Plasmene metasurface absorbers: electromagnetic hot spots & hot carriers

Qianqian Shi,† Timothy U. Connell,‡ Qi Xiao,¶ Anthony S. R. Chesman,¶ Wenlong Cheng,† Ann Roberts,∥ Timothy J. Davis,∥ and Daniel E. Gómez*,‡

†Department of Chemical Engineering, Faculty of Engineering, Monash University, Clayton, VIC 3800, Australia
‡School of Science, RMIT University, Melbourne, VIC, 3000, Australia
¶CSIRO Manufacturing, Clayton, VIC, 3169, Australia
§Melbourne Centre for Nanofabrication, Clayton, VIC, 3169, Australia
∥School of Physics, The University of Melbourne, Parkville, VIC, 3010, Australia

E-mail: daniel.gomez@rmit.edu.au

Abstract

Light-matter interactions are extremely important as they sustain life on Earth and can be tailored for diverse applications in areas such as solar energy conversion, chemical sensing, and information storage. One key process of these interactions is the absorption of photons. We demonstrate a novel material capable of absorbing up to 98% of incident visible light. The material comprises a thin sheet of a tightly-packed two-dimensional lattice of metal nanoparticles, called plasmene, supported by a thin (sub-wavelength) dielectric film deposited on top of a mirror. We demonstrate how the resulting metasurface absorbers are useful in surface-enhanced spectroscopy and in the generation of plasmonic hot carriers. These structures hold great promise for applications in structural color, sensing and photocatalysis.
Keywords

Plasmonics, metasurfaces, optical magnetic mode, perfect absorption, plasmene, hot carriers

Solar-energy harvesting in photovoltaics and photocatalysis begins with the absorption of light by matter.¹ Light absorption creates electronically excited states from which useful work can be extracted if the excited charge carriers can readily access chemical (catalytic site) or physical (electrode) interfaces. To maximize solar-energy conversion efficiencies, it is thus desirable to create light-harvesting devices in which the thickness of the absorbing layer is much smaller than characteristic charge-carrier scattering lengths, while simultaneously preserving a high magnitude of light absorption.²

One class of structure that embodies these properties is the electromagnetic metasurface absorber,³ in which near-complete light absorption occurs across a sub-wavelength path length due to optical impedance matching between the material and free space, at a specific set of frequencies. Optical impedance matching can be achieved by placing a surface comprising nanoscale resonators (metasurface) at a specific distance from a reflector, leading to the excitation of optical resonances that efficiently suppress the reflection of light.⁴ The presence of the mirror eliminates transmission, and consequently nearly all light is absorbed at the frequency of the optical resonance. This concept has been demonstrated using metallic (plasmonic) nanostructures as the metasurface building block, resulting in strong absorption bands in the infrared⁵–⁸ and visible⁹–¹¹ range of the electromagnetic spectrum. Notably, there are remarkable examples where broadband light absorption has been achieved.⁷,¹²–¹⁴

In most demonstrations of plasmonic metamaterial absorbers, the metallic nanostructures have been lithographically defined into periodic arrays, or consist of randomly-distributed nanoparticles, which result from the vacuum deposition and subsequent annealing of thin metal layers. In contrast, creating these structures using colloidal suspensions of high-quality nanocrystals would enable the facile fabrication of plasmonic metamaterial absorbers using simple and scalable deposition processes.¹⁵ Furthermore, plasmonic nanoparticles can be synthesized with well-defined three-dimensional shapes and multi-element composition,
creating the prospect for the fabrication of novel metasurfaces with enhanced functionality. A theoretical study suggested that, in order to observe perfect absorption of electromagnetic energy, the absorption cross-section of a single metal nanoparticle in a metasurface must be comparable to the area of the inter-particle separation distance. This implies that the use of metal colloids as the building blocks of plasmonic metamaterial absorbers requires their assembly into optically–dense surfaces. To date, colloid-based plasmonic metamaterial absorber structures have been realized by the deposition of nanocubes using a layer-by-layer self-assembly approach driven by the electrostatic attraction of colloids to the supporting substrates.

Plasmene is a class of highly ordered and tightly-packed two-dimensional sheets of metal nanoparticles, which are formed by a two-step polystyrene-based drying-mediated self-assembly method. These two-dimensional arrays are of single-particle thickness and form over macroscopic (i.e. \( \sim \) mm) lateral dimensions. They also demonstrate several unique fundamental properties, such as an unusually high mechanical strength (\( \sim 1 \) GPa Young’s modulus) and the capacity to support both propagating and gap plasmon modes, controllable by the size, geometry and the orientation of their constituent unit cell. The fabrication of plasmene is significantly simpler than most existing (multi-step) self-assembly strategies, which could enable its fabrication at scale.

Here we demonstrate the fabrication of plasmene metasurface absorbers, which consist of a plasmene metasurface placed above a reflective ground plate at a distance where the incident electromagnetic field and the reflected field from the system are out of phase (Figure 1). The resulting material absorbs up to 98% of incident visible light at the frequency of the optical resonance of the metasurface. By engineering the geometry of the plasmene building blocks, it is possible to control the frequency of maximum absorption and achieve polarization sensitive absorption. We further show that plasmene metasurface absorbers can find application in plasmonic hot–carrier photo-catalysis.

Plasmene metasurfaces with building blocks of Au nanocubes (Figure 1B) were synthe-
sized following well-established protocols.\textsuperscript{23,24} Suspensions of these nanocrystals in water exhibit extinction bands in the visible that are characteristic of the excitation of localized surface plasmon resonances (Figure 1D).\textsuperscript{25}

In solutions of low particle concentration, the inter-particle distances between neighboring particles is much larger than the near-fields generated by individual particle plasmons. Consequently, the optical properties of these particles are well-described by considering the interaction of an isolated nanocube with an incident light field. This interaction excites localized surface plasmon resonances, creating a surface charge distribution $\sigma(r)$ along the surface points $r$ of the nanostructure. Given that the nanoparticle dimensions are significantly smaller than the wavelength of visible light, this charge distribution can be written in terms of the (electrostatic) eigenmodes $\sigma_m(r)$ (or self-sustained oscillations) of the particle according to $\sigma(r) = \sum_m a_m(\omega)\sigma_m(r)$, where $a_m(\omega)$ are the excitation amplitudes that describe the coupling of the incident light field with a particular eigenmode (here $m$ is an index that indicates the $m$-th mode sustained by the nanoparticle). Modes with strong dipolar character couple strongly with uniform electric fields and thus have large values of $a_m(\omega)$. Consequently, these are manifest in optical extinction spectra, as shown in Figure 1D corresponding to Au nanocubes in Figure 1B. The calculated lowest-order (three-fold) degenerate eigenmodes $\sigma_m(r)$ of the nanocubes clearly have a strong dipolar character, with charge accumulation at each of the three orthogonal directions of the cube (Figure 1D inset). For these particles, the electrostatic eigenmode description (particles in a uniform medium with the refractive index of water; eigenvalue for this mode 1.728) predicts that these dipole resonances occur at 560 nm, which is in good agreement with the experimental value.

Plasmene is formed by the deposition of a chloroform solution of Au nanoparticles onto the surface of a water droplet (Figure 1A). A change in polarity resulting from the evaporation of the chloroform results in the self-assembly of an extended two-dimensional array on the surface of the water droplet, with subsequent evaporation of water yielding a quasicrystalline lattice of plasmene, as depicted in the electron microscopy image of Figure 1C.
(more detail in the Methods Section). The extinction spectrum \(1 - T\) of a plasmene layer on a glass surface clearly demonstrates both a red-shift and spectral broadening (Figure 1D). This results from a combination of at least two effects: (i) the interaction of the nanoparticles with a substrate, as well as (ii) long and short-range interactions in the nanoparticle assembly leading to collective plasmonic effects.\(^{15}\) When the nanocubes are placed on a substrate, the degeneracy of the dipolar modes shown in Figure 1D is lifted, leading to hybridization between bright (dipolar) and dark (multipolar) single-particle plasmon modes. In the case of Ag nanocubes, it has been shown that this hybridization results in substantial spectral red-shifts and the emergence of resonances that were absent in the solution spectrum.\(^{26,27}\)

Collective plasmon resonances in the two-dimensional metasurface are in general difficult to describe with analytical models, more so in particular when the metasurface is quasi-crystalline, due to a lack of perfect translation symmetry.\(^{28}\) In general, the interaction of the metasurface with light leads to an induced dipole moment \(\mathbf{p}_n\) on the \(n\)-th particle of the metasurface, which is determined by its electric polarizability \(\alpha\) and the self-consistent electric field acting on it: the incident field \(\mathbf{E}_{\text{inc}}\) and the superposition of the fields produced by all the other particles on the metasurface. As a result of this superposition, it is in general possible to express the induced dipole moment in terms of the incident field according to:

\[
\mathbf{p}_n = \frac{1}{1/\alpha - G} \mathbf{E}_{\text{inc}},
\]

where \(G\) represents a lattice sum describing the interaction of the particles in the metasurface.\(^{29}\) While the polarizability \(\alpha\) describes the surface plasmon resonance of a single particle, the quantity \((1/\alpha - G)^{-1}\) accounts for the collective plasmon modes of the metasurface, which due to the effect of the inter-particle interactions in the lattice (accounted for by the term \(G\)), will lead to a resonance frequency red-shift with respect to that of the isolated particle. Following this analysis, it can be shown that the maximum amount of light that a single plasmene sheet can absorb (when placed in a symmetric dielectric environment) is limited
To experimentally realize plasmene metasurface absorbers of light, the mirror and spacer layer of the diagram of Figure 1A were deposited by physical vapor deposition. The spacer layer consisted of TiO$_2$, a dielectric with a high refractive index that is transparent to visible light. Self-assembly of a plasmene sheet on the TiO$_2$ thin film completed the structure (complete details in the Methods section). Figure 2A shows the measured absorption spectra of two samples constructed using Al as the mirror, Au nanocubes as the plasmene building blocks, and TiO$_2$ of different thicknesses. These spectra were determined by measuring the transmission ($T$) and reflection ($R$) spectra of each sample (the latter carefully referenced to a surface with a known reflectance spectrum), giving the absorption ($A$) as: $A = 1 - R - T$ by virtue of the conservation of energy (more detail in the Methods Section, the transmission spectra are shown in Figure ??). With a dielectric spacer of 30 nm thickness, the spectrum showed two dominant absorption bands at 480 and 703 nm reaching absorption magnitudes of 86% and 91%, respectively. Increasing the dielectric spacer thickness to 58 nm slightly increased the maximum absorption to 94% at 700 nm. Interestingly, while the absorption band at $\sim$700 nm underwent a slight hypsochromic shift, the higher energy band ($\sim$480–500 nm) showed a bathochromic shift as the TiO$_2$ thickness increased, consistent with a distance-dependent interaction between the plasmene sheet and the metal layer.$^{18}$ Changing the chemical composition of the mirror layer in the metasurface absorber from Al to Au caused a hypsochromic shift in the low energy absorption band (approx. 10 nm) along with a small increase in magnitude (Figure 2B). When compared to the extinction spectrum of a nanocube plasmene sheet deposited on glass (Figure 1D), the absorption bands of Figures 2A-B are noticeably sharper.

The absorption spectrum of plasmene is spectrally tailored by the geometry and size of the nanoparticle building blocks. For increasing size of the building blocks, a redshift in the plasmene optical resonances is expected.$^{24,30,31}$ The geometrical effect is illustrated in Figure 2 C-E, where we show a metasurface absorber made with bipyramidal-shaped Au
nanocrystals (electron microscope image of the building blocks shown in Figure 2C). Due to their long aspect ratio (Figure 2C), Au bipyramid nanoparticles exhibit multiple localized surface plasmon resonances (Figure 2D). A plasme metasurface absorber incorporating bipyramidal building blocks exhibited an absorption band with a maximum of 98% incident light absorption at 524 nm. (A second absorption band is expected to occur at higher wavelengths, but is beyond the detection range of the instrumentation used). Nano–bipyramids can self-assemble to form plasmene sheets in four different packing orders, and due to their high structural aspect ratio, these assemblies form plasmene sheets with optical properties that are sensitive to the polarization of the incident electromagnetic field. This is illustrated in Figure 2E, where it can be observed that the absorption of light depends on the polarization of the incident electromagnetic field. This effect is also clearly visible to the naked eye, as we illustrate with the optical microscope images shown in the inset of Figure 2E.

The scattering of light imposes a lower limit on the reflectivity at the peak absorption. Scattering can occur as a consequence of structural disorder or the existence of edges in the plasmene lattice. The former may arise from the size distribution of the building blocks, while the latter may occur due to the finite extent of the plasmene sheets or the unintentional formation of stacked multiple layers. The black line of Figure 2(E) shows the measured dark-field scattering spectrum of a plasmene metasurface absorber, which we calibrated against a surface of known reflectance and scattering amplitude (details in Methods section). The figure shows clearly that scattering in these structures is strongly suppressed (< 1% of the total incident power) due to the regular ordering of the nanocrystal building blocks in the plasmene metasurface.17

In order to gain insight into the physical mechanism that enables almost complete impedance matching in plasmene metasurface absorbers, we have modeled the optical properties of nanocube plasmene metasurface absorbers using a finite element approach for solving Maxwell equations. The model consisted of a periodic array of nanocubes of side length 40 nm ordered in a cubic lattice with a 80 nm period and a 30 nm spacer layer. Figure 3
shows the calculated maps of electric ($|E|$) and magnetic ($|H|$) field distributions around a single particle in the plasmene metasurface absorber. The results predict the existence of two optical resonances, in agreement with the experimental observations of Figure 2. For a wavelength of 520 nm, the electric field is strongly localized at the edges of the nanocube distant to the dielectric film. This localization is reversed at 700 nm, where the electric field is strongly localized at the edges of the cube in the dielectric-cube interface. The magnetic field exhibits strong localization in the TiO$_2$ layer, analogous to a magnetic dipole. This optical magnetic response originates from the interaction of the induced oscillating surface charges on the cubes with their mirror images on the metal support. The radiation from both dipoles (one located on the metasurface and its mirror image) are out of phase and cancel, leading to suppression of reflection, resulting in complete absorption of the energy by the metasurface.

For metasurfaces with a nanostructured layer, in which the inter-particle spacings are larger than the spatial extent of the plasmonic near-fields, perfect absorption has been modeled with a coupled-mode theory, wherein each individual mirror-coupled nanocube acts like a magnetic dipole. The collective action of an ensemble of these nanocubes results in an effective magnetic response, which enables almost complete impedance matching between the metasurface and free space, resulting in near-perfect absorption. In metasurfaces with a sparse surface coverage, these magnetic modes can be both excited and scattered at the edges of the nanocube, allowing for some of the radiation to escape and couple into free space. Given the deep sub-wavelength separation between the building blocks, the plasmene metasurface can be considered an effective magnetic metasurface, that is different from a metal film of a similar thickness (see Figure ??). In effect, the plasmene metasurface absorbers can be conceptualized as being a class of asymmetric Fabry-Pérot resonators, where one of the mirrors can support optical resonances. This implies that (to zeroth–order) an optical resonance of the asymmetric Fabry-Pérot resonators occurs when the total phase shift $\Delta\phi$ experienced by the electromagnetic field is a multiple integer of $2\pi$, a condition that is illus-
trated in Figure 3, and expressed mathematically as: $\Delta \phi = m2\pi = 2\varphi_{\text{propagation}} + \varphi_m + \varphi_P(\lambda)$, where $m$ is an integer ($m = 0, 1, 2, \ldots$), $\varphi_{\text{propagation}}$ is the phase accumulated during propagation in the TiO$_2$, $2\varphi_m$ the phase shift that occurs upon reflection from the mirror and $\varphi_P(\lambda)$ the wavelength ($\lambda$) –dependent phase shift that occurs upon reflection from the plasmene metasurface.\textsuperscript{4,34,35} The magnitude of each of these phase shifts depends on the material properties of the mirror and spacer layer in addition to the optical properties of the plasmene metasurface.

Due to the strong local electromagnetic fields produced in the plasmene metasurface absorber, these materials can find application in surface-enhanced Raman spectroscopy (SERS), wherein an electromagnetic enhancement of the measured signals originates from so-called hot spots.\textsuperscript{36} For a simple proof-of-principle demonstration, the metasurface absorbers were firstly subjected to a plasma treatment for the removal of organic ligands. As a model Raman analyte, we employed 4-aminothiophenol (4-ATP, under illumination with a 782 nm laser) and in figure 4A, we show the SERS spectra of 4-ATP obtained with Au nanocube plasmene metasurfaces (supported on Al) and with bare glass and TiO$_2$ for comparison. The spectra consists of a set of peaks, the most intense of which are located at 1078, 1141, and 1578 cm$^{-1}$, which are consistent with previous studies.\textsuperscript{24} Clearly, the recorded SERS signals are strongest for plasmene metasurface absorber substrates, which is a consequence of: (i) the strong absorption of light by these materials at the excitation wavelength, and (ii) their strong localization of electromagnetic fields (i.e. hot spots, Figure 3).

Nanomaterials that harness radiant energy to drive chemical transformations are of great importance to the development of highly efficient heterogeneous photocatalysts,\textsuperscript{37} which have great potential for enabling a solar-powered chemical manufacturing industry.\textsuperscript{38,39} Non-radiative power dissipation in plasmene metasurface absorbers can result in the excitation and emission of hot electrons and holes.\textsuperscript{40,41} One approach for capturing these energetic charge carriers is to create metal-semiconductor contacts, which can lead to Schottky junctions [see Figure 4(B, left)], where electrons generated in a metal can escape into the semicon-
ductor if their energy is higher than the energy barrier at the interface ($\phi_B$, Figure 4B) and their momentum lies within the escape cone. While the exact mechanism for hot-carrier generation and emission with metal nanostructures is still a subject of intense debate, it is clear that absorption of electromagnetic energy is of fundamental importance in this process.

In Figure 4B, we show the photo-current measured with plasmene metasurface absorbers when these were employed as working electrodes in a three-electrode photo-electrochemical cell (Pt wire counter-electrode and a Ag/AgCl reference, details in the Methods section). Following non-radiative power dissipation in the plasmene metasurface absorbers, hot electrons are injected into the TiO$_2$ and subsequently collected by the mirror, from which they are transported to the counter-electrode, where a corresponding reduction reaction occurs in solution. The positive hot-hole left in the plasmene metasurface can be filled by a sacrificial electron donor in solution. These processes result in a measurable photo-current, as demonstrated in Figure 4. This figure shows the measured photocurrents for three cases: (i) Al/TiO$_2$/plasmene, (ii) Al/TiO$_2$, and (iii) ITO/TiO$_2$/plasmene. These measurements were performed under visible light irradiation (495 nm long pass filter) with an applied potential of 1.0 V (with respect to the reference electrode) and under conditions where the electrolyte consisted of aqueous 0.5 M Na$_2$SO$_4$ and 20 v/v% methanol as the sacrificial electron donor (details in the Methods section). The long pass filter negates direct excitation of charge carriers in TiO$_2$, accounting for the almost non-existent photo-response observed with the Al/TiO$_2$ support alone. Significant photocurrents were only observed when Au plasmene metasurfaces were present, suggesting that the interaction of light with the plasmene metasurface initiates subsequent charge-separation and transport. The anodic currents measured with the plasmene metasurface absorber (i.e. Al/TiO$_2$/plasmene, 0.44 $\mu$A cm$^2$) were 6.3$\times$ larger than those obtained with the ITO/TiO$_2$/plasmene (0.07 $\mu$A cm$^{-2}$) electrode, a consequence of the greater absorption of electromagnetic energy exhibited by the plasmene metasurface absorber. The presence of the mirror support, as discussed previously, is required for achieving near-perfect absorption of light at the wavelength of the optical reso-
nance, which is in turn the primary step leading to the observation of hot-carrier phenomena with these structures. This simple proof-of-concept demonstration can be readily extended for the application of plasmene metasurface absorbers in plasmonic hot-carrier effects for novel photo-redox chemistry, and photo-detection schemes.

In summary, we have fabricated and measured the absorption spectra of plasmene metasurface absorbers of light, which can absorb up to 98% of incident visible light at the wavelength of their optical resonance. We have shown that these resonances can be engineered by the geometry of the building blocks of plasmene to result in polarization-selective near-perfect absorption of light. We showed how these self-assembled metasurface absorbers lead to enhanced spectroscopy and hot-carrier photocurrents, demonstrating how function can be derived from metasurface design. The intense electromagnetic near-fields resulting from this near total extinction of light may also find application in surface-enhanced spectroscopy, chemical and biological sensing, and for exploiting plasmonic hot-carrier extraction. Notably, as the mirror and TiO$_2$ layers can be deposited by solution-based approaches (such as electroplating, spin-coating and sol-gel methods), this report provides a pathway to the scalable, vacuum-free fabrication of metasurface electromagnetic absorbers.

1 Methods

Materials Gold(III) chloride trihydrate (HAuCl$_4$·3H$_2$O, ≥99.9 %), sodium borohydride (NaBH$_4$), trisodium citrate, hexadecyltrimethylammonium bromide (CTAB), silver nitrate (AgNO$_3$), L-ascorbic acid, and cetyltrimethylammonium chloride solution (CTAC, 25 wt% in H$_2$O) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, 32 wt %) was purchased from AJAX. Ammonium hydroxide (NH$_3$·H$_2$O, 25 wt %) used in the purification process of Au NBP was purchased from Chem Supply. Hydrogen peroxide (H$_2$O$_2$, 30 wt %) used in the purification process of Au NBP, and chloroform were purchased from Merck KGaA. Tetrahydrofuran (THF) was purchased from UNILAB. Thiol-terminated polystyrene (SH-PS) (Mn
was purchased from Polymer Source Inc. All chemicals were used as-received unless otherwise indicated. Milli-Q water was used in all aqueous solutions. All glassware used in the experiments were cleaned in a bath of freshly prepared aqua regia and were rinsed thoroughly with Milli-Q water prior to use.

**Synthesis of Nanocrystal Building Blocks**

*Synthesis of Au nanocubes* A seed-mediated method was used to synthesize Au nanocubes. Briefly, a seed solution was prepared by adding NaBH₄ (0.6 ml, 0.01 M) to an aqueous solution prepared by mixing HAuCl₄ (0.1 ml, 25 mM) and CTAB (7.65 ml, 0.1 M). The seed solution was then kept at 30 °C for 1 hour. The growth of Au nanocubes was triggered by adding 5 µl of a 10-fold diluted seed solution into a growth solution prepared by adding CTAB (1.6 ml, 0.1 M), HAuCl₄ (0.2 ml, 7 mM), and ascorbic acid (1.2 ml, 0.1 M) to water (8 ml). The resulting solution was then left undisturbed overnight, followed by centrifugation at 8000 rpm for 10 min and redispersal in Milli-Q water (10 ml) for further use.

*Synthesis of Au Nanobipyramids (NBP)* The synthesis of Au nanobipyramids involved a seed-mediated method and a three-step purification, as reported. A Au-seed solution was synthesized by adding NaBH₄ (1 ml, 100 mM) to a solution prepared by adding HAuCl₄ (0.4 ml, 25 mM) to aqueous trisodium citrate (40 ml, 0.25 mM). The resulting solution was then kept stirring at room temperature for 2 hours. Later, a portion of this seed solution (0.8 ml) was added to a CTAB growth solution (0.1 M, 100 ml) that contained aliquots of HAuCl₄ (2 ml, 25 mM), AgNO₃ (1 ml, 10 mM), HCl (2 ml, 1.0 M), and ascorbic acid (0.8 ml, 0.1 M). The growth solution was kept at 30 °C overnight, and then centrifuged at 7830 rpm for 10 min, with the precipitate re-dispersed in an aqueous solution of CTAC (100 ml, 80 mM). Purification of the Au NPBs was achieved using a three-step method reported previously. The final solution was washed and re-dispersed in Milli-Q water for further use.

**Preparation of Metal-Semiconductor Substrates** All films were deposited in an electron beam evaporation system (Intlvac, Nanochrome II) using a 10 kV power supply in a Class 10,000 clean-room. Glass substrates were cleaned by sequential ultra-sonication in
acetone and isopropanol, and then dried under a stream of nitrogen gas. The substrates were also cleaned by a plasma treatment step prior to the deposition of the metal-semiconductor films. In order to achieve good adhesion of the mirror layer to the substrate, a thin layer of Cr (5 nm, deposited 0.5 Å/s) was deposited. The Al or Au mirrors (100 nm, deposited 1.0 Å/s), and TiO$_2$ spacer (30 or 60 nm, deposited 0.5 Å/s) were deposited sequentially. Dielectric film thickness was confirmed by spectroscopic ellipsometry (J. A. Woolam Co., M-2000DI).

**Plasmene assembly** Plasmene metasurfaces were created by a drying-mediated self-assembly method at an air-water interface. First, a two-step ligand-exchange method was used to replace CTAB ligands with SH-PS (Mn=50,000 for Au nanocubes and 20,000 for NBP). Briefly, 10 ml of the CTAB-capped Au nanocube solution (or 12 ml of the Au NBP solution) was centrifuged and re-dispersed in 5 ml (or 6 ml for Au NBP) SH-PS-THF (4 mg/ml) solution. The solution was then kept at room temperature overnight and purified by repeated centrifugation-precipitation cycles to remove uncapped ligands and precipitate the SH-PS capped nanoparticles. Finally, the solution was concentrated and re-dispersed in a small amount of chloroform. To assemble a plasmene sheet, one drop of nanoparticle solution was deposited onto a water droplet sitting on the mirror/spacer substrate. After the full evaporation of the water and chloroform, a plasmene sheet was obtained. In figure S3 of the supporting information section we show the effect of the volume of the supporting water drop on the resulting lateral dimension of the plasmene.

**Characterization** Normal incidence images of the resulting structures were obtained by scanning electron microscopy (FEI, NovaNanoSEM 430). SEM images of plasmene were obtained by a FEI Helios Nanolab 600 FIB-SEM operating at 5 kV.

**Optical Measurements** The optical transmission and reflectance spectra of the metasurface absorber plasmene sheets were measured using an upright microscope (Nikon LV100), coupled to a spectrograph (Andor, SR-303i-A) equipped with a CCD (iDUS DU420A-BEX2-DD). For all the measured spectra, the light source was a broadband 100 W halogen lamp.
The illumination and collection of reflectance ($R$) was done with a 50× objective (NA 0.55), and these measurements were referenced to a mirror with a known reflectance spectrum (Thorlabs BB1-E02). The transmission ($T$) spectra were calibrated using a bare glass substrate. The absorption data shown in this paper were calculated as: $A = 1 - R - T$ and are consequently not arbitrary values. Scattering spectra were measured using the same objective but placing a dark-field iris in front of the light source. These spectra were referenced to a white diffuse Reflectance Standard (Labsphere, Spectralon SRS-99-020).

**SERS measurements** The plasmene metasurface absorbers were first plasma-treated for 4 min and then submerged into 1 mL of 10 μM ATP ethanol solution and left undisturbed overnight. The samples were rinsed with ethanol and dried before testing. SERS spectra were recorded by using a Renishaw RM 2000 Confocal micro-Raman System equipped with an excitation laser wavelength of 782 nm and using a 50× objective.

**Photo–electrochemical Measurements** Prior to all experiments, the plasmene metasurface absorbers were first plasma-treated for 4 min. The plasmene metasurface absorbers and a platinum wire were employed as the working electrode and counter electrode, respectively, with a Ag/AgCl reference electrode in a photo-electrochemical cell. The exposed surface area of the working electrode was 1 cm in diameter. The electrolyte solution used was 0.5 M Na$_2$SO$_4$ (anhydrous, Sigma-Aldrich, ≥ 99%) with 20 v/v % amount of methanol (Sigma-Aldrich, ≥ 99.9%) or ethanol (Sigma-Aldrich, ≥ 99.9%) as the sacrificial electron donor. The 0.5 M Na$_2$SO$_4$ was employed to reduce the electrical resistance in the electrolyte solution. Prior to the photocurrent measurements, the solutions were purged with N$_2$ gas to remove electron scavenging O$_2$. The working potential was set at +1.0 V versus the Ag/AgCl reference electrode, and the devices were illuminated with light from a 300 W Xenon lamp (Newport Model no. 669092) using a 495 nm long-pass filter (Thorlabs FGL-495). The applied voltage and photocurrent were recorded with a potentiostat (AutoLab PGSTAT204). Figure S4 shows SEM images of the plasmene before and after UV ozone treatment demonstrating its structural stability.
**Numerical Simulations** The three-dimensional numerical simulations shown in Figure 3 were undertaken using the Finite Element Method implemented in COMSOL Multiphysics 5.3a. We used tabulated data for the refractive index of Au\(^{46}\) and Al\(^{47}\) for the substrate, and 1.0 for the medium above the structure. The refractive index of the TiO\(_2\) layer was assumed to be fixed at 2.4. The cubes were rounded to have a radius of curvature of 2 nm. Although the arrangement has significant irregularities, periodic boundary conditions were assumed on the relevant sides of the modeled region with the period taken to be 80 nm. The larger period was selected to avoid overestimating the degree of coupling between the particles which depends not only on the spacing, but also the morphology of the particles which can be seen to deviate from cuboids. A port boundary was used at the excitation surface and the surface adjacent to the Al was taken to be a scattering boundary. No apparent backscattering from the terminating boundaries was apparent. The normally incident plane was assumed to be linearly polarized parallel to one of the horizontal edges of the cubes.

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**Competing financial interests** The authors declare no competing financial interests.
Figure 1: The self-assembly of plasmene sheets on mirror/dielectric substrates (supported on glass), resulting in the formation of near-perfect absorbers. **A** The drying-mediated self-assembly of plasmene. Electron microscope images of **B** Au nanocubes (side length $\sim 40$ nm), and **C** a plasmene sheet. The scale bar corresponds to 100 nm in both images. **D** Normalized absorption spectra of Au nanocubes in solution and the extinction (1-T) spectrum of a Au nanocube plasmene sheet on glass. **Inset.** Calculated lowest-order degenerate eigenmodes $\sigma_m(r)$ of Au nanocubes.
Figure 2:  

(A) Absorption spectra of plasocene metasurface absorbers made with Au nanocubes / TiO$_2$ / Al mirror, with varying TiO$_2$ thicknesses affecting the absorption spectra.  

(B) Effect of mirror type on the absorption spectra of the absorbers (TiO$_2$ thickness fixed at 30 nm.) Effect of plasocene building block geometry on optical properties. Electron microscope images of (C) Au bipyramids in solution (scale bar 100 nm) and a plasmene sheet made with Au bipyramids (scale bar 400 nm), illustrating the lattice orientation that is responsible for the observed polarization dependence. The black arrow denotes the $0^\circ$ polarization referred to in (E).  

(D) Absorption spectrum of a plasocene metasurface absorber made with bipyramids, shown for two TiO$_2$ thickness. Also shown is the (normalized) absorption spectrum of Au bipyramids in solution (shaded area). the inset shows the three dominant eigenmodes of a bipyramid.  

(E) Absorption spectra for plasocene sheets made with Au bipyramids measured for two polarizations. The black line corresponds to the measured dark-field scattering spectrum. For the cases shown here, the mirror was made with Al and the spacer consisted of 30 nm of TiO$_2$. Inset. Optical microscope images of the measured regions demonstrating a drastic change in color. The scale bar corresponds to 10µm.
Figure 3: Diagram illustrating the phase changes experienced by electromagnetic radiation as it reflects and propagates within a plasmene metasurface absorber. (Right) Spatial maps of the magnitude of the electric ($|E|$) and magnetic ($|H|$) fields at two wavelength. The magnetic field distribution at $\sim 700$ nm clearly shows that at this wavelength, normally-incident light excites a magnetic mode in the structure.

Figure 4: Surface enhanced Raman spectroscopy (A) and Photocurrent generation (B) with plasmene metasurface absorbers. (A) SERS spectra of 4-ATP obtained at an excitation wavelength of 782 nm when using a bare glass support, a thin film of TiO$_2$ or plasmene metasurface absorbers with different TiO$_2$ thickness as indicated in the figure legend. (B, Left) Energy diagram of a metal–semiconductor Schottky junction, characterized by a barrier height $\phi_B$. $E_F$ is the Fermi level of the metal and $E_c$ and $E_v$ are the conduction and valence band energies of the semiconductor. Non-radiative dissipation can excite a hot electron ($e_{hot}$) which can be injected into the semiconductor, leading to measurable photocurrents in a photoelectrochemical cell. (B, Right) Measured current densities under visible light ($>495$ nm) illumination for photo–anodes made of Al/ TiO$_2$/plasmene (blue), Al/TiO$_2$ (black) and ITO/TiO$_2$/plasmene (orange).
References


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