinsic graphene absorption in the MWIR ($\sim 1.9\%$, calculated for graphene with same Fermi level and scattering rate). By tuning the Fermi level of graphene to 1 eV, absorption could be further increased to 56% (Fig. 4.12b, dark yellow curve). Figure 4.12c-d show 2D maps of the graphene absorption, showing a more general trend of the absorption by varying the antenna array period (Fig. 4.12c) and Fermi level of graphene (Fig. 4.12d). The device architecture with a bottom optical cavity investigated here shows great potential in further boosting the light absorption in graphene and realizing MWIR graphene photodetectors with high responsivity and speed, operating at room temperature, which could be a topic for future studies. In addition, we note that the concept of such architecture could readily be extended into the LWIR region by scaling and optimizing the structure dimensions for optimal graphene absorption in the LWIR.

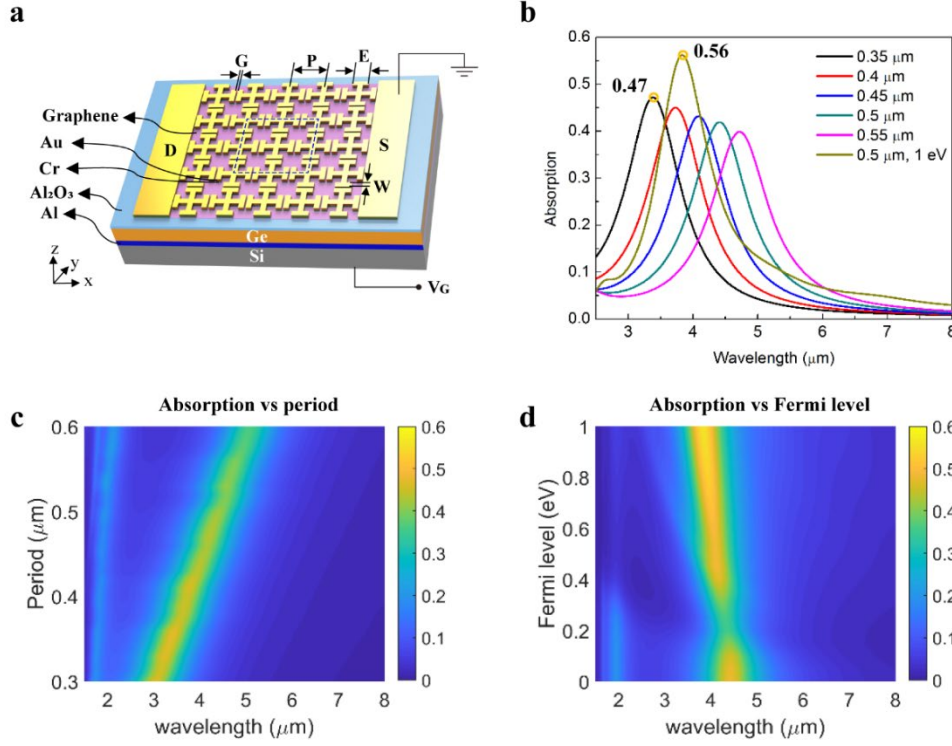


Figure 4.12. Enhancement of graphene absorption for graphene photodetectors with integrated JC antennas and bottom optical cavity. **a** Schematic of graphene photodetectors with integrated JC antennas and bottom optical cavity consisting layers of alumina (30 nm), germanium (100 nm), and aluminum (100 nm), from top to bottom. **b** Simulated graphene absorption spectra as antenna array period P varies from 350 nm to 500 nm, in steps of 50 nm. Other parameters are $E = 9P/20$, $W = 3P/20$, $G = 40$ nm. Graphene Fermi level is 1 eV for the dark yellow curve and is 0.1366 eV for other curves. Yellow circles indicate peak absorption for corresponding curves. **c** 2D map of simulated graphene absorption spectrum, as the antenna array period P is varied from 300 nm to 600 nm. $E = 9P/20$, $W = 3P/20$, $G = 40$ nm. **d** 2D map of simulated graphene absorption spectrum, as Fermi level is swept from 0 eV to 1 eV. $P = 500$ nm, $W = 75$ nm, $E = 225$ nm, $G = 40$ nm.

4.5 Conclusions

In conclusion, we demonstrate a polarization-independent graphene photoconductor with integrated Jerusalem-cross nanoantennas operating in the mid-wave infrared. Photoresponse is measured at both room and cryogenic temperatures, with maximum responsivities of 4.6 mA/W (14.5 V/W) and 1.9 A/W (4.4×10^3 V/W) at room temperature and 78 K respectively. Compared to previously reported work where end-to-end rod antennas are employed, the unique shape of the JC-antennas, with their elongated ends, and the narrower gaps (~ 40 nm) between adjacent antennas, render a stronger and polarization-independent optical absorption enhancement in graphene. Our photocurrent measurements confirm the largely polarization-insensitive photoresponse of the detector. Unlike previously demonstrated detectors based on trapping centres or photogating effects which show response times of milliseconds or even hundreds of seconds, our detector shows a fast response with a measured rise time of 11.4 μ s, which would be sufficient for many applications (*e.g.* imaging). Notably, our graphene detector with integrated JC antennas also exhibits a strong and broadband photoresponse at visible and near-infrared wavelengths, which we attribute to the improved carrier collection by the antennas. We believe our work provides guidelines to the design of antenna-assisted graphene photodetectors with improved responsivity and versatile optical properties.

Chapter 5

Metasurface with Metallic Nanoantennas and Graphene Nanoslits for Sensing of Protein Monolayers and Sub-Monolayers

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Metasurface with metallic nanoantennas and graphene nanoslits for sensing of protein monolayers and sub-monolayers

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Abstract: Biomolecule sensing plays an important role in both fundamental biological studies and medical diagnostic applications. Infrared (IR) spectroscopy presents opportunities for sensing biomolecules as it allows their fingerprints to be determined by directly measuring their absorption spectra. However, the detection of biomolecules at low concentrations is difficult with conventional IR spectroscopy due to signal-to-noise considerations. This has led to recent interest on the use of nanostructured surfaces to boost the signals from biomolecules in a method termed surface enhanced infrared spectroscopy. So far, efforts have largely involved the use of metallic nanoantennas (which produce large field enhancement) or graphene nanostructures (which produce strong field confinement and provide electrical tunability). Here, we propose a nanostructured surface that combines the large field enhancement of metallic nanoantennas with the strong field confinement and electrical tunability of graphene plasmons. Our device consists of an array of plasmonic nanoantennas and graphene nanoslits on a resonant substrate. We perform systematic electromagnetic simulations to quantify the sensing performance of the proposed device and show that it outperforms designs in which only plasmons from metallic nanoantennas or plasmons from graphene are utilized. These investigations consider the model system of a representative protein - goat anti-mouse immunoglobulin G (IgG) – in monolayer or sub-monolayer form. Our findings provide guidance for future biosensors for the sensitive quantification and identification of biomolecules.

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1. Introduction

The identification of biomolecules and the monitoring of the binding processes they undergo are crucial for understanding the molecular mechanisms of cellular functions (e.g. for fundamental biological studies) and for medical diagnostic applications. Many techniques have thus been developed for the sensitive detection of biomolecules, including electro-chemical reactions [1, 2], field effect transistors [3-7], surface plasmon resonances [8-14] and optical fibers [15]. In general, however, these methods suffer from lack of specificity in terms of what is being measured. On the other hand, infrared (IR) spectroscopy [16-22] is a highly specific sensing modality as it allows direct measurement of the vibrational fingerprints of molecules. It is also non-invasive, label-free, and has been used for a wide variety of biological samples, including proteins [16], lipids [23] and bacteria [24]. Nonetheless, conventional IR

spectroscopy faces the challenge of low signal-to-noise for measurements of small quantities of biomolecules (e.g. monolayers), which originates from the large mismatch between the wavelength of light ($\sim$ micrometers) and the size of biomolecules (<10 nm). This has led to the development of a method that leverages the large optical field enhancement that can occur in the vicinity of metallic nanostructures [25-29] that is known as surface-enhanced infrared absorption (SEIRA) [30-32]. The detection of small quantities of molecules has been demonstrated based on this method [9, 33-39]. Metallic nanostructures have some drawbacks for SEIRA, however [28, 40-42]. The spectral bandwidth over which they boost IR absorption is relatively narrow and generally fixed at the time of manufacturing. The field confinement of noble metal plasmons in the mid-infrared molecular fingerprint region is also relatively weak. Recently, graphene has emerged as an attractive candidate for biosensing as it supports mid-infrared plasmons that can be dynamically tuned by electrostatic gating [43, 44]. In addition, graphene plasmons exhibit unprecedented spatial confinement [45, 46]. These unique properties of graphene have been exploited for the quantification and identification of biomolecules down to monolayers, with key improvements over plasmonic sensing devices employing metallic nanostructures [47-49]. Despite these impressive features, one major disadvantage of biosensors based on graphene plasmons is the fact that the field enhancement that accompanies graphene plasmon is small compared to that occurring with plasmons on noble metals. For example, Rodrigo et al [48] reported a tunable biosensor based on a graphene ribbon array, demonstrating the chemically-specific detection of protein monolayers by leveraging the tunability and spatial confinement of graphene plasmons. In that paper, the authors noted that the extinction change caused by the presence of proteins was an indicator of the sensitivity of their biosensor. This was reported to be below 1%, i.e. the extinction change was fairly modest due to the relatively small near-field enhancement of their device (~ 30 times). One may anticipate that this approach would face challenges related to signal-to-noise ratio, especially for the detection of proteins in sub-monolayers. This leads to the question of whether one can realize a single device that exhibits both the large field enhancement of conventional metal plasmons and the strong field confinement of graphene plasmons. Here, we address this question by investigating a nanostructured surface, which we term a metasurface, that consists of an array of plasmonic nanoantennas and graphene nanoslits on a resonant substrate. In this device, the excitation of antenna plasmons and the subsequent coupling to graphene plasmons generate electric fields with both high intensity and strong spatial confinement near the graphene nanoslits. This results in strongly enhanced absorption by the adsorbed molecules, i.e. by the proteins that are being sensed, which improves the sensitivity of the device for sensing. We perform systematic electromagnetic simulations to quantify the sensing performance of our metasurface for protein quantification and identification of goat anti-mouse immunoglobulin G (IgG) down to sub-monolayer densities. For comparison, we also study the sensing performance of three other metasurfaces in which only plasmons from metallic nanoantennas or plasmons from graphene are employed. These consist of: a plasmonic nanoantenna array, a plasmonic nanoantenna array on a graphene sheet, and a graphene nanoribbon array. We find that among the metasurfaces investigated, the proposed metasurface exhibits the best performance for sub-monolayer protein detection due to the large field enhancement and strong field confinement. We also demonstrate that tuning the graphene Fermi level via external gate bias would allow our metasurface to achieve optimal sensing of different molecular fingerprints.

2. Biosensor structure and optical properties

The biosensor we proposed is shown schematically as Figure 1. It consists of a rectangular array of Ti/Au (5 nm/45 nm) linear antennas on a monolayer of graphene over a resonant substrate

comprising an alumina film (300 nm thick) on aluminum (100 nm). The graphene within the antenna gaps is removed, forming an array of graphene nanoslits (Fig. 1(a)) for the excitation of graphene plasmons upon illumination. Here, the alumina layer acts both as a gate dielectric for electrical tuning of the graphene Fermi level and a low-loss spacer for the optical cavity. For all the simulations performed in this work, the antenna gap G , antenna width W , period P_y and width of graphene nanoslit W_s are fixed as $G = 30$ nm, $W = 240$ nm, $P_y = 2$ μ m, $W_s = 22$ nm.

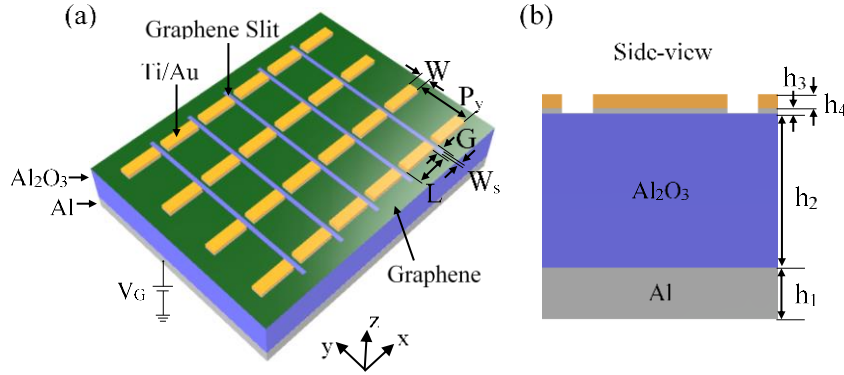


Fig. 1. (a) Schematic of biosensor structure that consists of an array of Ti /Au ($h_3 = 5$ nm/ $h_4 = 45$ nm) linear antennas and graphene slits on top of alumina ($h_2 = 300$ nm) and aluminum ($h_1 = 100$ nm) films. Antenna gap G , antenna width W , period P_y and width of graphene slit W_s are fixed as $G = 30$ nm, $W = 240$ nm, $P_y = 2$ μ m, $W_s = 22$ nm. (b) Side-view of structure.

In this work, we also investigate three other metasurfaces and compare their sensing performance to the proposed metasurface (metasurface I, Fig. 2(a)). These are schematically shown as Fig. 2(b-c) and consist of: plasmonic nanoantenna array (metasurface II, Fig. 2(b));

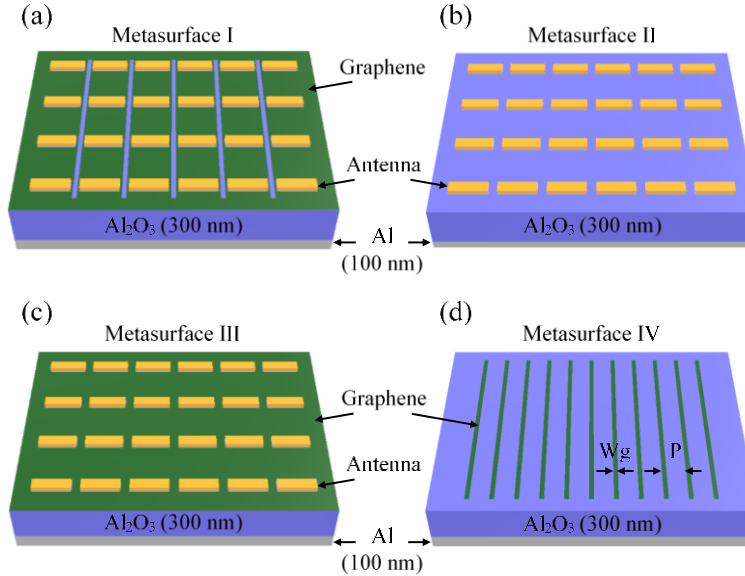


Fig. 2. Schematic of the four metasurface structures. (a) Metasurface I: plasmonic nanoantenna array with graphene slits, (b) Metasurface II: plasmonic nanoantenna array, (c) Metasurface III: plasmonic nanoantenna array on graphene sheet, (d) Metasurface IV: graphene ribbon array.

plasmonic nanoantenna array on graphene sheet (metasurface III, Fig. 2(c)); and graphene ribbon array (metasurface IV, Fig. 2(d)). All metasurfaces are on the same substrate.

We first investigate the optical field enhancement in the mid-infrared region where most biomolecules have their vibrational fingerprints. Electromagnetic simulations are conducted using the finite difference time domain method implemented in a commercial package (Lumerical FDTD). The computational domain consists of a single unit cell of the structure. Periodic boundaries are used at the x- and y- boundaries. Perfectly matched layers (PMLs) are used at the z- boundaries to avoid unwanted backscattering of the electromagnetic fields. Illumination is from a plane wave linearly polarized along the x axis at normal incidence. In the simulations, graphene is modelled as a two-dimensional surface with a surface conductivity given by the Kubo formula[50, 51]:

$$\begin{aligned}\sigma(\omega, \mu_c, \Gamma, T) &= \sigma_{intra}(\omega, \mu_c, \Gamma, T) + \sigma_{inter}(\omega, \mu_c, \Gamma, T) \\ &= \frac{ie^2(\omega - i2\Gamma)}{\pi\hbar^2} \left[\frac{1}{(\omega - i2\Gamma)^2} \int_0^\infty \varepsilon \left(\frac{\partial f_d(\varepsilon)}{\partial \varepsilon} - \frac{\partial f_d(-\varepsilon)}{\partial \varepsilon} \right) d\varepsilon \right. \\ &\quad \left. - \int_0^\infty \left(\frac{f_d(-\varepsilon) - f_d(\varepsilon)}{(\omega - i2\Gamma)^2 - 4(\varepsilon/\hbar)^2} \right) d\varepsilon \right]\end{aligned}\quad (1)$$

where ω is angular frequency, μ_c is chemical potential, Γ is scattering rate, T is temperature, e is the electron charge, $\hbar = h/2\pi$ is the reduced Planck's constant, $f_d(\varepsilon) = (e^{(\varepsilon - \mu_c)/k_B T} + 1)^{-1}$ is the Fermi-Dirac distribution, and k_B is Boltzmann's constant. The values for μ_c , Γ and T are set to be 0.3 eV, 0.022 eV and 300 K, unless otherwise stated.

The electric field intensity enhancement distributions are provided as Fig. 3 for all four metasurfaces. For metasurfaces I-III, the antenna length is the same, i.e. $L = 1.25 \mu\text{m}$. For metasurface IV, graphene ribbon width is $W_g = 24 \text{ nm}$ and period is $P = 80 \text{ nm}$. Each structure is illuminated at its resonant wavelength. It can be seen that for the proposed metasurface (metasurface I, Fig. 3(a)), the electric field is strongly enhanced and confined in the vicinity of the graphene slit, with a maximum intensity enhancement factor of 6.1×10^5 . Note that the colorbar is set to have a maximum value of 1×10^5 in Fig. 3(a-c) to enable intuitive comparison. The enhancement results from the resonant excitation of antenna surface plasmon polaritons and subsequent coupling to graphene plasmons. In comparison, the maximum electric field intensity enhancement factors are 4.1×10^5 , 1.4×10^5 and 104 for metasurfaces II (Fig. 3(b)), III (Fig. 3(c)) and IV (Fig. 3(d)) respectively. The field intensity enhancement provided by our proposed metasurface that combines graphene plasmons with antenna plasmons is more than three orders of magnitude greater than that generated by metasurface IV in which only graphene plasmons are excited, and is comparable to that of the device (metasurface II) in which only antenna plasmons are excited. We note that the ratio between field intensity at the bottom of the antenna (where it meets the substrate) to the top of the antenna is greater for our proposed metasurface than that for the antenna-only structure (metasurface II, Fig. 3(b)). We also note that with the addition of the graphene sheet underneath the antennas (i.e. metasurface III), the maximum field intensity enhancement (Fig. 3(c)) is markedly reduced, taking a value that is less than one quarter of that of the proposed metasurface.

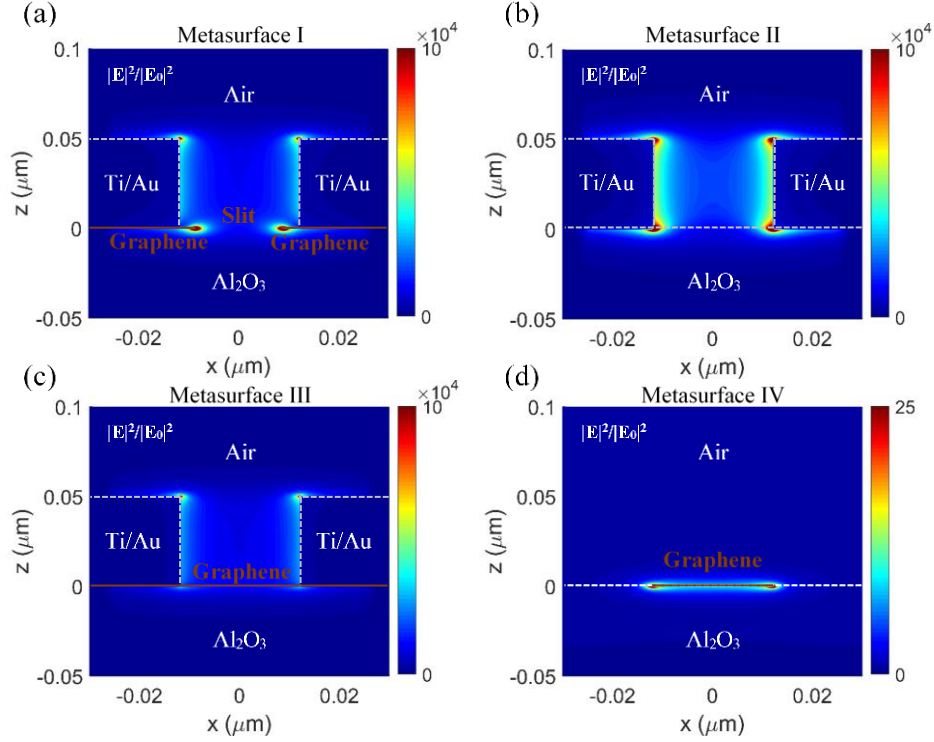


Fig. 3. Simulated electric field intensity enhancement distributions on XZ cross-section for structures with (a) metasurface I, plasmonic nanoantenna array with graphene slits, (b) metasurface II, plasmonic nanoantenna array, (c) metasurface III, plasmonic nanoantenna array on graphene sheet and (d) metasurface IV, graphene ribbon array, with ribbon width $W_g = 24$ nm and period $P = 80$ nm. Antenna length ($L = 1.25$ μm) is same for (a-c). Each structure is illuminated at its resonant wavelength, i.e. $\lambda = 6531$ nm, 6540 nm, 6014 nm and 6180 nm, for panels a-d, respectively. White dotted lines indicate antenna boundaries and/or substrate surface. Dark red solid lines represent graphene.

3. Sensing performance for protein monolayers

To study the sensing performance of the proposed metasurface, goat anti-mouse immunoglobulin G (IgG) is employed as a representative target protein to be sensed. We furthermore assume that sensing is performed by measuring the reflection spectrum of the metasurface. We thus simulate the reflection spectrum from our metasurface with an adsorbed protein monolayer (or sub-monolayer). The protein permittivity is modelled as a Lorentz series with two oscillating terms that account for amide I and II bands [48]:

$$\epsilon_{\text{protein}}(\omega) = n_{\infty}^2 + S_1^2 / (\omega_1^2 - \omega^2 - i\omega\gamma_1) + S_2^2 / (\omega_2^2 - \omega^2 - i\omega\gamma_2) \quad (2)$$

where $n_{\infty}^2 = 2.08$ is the permittivity at infinite frequency; $\omega_1 = 1668\text{cm}^{-1}$, $\omega_2 = 1532\text{cm}^{-1}$, $\gamma_1 = 78.1\text{cm}^{-1}$, $\gamma_2 = 101\text{cm}^{-1}$, $S_1 = 213\text{cm}^{-1}$, $S_2 = 200\text{cm}^{-1}$ are the resonant frequencies, damping rates and oscillation strengths for the amide I and II bands respectively.

Figures 4 (a)-(d) show the simulated reflection spectra for metasurfaces I, II, III and IV respectively, including a coating that comprises a monolayer of protein IgG. The antenna

lengths and graphene ribbon widths are chosen so that the resonance wavelengths of the four metasurfaces span approximately the same spectral range. In the simulation, the protein monolayer is modelled as a 8-nm thick film whose permittivity is as given by Eqn. (2) that conformally coats each metasurface [48]. It can be seen that each spectrum exhibits a reflection dip in the spectral range $\lambda \approx 7$ to $9 \mu\text{m}$. This corresponds to the antenna and/or graphene plasmon resonant wavelength. In addition, the reflection spectra exhibit dips that originate from plasmonically enhanced light absorption by the protein. We indicate these features via green and orange shaded regions in Fig. 4(a-d). These are at wavelengths near the amide I ($\sim 6 \mu\text{m}$) and II bands ($\sim 6.5 \mu\text{m}$) of the protein IgG, and thus represent its spectroscopic fingerprint. It can be seen that these dips become weaker as the antenna resonance shifts away from the protein absorption bands as a result of the weaker coupling between the plasmonic resonance modes and the protein vibration modes [38]. In addition, dips caused by protein absorption of metasurface IV (Fig. 4(d)) are much weaker than those of metasurface I, II and III (Fig. 4(a-c)), due to the much weaker field enhancement of pure graphene plasmons.

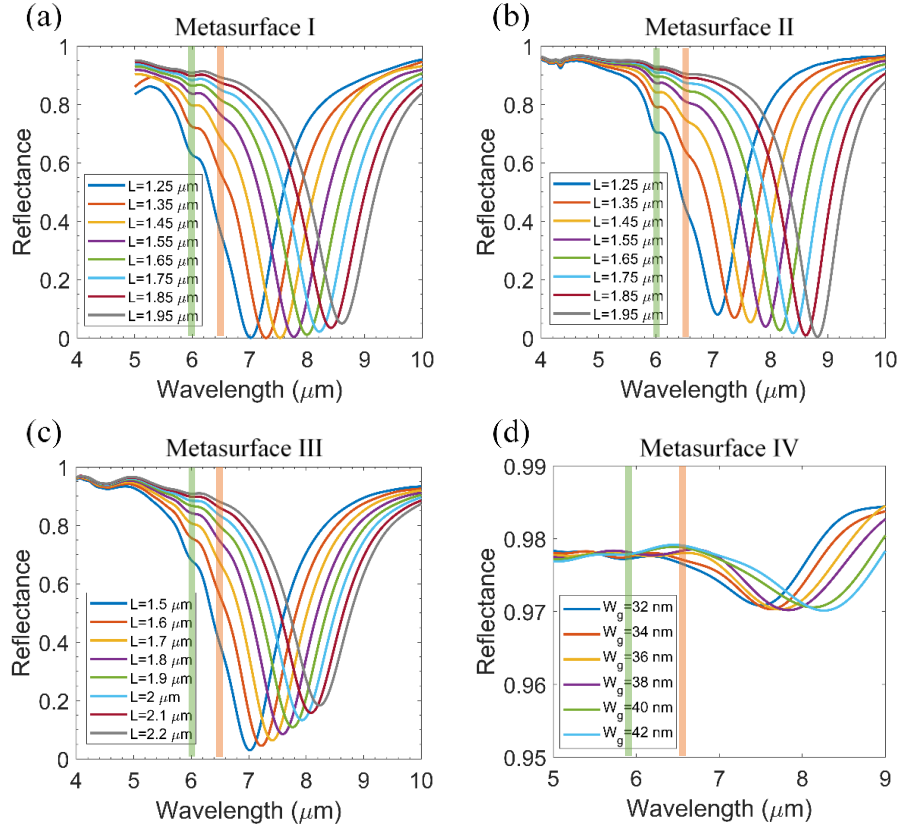


Fig. 4. Simulated reflection spectra for metasurfaces I (a), II (b), III (c) and IV (d). Antenna lengths are $L = 1.25 \mu\text{m} \sim 1.95 \mu\text{m}$ for (a-b), and $L = 1.5 \mu\text{m} \sim 2.2 \mu\text{m}$ for (c). For metasurface IV, graphene ribbon widths are $W_g = 32 \text{ nm} \sim 42 \text{ nm}$ and period is 80 nm . For all cases, a monolayer of protein IgG is coated on the metasurface. Green and orange shaded areas indicate the amide I and II bands of the protein.

To quantify the intensity of the amide band features of the reflection spectra, we calculate the second derivatives of these spectra. It can be seen that this results in spectral peaks (Figure 5) that can be readily compared. Indeed, the peak second derivative is positively correlated with the protein absorption as can be seen in Fig. 6 for metasurface I. This means that larger peak value in the second derivative curves corresponds to larger total protein absorption, providing the opportunity to quantify the amount of proteins.

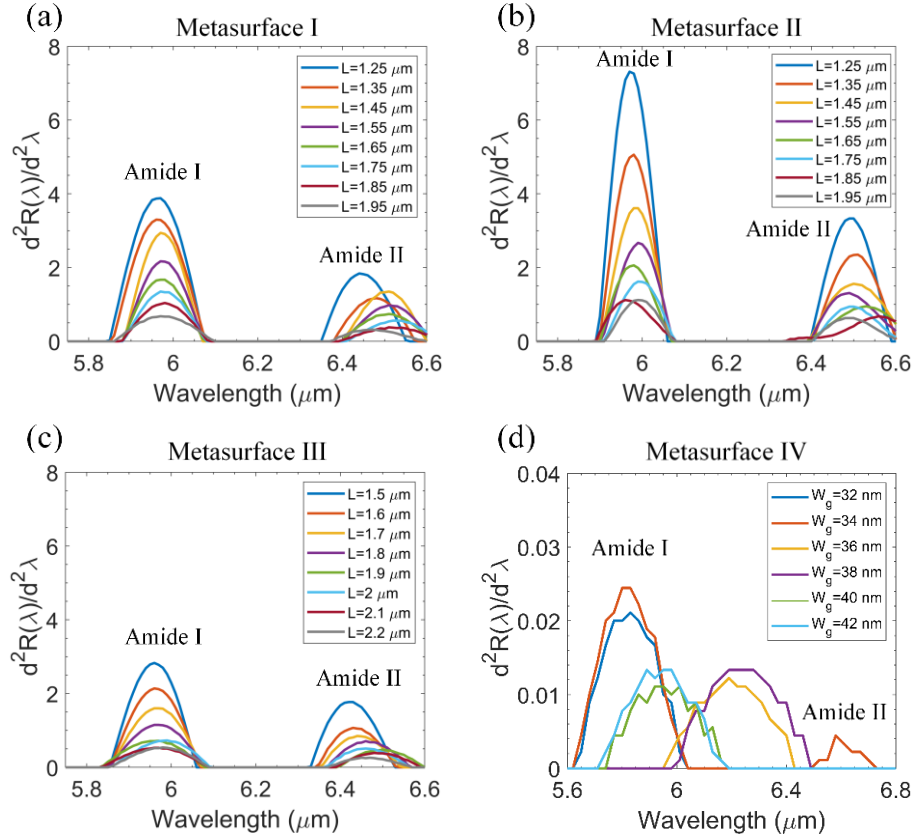


Fig. 5. Second derivatives calculated for the reflection spectra from Fig. 4 for metasurface (a) I, (b) II, (c) III and (d) IV. Note that only positive values are presented in all figures for brevity.

Figures 5(a)-(d) show the second derivative spectra calculated from the curves of Fig. 4(a)-(d), respectively. Note that only positive values have been shown to facilitate interpretation of these curves. Positive values of the second derivative correspond to the regions of upward concavity in the reflection spectra and thus include the features associated with protein absorption. Peaks in the second derivative spectra of Fig. 5 can be seen to occur at wavelengths corresponding to the amide I and amide II bands of the protein. It can be seen that these peaks decrease in strength as the antenna resonance shifts away from the absorption bands of the protein. It can also be seen that metasurface I (Fig. 5(a)) has a second derivative spectrum whose

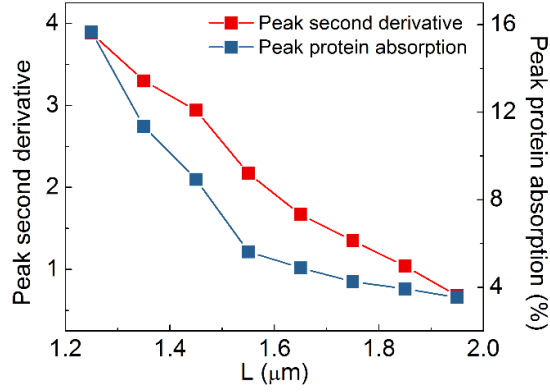


Fig. 6. Peak second derivative (red) and the corresponding protein absorption (blue) as a function of antenna length at the amide I band. Results obtained from metasurface I.

peaks are larger than metasurface III (Fig. 5(c)) but smaller than metasurface II (Fig. 5(b)). However, we show later on that the electrical tunability of metasurface I allows the device to be optimized and produces second derivatives greater than that of metasurface II. More importantly, the electrical tunability of metasurface I by gate voltage allows us to generate distinctive characterization spectra, i.e. reflectance spectra measured at different gate voltages, that would be very advantageous for sensing and identification. Here, the smaller second derivatives of metasurface I than that of metasurface II is probably due to the fact that the plasmonic mode volume is smaller for metasurface I than metasurface II, leading to weaker interplay between plasmonic polaritons and phonon-polaritons in IgG thin film. This can be further understood by examination of the intensity distributions of Fig. 3(a) and 3(b). It can also be seen that the maximum values of the second derivative peaks for metasurface IV (Fig. 5(d)) are about two orders of magnitude smaller than those of metasurface I. This indicates that this metasurface, which employs graphene plasmons only, would have much lower sensitivity in a protein sensing application.

4. Sensing performance for protein sub-monolayers

We next compare the sensing limitations of metasurface I, II and III by considering proteins in sub-monolayer form. We note that metasurface IV is not considered here since it already shows much lower sensitivity for the sensing of protein monolayers. We model each (single) IgG protein as a cuboid with dimensions of 4 nm (width) $\times$ 14 nm (length) $\times$ 8 nm (height) [52]. The proteins are positioned within the antenna gaps in the vicinity of antenna/graphene slit edges where the electric field is maximum. Figure 7(a-c) show the simulated reflection spectra for metasurfaces I, II and III respectively, with varying protein surface percentage coverage. The green and orange shaded regions indicate the amide I and II bands of the protein. To enable a fair comparison to be made, the lengths of the antennas of the three metasurfaces are chosen so they have the same resonant wavelengths.

We calculate the second derivatives of the spectra in Fig. 7(a)-(c) for quantitative comparison. The results are shown as Fig. 7(d)-(e). The amide I peak (centered around 6 μm) can be seen for all three metasurfaces and decreases as the protein density decreases (Fig. 7(d),(e)). For the same protein density, metasurface I shows the largest amide I peak value. We can also see a

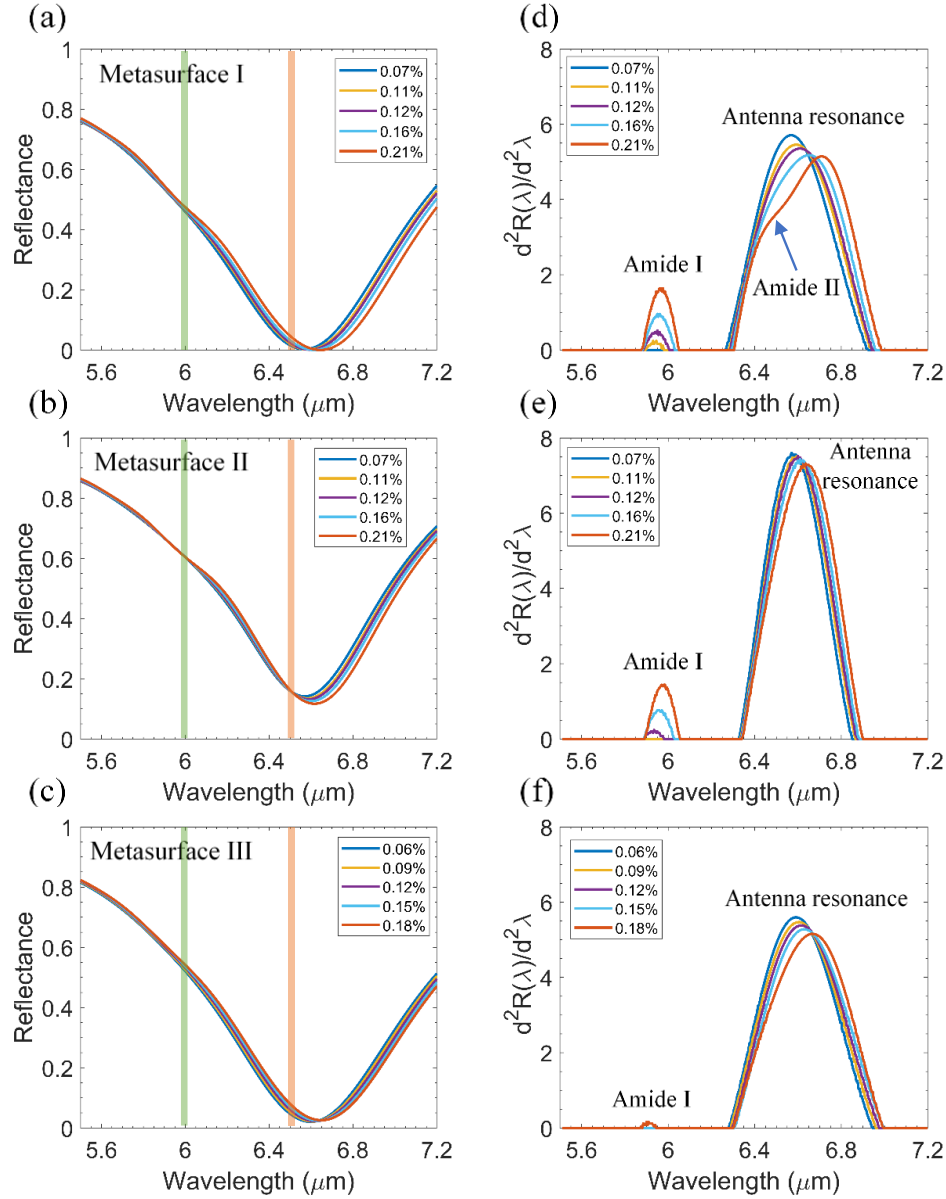


Fig. 7. Sensing performance for protein sub-monolayers. (a-c) Reflection spectra simulated for metasurface I, II and III coated with protein with varying surface percentage coverage. Antenna lengths are $L = 1.25 \mu\text{m}$, $1.25 \mu\text{m}$ and $1.5 \mu\text{m}$ for metasurface I, II and III respectively. Green and orange shaded regions indicate the amide I and II bands of the protein. (d-f) Second derivatives calculated from the simulated reflection spectra in (a-c) respectively.

weaker feature corresponding to the absorption of the protein amide II band for metasurface I (Fig. 7(d), indicated by the blue arrow). Furthermore, all three metasurfaces show large peaks associated with the antenna resonances that redshift as the protein density increases. The shift of antenna resonance can also be used to detect the presence of proteins. In Fig. 8(a-b), we show the antenna resonance wavelength shift (Fig. 8(a)) and the amide I peak values (Fig. 8(b)) as a

function of protein density. The antenna resonance wavelength shift is calculated with respect to the resonance wavelength that occurs in the absence of the protein coating. It can be clearly seen that metasurface I shows the greatest antenna resonance shift and amide I peak values for all values of protein density, indicating the highest device sensitivity among the three metasurfaces. One can also compare the metasurfaces in terms of the minimum protein density (surface percentage coverage) needed for the second derivative to be non-zero. From Fig. 8(b), it can be seen that for metasurface I this takes a value of 0.11%, compared to 0.12% for metasurface II and 0.18% for metasurface III.

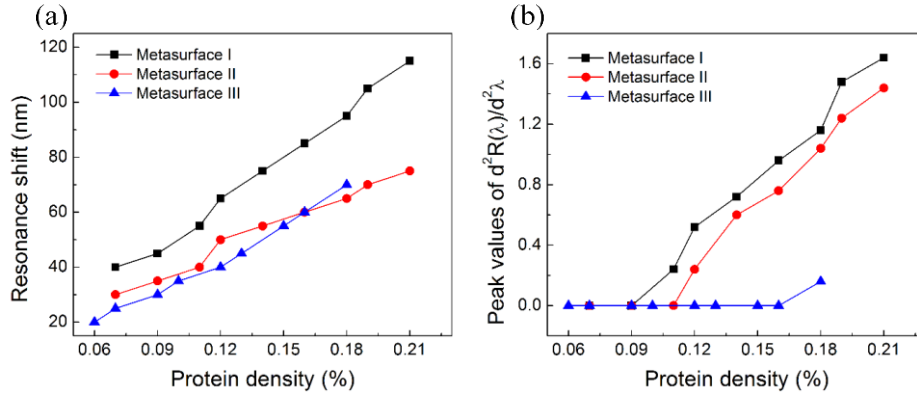


Fig. 8. Antenna resonance shift (a) and amide I peak values (b) as a function of protein density for metasurface I, II and III.

5. Electrical tuning of sensitivity for the proposed metasurface

Lastly, we show that varying the graphene Fermi level presents a means for further improving the performance of the device for detecting protein adsorption. This would be achieved by electrostatic gating. To exploit the tunability of graphene plasmon and achieve tuning of the resonance across the absorption bands of the protein, we tune the graphene plasmon closer to the protein absorption bands by changing the width of the graphene slits. Figure. 9(a) shows the reflectance spectra of metasurface I coated with protein IgG monolayer, with the width of graphene slits W_s varied from 19 nm to 5 nm. It can be seen that both the graphene plasmon resonance (indicated by red arrow) and the plasmonic resonance of the nanoantennas (indicated by yellow arrow) undergo redshift as W_s decreases. In particular, when $W_s = 5$ nm (dark blue curve), the graphene plasmon resonance locates in-between the two absorption bands. The corresponding second derivatives are shown in Fig. 9(b). As the graphene slit width decreases from 19 nm to 5 nm, the two peaks corresponding to amide I & II bands of the protein first decrease and then increase. This is due to the fact that as the plasmonic resonances undergo redshift, the coupling between the graphene plasmon mode and the protein film becomes stronger while the coupling between the antenna resonance mode and the protein film becomes weaker. Consequently, there exists a value of W_s for which the overall protein absorption is lowest and the corresponding second derivative value reaches minimum. We also note that in order to obtain a distinct protein signature, it is desirable to design the plasmonic resonances

away from the protein fingerprints region so that the reflectance dips caused by the protein absorption could be readily distinguished from that caused by the plasmonic resonances.

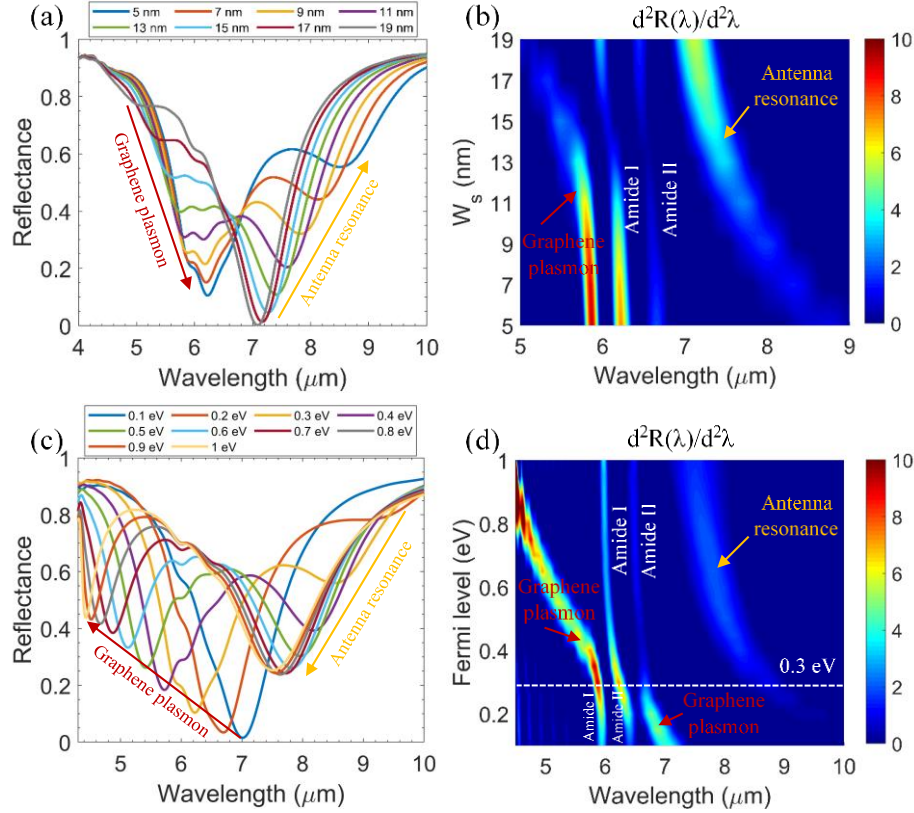


Fig. 9. Tuning of plasmonic resonance and device sensitivity via graphene slits for metasurface I. (a-b) Simulated reflectance spectra of metasurface I coated with protein IgG monolayer (a) and corresponding second derivatives (b), with width of graphene slits W_s varied from 19 nm to 5 nm. Antenna length $L = 1.25 \mu\text{m}$. (c-d) Simulated reflectance spectra of metasurface I coated with protein IgG monolayer (c) and corresponding second derivatives (d), with Fermi level of graphene E_f varied from 0.1 eV to 1 eV. Antenna length $L = 1.25 \mu\text{m}$. Graphene slit width $W_s = 5 \text{ nm}$. Graphene plasmon resonance and antenna resonance are indicated by the red and yellow arrows respectively.

Based on these simulations, we choose the width of the graphene slits W_s to be 5 nm for the demonstration of electrical tuning of plasmonic resonances and device sensitivity, because it corresponds to graphene plasmon resonance closest to the protein absorption bands. Figure 9(c) shows the simulated reflectance spectra of metasurface I with the Fermi level of graphene varied from 0.1 eV to 1 eV. The graphene slit width and antenna length are fixed at $W_s = 5 \text{ nm}$ and $L = 1.25 \mu\text{m}$ respectively. It can be seen that both the graphene plasmon resonance and antenna resonance undergo blueshift as the Fermi level of graphene increases from 0.1 eV to 1 eV. Specifically, the wavelengths of graphene plasmon resonance and antenna resonance are shifted from $7.01 \mu\text{m}$ to $4.43 \mu\text{m}$ and from $8.95 \mu\text{m}$ to $7.51 \mu\text{m}$, corresponding to a tuning range of $2.58 \mu\text{m}$ and $1.44 \mu\text{m}$, respectively. Notably, the graphene plasmon resonance is tuned across the two absorption bands of IgG protein, allowing active control of device sensitivity for

detecting different protein fingerprints. Figure 9(d) shows the corresponding calculated second derivatives from Fig. 9(c). It can be seen that, as the graphene plasmon resonance is shifted toward the protein absorption bands, the peak values corresponding to amide I (grey dashed lines) and amide II (grey dotted lines) bands of the IgG protein becomes larger. In particular, the peak second derivative corresponding to amide I reaches a maximum value of 9.41 when the Fermi level is tuned to 0.3 eV. Similarly, the peak corresponding to amide II reaches a maximum value of 4.74 when the Fermi level is tuned to 0.2 eV. This means that by fine tuning the graphene Fermi level to the appropriate values, the metasurface could be configured to be optimal for the detection of different molecular fingerprints. The distinctive pattern of the second derivative spectrum vs Fermi level is advantageous for the accurate detection of protein fingerprints in sensing experiments as one can tune the Fermi level of graphene and see whether the obtained second derivative pattern matches that of simulation. This approach would not be possible for metasurface II, for which only metallic antennas are used for sensing. It should be noted that the two peaks corresponding to amide I & II bands undergo slight red (blue) shift as the graphene plasmon resonance moves closer to the absorption bands from shorter (longer) wavelength. This phenomenon is more evident in the region near $E_f = 0.3$ eV, at which the graphene plasmon resonance is in-between the two protein absorption bands.

6. Conclusions

In conclusion, we propose a biosensor metasurface that consists of an array of plasmonic nanoantennas and graphene nanoslits on a resonant substrate. Systematic simulations are carried out to study the performance of the proposed metasurface for sensing the protein goat anti-mouse immunoglobulin G (IgG). Three other metasurface designs are also investigated for comparison. These consist of a plasmonic nanoantenna array, a plasmonic nanoantenna array on a graphene sheet, and a graphene ribbon array. The proposed metasurface combines the large electric field enhancement of metal plasmons with the strong spatial confinement of graphene plasmons, providing an opportunity for the sensitive quantification and identification of biomolecules down to sub-monolayer densities. We show by simulation that in the sensing of a monolayer of protein IgG, the proposed metasurface exhibits a sensitivity (strength of reflection dips associated with protein absorption) that is higher than that of the other metasurfaces. Indeed, the sensitivity is in excess of two orders of magnitude greater than that of the metasurface with graphene ribbon array. For the sensing of sub-monolayer of IgG, the proposed metasurface shows the highest sensitivity and best specificity among the four different metasurfaces, enabling fingerprint detection of proteins with densities down to a surface percentage coverage of 0.11%. The use of graphene nanoslits also allows an active tuning of the structure's resonance by electrostatic gating and provides a degree of freedom to configure the metasurface to be optimal for the detection of different molecular fingerprints, which is not possible for metasurface with plasmonic nanoantenna array. We believe the sensing strategy we propose in this paper, in which metal plasmons and graphene plasmons are combined synergistically, provides guidance for the future development of biosensors with ultra-high sensitivity and specificity.

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Appendix of Chapter 5

A5.1. Discussion on how to improve the resonance quality factor.

The quality factor of the resonances could be further improved by employing a few types of structures such as broken symmetry resonators and high contrast gratings. In addition, recently, the bound states in the continuum (BICs) has received much attention due to its ability to produce resonances with high quality factor and its demonstration in biosensing applications.¹⁸²⁻¹⁸⁴ We think that the BICs in dielectric resonators could also be used in combination with graphene for detection of biomolecules with high sensitivity.

A5.2. Discussion on the feasibility for fabrication of metallic nanoantennas and graphene nanoslits.

The nanofabrication of the proposed biosensor includes the fabrication of metallic nanoantennas and graphene nanoslits. The metallic nanoantennas with 30-nm gaps between adjacent antennas can be fabricated using high-resolution electron beam lithography, e.g. with Vistec EBPG5000 Plus EBL. The smallest graphene nanoslits we have studied, with a slit width of 5 nm, might not be easy to fabricate using standard etching method with electron beam resist as the mask. Such standard etching method would require sophisticated optimization of the etching processes to reach a 5-nm structure resolution. Alternatively, it would be less difficult to fabricate the 5-nm graphene slit using high-resolution focused ion beam lithography.

Chapter 6

Summary and Future Works

6.1 Summary of Results

In this thesis, we present nano-optical approaches to enhance the performance of graphene-based photodetectors operating in the two atmospheric transparent windows, i.e. long-wave infrared (LWIR) and mid-wave infrared (MWIR), by the use of two structures, namely magnetic mirrors and Jerusalem Cross nanoantennas (JC-antennas). These structures serve to boost the optical absorption in graphene and/or improve carrier collection, thereby increasing responsivity of the graphene photodetectors. We also present an approach to improve the sensitivity of graphene biosensors by combining graphene plasmons and noble metal plasmons synergistically and show their potential in quantification and identification of a representative protein – goat anti-mouse immunoglobulin G (IgG) – with densities down to sub-monolayers.

In the first work (Chapter 3), we propose and demonstrate a LWIR magnetic mirror consisting of an array of amorphous silicon (a-Si) cuboids on gold substrate. We demonstrate the magnetic mirror functionality by measuring a zero-phase shift of reflection at $\lambda = 8.4 \mu\text{m}$ using a home-built interferometer setup. The magnetic mirror also shows high reflectance with a measured reflectance of $\sim 90\%$ at the same wavelength. A modified multipole analysis method is devised and employed to provide insights into the magnetic mirror behaviour. We demonstrate by simulation that the optical absorption in graphene placed on our magnetic mirror can be enhanced by more than three orders of magnitude compared to the absorption that would occur were the graphene instead placed on a gold mirror. In the second work (Chapter 4), we demonstrate a MWIR polarization

independent graphene photodetector with integrated plasmonic nanoantennas we term JC-antennas. The JC-antennas serve to enhance the optical absorption as well as to increase the carrier collection. The demonstrated graphene photodetector shows MWIR photoresponse at room temperature (4.6 mA/W or 14.5 V/W), with improved responsivity at cryogenic temperatures (1.9 A/W or 4.4×10^3 V/W). Our detector also exhibits fast and broadband photoresponse that extends to visible and near-infrared wavelengths. In the third work (Chapter 5), we investigate a graphene biosensor device comprising graphene nanoslits and metallic nanoantennas on a resonant substrate. By leveraging both the strong field confinement of graphene plasmon and the large field enhancement of noble metal plasmon, we show that the proposed biosensor is able to detect protein G (IgG) in sub-monolayer form. Systematic electromagnetic simulations are performed to quantify the sensing performance of the proposed device and show that it outperforms designs in which only plasmons from metallic nanoantennas or plasmons from graphene are utilized.

6.2 Future Works

Below, we make some suggestions on future research directions in relation to the three works that are done in this thesis.

In the first approach, we experimentally demonstrate the magnetic mirror functionality and show through simulation that this structure could be used to enhance the optical absorption in graphene placed on top of the structure. The experimental demonstration of the integration of the magnetic mirror with graphene photodetector remains to be done and could be a research direction for future study. Our magnetic mirror could be used as a substrate in a graphene photodetector, allowing both the optical absorption of graphene to be enhanced and the Fermi level of graphene to be

electrostatically modulated by applying a voltage to the metal. To avoid the potential issue associated with the difficulty of transferring graphene on nanostructured surface, i.e. a-Si cuboid surface, one can have a device in which the magnetic mirror structure is fabricated on one side of a silicon wafer and the graphene is transferred on the other side of the wafer. The cuboid side length is varied to form a reflective metalens array. The incident light from the graphene side will first propagate through the wafer and then be reflected from the metalens array on the other side of the wafer and be focused on the detector plane, i.e. solid immersion type of focusing.¹⁸⁵ This device also provides further potential to be monolithically integrated with infrared focal plane arrays (IR FPAs).

The graphene absorption in our plasmonic antenna integrated graphene photodetector (in Chapter 4) could also be substantially improved by introducing a bottom optical cavity as predicted by the simulation in Fig. 4.12 of Chapter 4. One can expect that the design with optical cavity would exhibit even higher room temperature responsivity and detectivity. Recently, miniaturized spectrometers have drawn much interest due to their potential applications including lab-on-a-chip system, drones, and wearable devices. Computational spectroscopy approaches could allow the realisation of fully functional spectrometers with dimensions as small as tens of micrometres.¹⁸⁶ In such design, instead of using complex or dispersive optics for light sorting, the sensing material itself is engineered into pixels with varying spectral responses. The measured photocurrents, together with precalibrated response functions from the pixels, are then processed in a reconstruction algorithm to reconstruct the incident signal. The MWIR graphene photodetector we demonstrated in this thesis could also be used in computational spectral reconstruction applications. In our case, the spectral response of the detector is modulated by the plasmonic resonances of the JC-antennas, which could be conveniently shifted by tuning the Fermi level of graphene, forming a series of distinct

response functions. The electrical tunability of the detector spectral response provides the possibility for the spectral reconstruction to be achieved with single pixel. Based on our detector demonstration, the pixel size could be miniaturized down to $30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$, though further down scaling might also be possible.

The graphene biosensor we investigated in Chapter 5 could also be demonstrated experimentally. The device fabrication could be done by standard nanofabrication techniques and graphene transfer method we employed in this thesis. The reflectance spectrum measurement could be carried out with Fourier transfer infrared spectrometer (FTIR) attached to a microscope.

Finally, in light of current global coronavirus pandemic, we envision that the mid-infrared graphene photodetectors and biosensors investigated in this thesis would have good potential to help us better cope with COVID-19 and future pandemics by providing low-cost and sensitive tools for temperature monitoring and virus testing. On the one hand, it is a good hope that the cost of graphene-based mid-infrared photodetectors will be much cheaper than current commercial MCT detectors and thus make it more affordable for individuals and more economical for government organizations and businesses to setup temperature monitoring systems. On the other hand, it has been reported that coronaviruses have an average diameter of 120 nm. Thus, it is possible that the graphene biosensor structure studied in this thesis could help the testing of infection cases in the future by providing faster and more accurate detection of the viruses through fast optical measurement.

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