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Micropatterning of the Ferroelectric Phase in a Poly(vinylidene difluoride) Film *via* Plasmonic Heating with Gold Nanocages

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Abstract: *Polymer thin films with patterned ferroelectric domains are attractive for a broad range of applications, including the fabrication of tactile sensors, infrared detectors, and non-volatile memories. Here we report the use of gold nanocages (AuNCs) as plasmonic nanostructures to induce ferroelectric-paraelectric phase transition in a poly(vinylidene fluoride) (PVDF) thin film by leveraging their photothermal effect. This technique allows us to generate patterned domains of ferroelectric PVDF within just a few seconds. The incorporation of AuNCs significantly enhanced the pyroelectric response of the ferroelectric film under near-infrared irradiation. We also demonstrated the use of such patterned ferroelectric films for near-infrared sensing/imaging.*

Keywords: ferroelectric • IR imaging • nanostructures • phase transition • surface plasmon resonance

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Plasmon-assisted phase transition was used to pattern a freestanding ferroelectric thin film into arrayed domains in a few seconds by incorporating a very small (0.08% by wt.) amount of Au nanocages into the film. The patterned array of ferroelectric domains could serve as discrete pixels for infrared sensing/imaging.

Photothermal conversion based on plasmonic nanostructures has been explored to induce localized heating of the host medium, which is highly attractive for a broad range of applications including biomedicine,^[1] steam generation,^[2] optofluidics,^[3] and acceleration of chemical reactions.^[4] The heat transfer from a plasmonic nanoparticle to the host medium starts with the absorption of photons *via* localized surface plasmon resonance (LSPR) and conversion of part of the photon energy to heat, which is then transferred to the surrounding medium.^[5] Previous studies have demonstrated the use of such plasmonic heating to induce phase transition in water,^[2b] thermoresponsive copolymers^[6] and phase-changing materials^[7]. These plasmon-assisted phase transitions in the host media can lead to various interesting physical changes in material properties, offering a powerful tool to design and fabricate functional devices for an array of applications.

Ferroelectric polymers have attracted much interest as the next-generation piezo-/pyroelectric materials due to their feasibility for solution processing, flexibility, low cost, and non-toxicity. Poly(vinylidene fluoride) (PVDF), one of the most commonly used ferroelectric polymers, possesses α , β and γ phases.^[8] Its piezo-/pyroelectric properties have enabled the fabrication of film-based tactile sensors, infrared detectors, energy harvesting devices, and non-volatile memories. To realize these applications, it is critical to pattern the ferroelectric phase (either β or γ) rather than the paraelectric α phase. So far, such patterning has been mainly achieved by irradiation etching^[9] and imprinting lithography.^[10] The former method may deteriorate the ferroelectric properties while it is not easy to obtain a freestanding and smooth polymer film using imprinting lithography without involving multiple steps. PVDF generally exhibits a phase transition from the ferroelectric to the paraelectric phase when heated temperatures near its melting point or the ferroelectric Curie temperature (*ca.* 170 °C).^[11] As an alternative approach, Wegener *et al.* reported the patterning of PVDF film by scanning of a focused laser beam across the top aluminum electrode.^[12] This method successfully generated depolarized stripes of 80–90 μm wide in a PVDF film, but the efficiency is expected to be relatively low due to the high reflectance of the metal electrode, and the one-direction heat transfer from the electrode to the film.

In this communication, we demonstrate the use of plasmonic nanostructures to harvest the photon energy as an effective means to induce ferroelectric-paraelectric phase transition in a ferroelectric polymer film. Specifically, we mixed AuNCs with PVDF and then cast the mixture

into thin films. We employed AuNCs as the plasmonic nanostructures owing to their tunable LSPR in the near-infrared (NIR) region and the remarkable photothermal effect.^[6, 13] When dispersed in a polymer matrix, AuNCs could be used to generate localized heating in the PVDF film upon laser irradiation, leading to ferroelectric-paraelectric phase transition in just a few seconds. This efficient plasmon-assisted phase transition allows us to pattern the ferroelectric β phase into an array of domains (*i.e.*, pixels) isolated by the paraelectric α phase over a large area, enabling the facile fabrication of NIR-responsive pyroelectric devices.

Figure 1a shows a TEM image of the AuNCs, which are characterized by a hollow interior and pores at the corners, together with an average outer edge length of *ca.* 48 nm and a wall thickness of *ca.* 6 nm. The homogeneous mixture of AuNCs and PVDF showed a slight blue color (Figure 1b), with no indication of aggregation. The as-obtained AuNC/PVDF composite films had a smooth surface (Figure S1). The films were characterized by FTIR spectroscopy. As shown in Figure S2, the β phase^[14] predominated the crystallization of PVDF during film casting and the addition of AuNCs had essentially no effect on the formation of the β phase. The UV-vis-NIR extinction spectrum (Figure 1c) recorded from the AuNC/PVDF film revealed a red shift of *ca.* 67 nm for the LSPR peak in comparison with that of AuNCs in an aqueous suspension due to the increase in effective refractive index for the surrounding medium.^[15] In the present work, we purposely tuned the LSPR peak of the composite film to *ca.* 800 nm to overlap with the wavelengths of lasers used in this work.

In an initial study, we investigated the plasmon-assisted heating process. The temperatures of a AuNC/PVDF film upon irradiation with the 808 nm laser were monitored using a K-type thermocouple and an infrared camera. We also carried out measurements for pristine PVDF in addition to composite films with four different mass ratios for AuNCs (0.01, 0.02, 0.04 and 0.08%). As shown in Figure S3, the temperature increased with both the mass ratio of AuNCs and laser power density. Within 20 s of irradiation, all the AuNC/PVDF films showed drastic increases in temperature, more significant than what was observed in the case of pristine PVDF film (see Figure S4 for IR images). When the laser power density was increased, the rise in temperature (ΔT) also increased accordingly for each composite film. We then quantitatively evaluated the ability of the composite films to convert light to heat by calculating the energy conversion efficiency (η , see Supporting Information). Furthermore, the AuNC/PVDF films exhibited good durability under long-term laser irradiation. As shown in Figure S5, the

photothermal conversion efficiency of the composite films did not change after five rounds of irradiation, whereas reduction in temperature rise was clearly observed for a reference sample containing indocyanine green rather than AuNCs. The much higher stability of AuNCs over organic dyes would ensure a long lifetime for the devices.

We then studied the phase transition during a plasmon-assisted heating process. We observed that exposure to 808 nm laser at 1 W cm^{-2} for less than 10 s was sufficient to induce the transition from the ferroelectric β phase to the paraelectric α phase due to the high photothermal conversion efficiency of AuNCs. The formation of the α phase in the composite film was evidenced from the time-elapsd FTIR spectra shown in Figure 2a. The peaks at 610, 765, 796, 973, 1144, 1167 and 1211 cm^{-1} for the α phase were clearly visible while the peaks at 839, 1176 and 1232 cm^{-1} for the β phase disappeared. For the thermally induced ferroelectric to paraelectric phase transition of PVDF, it has been reported to occur near its melting point (*ca.* 170°C) through an intermediate amorphous or liquid-crystalline phase.^[11a] When the laser energy added into the AuNC/PVDF film reached 800 J cm^{-3} , the corresponding temperature could be over 170°C (see Figure 2b). As such, the β -phase crystal could melt to form an amorphous phase or a liquid-crystalline phase, followed by recrystallization into the α phase. We calculated the α or β phase content in the laser-irradiated region from the absorbance of the respective vibrational bands at 765 cm^{-1} for the α phase and 839 cm^{-1} for the β phase. Upon irradiation for a short period of only 10 s, the β phase-dominated (*ca.* 73%) AuNC/PVDF film was transformed to the α phase-dominated (*ca.* 70%) film.

The efficient plasmon-assisted phase transition could also be employed for the fabrication of micropatterned ferroelectric domains. We could simply use a laser beam as a writing pen to create a patterned array of the β -phase PVDF isolated by the nonpolar α phase over a large area. To obtain a micropatterned ferroelectric thin film, a continuous laser beam was utilized to irradiate the AuNC/PVDF film on a motorized *x-y* stage (Figure 3a). The use of a 785 nm laser at a power of 25 mW and a stage moving speed of $20 \mu\text{m s}^{-1}$ successfully produced micropatterned β -phase domains in the composite film. The phase contents of the irradiated and non-irradiated regions were visualized using Raman spectroscopy as shown in Figure 3b. The representative absorption peaks of 839 and 796 cm^{-1} for the β and α phases, respectively, were selected and the integrated intensity for each peak was mapped (Figure 3, c and d). The pattern

clearly shows a transition from the β phase to the α phase in the laser beam path. The percentages of the α and β phases were calculated and plotted as dashed lines in Figure 3e. The line profile clearly shows a patterned distribution of the β phase, with a minimum feature size around 20 μm . Note that there was a transition gap of *ca.* 10 μm wide between the α and β phase-dominated regions, mainly due to the lateral thermal diffusion.

One of the major applications of the ferroelectric PVDF film is for the detection of infrared signals. Conventionally, the infrared sensor comprises a PVDF film sandwiched between two electrodes with the top electrode serving as an absorption layer to pass the heat to the pyroelectric film.^[16] This design may cause heat transfer loss and hinder the pyroelectric response of the detector. In our system, the pyroelectric film itself serves as the adsorption layer due to the incorporation of AuNCs. When the AuNC/PVDF film is exposed to NIR irradiation, heat will be generated directly in the film due to the photothermal effect so the level of polarization in the film will change as a result of change in temperature. Therefore, when the level of polarization decreases upon heating under open circuit conditions, the released surface charges will create a potential difference across the polar axis, similar to a charged parallel plate capacitor.^[17] For a parallel capacitor with a homogeneous electric field, the open circuit voltage V can be expressed as

$$V = \frac{p}{\epsilon_{33}} d \Delta T$$

where p is the pyroelectric coefficient, ϵ_{33} is the relative permittivity of the PVDF, d is the film thickness, and ΔT is the temperature change. Therefore, one direct approach to increase the open circuit voltage generated by the AuNC/PVDF film with a specific thickness is to increase the ΔT . At a given irradiation energy, ΔT is determined by the photothermal conversion efficiency (η) of the composite film. As such, we presume that enhancement in pyroelectric response can be obtained for the AuNC/PVDF film by increasing the mass ratio of AuNCs. To measure the pyroelectric responses to NIR irradiation, the PVDF films with different mass ratios of AuNCs were sandwiched between two electrodes, with the bottom electrode being a copper tape and the top electrode being a mesh of Ag nanowires (see Figure S6 for the characterization). As shown in Figure S7, a higher AuNC mass ratio indeed led to a larger temperature change as well as higher voltage value. The 0.08% AuNC/PVDF film developed a voltage of ~ 20 mV, which represents an increase of *ca.* 570% compared to the ~ 3 mV for a pristine PVDF reference sample.

Clearly, the incorporation of AuNCs could greatly enhance the pyroelectric response of a PVDF-based pyroelectric device to NIR light.

The plasma-assisted micropatterning of ferroelectric phase together with enhanced pyroelectric response further encourage us to fabricate a pixilated array for infrared imaging. As a proof-of-concept, we constructed a β -phase sensing array with 3×3 pixels as shown in Figure S8. The patterned copper layer served as both a mask for laser exposure and electrodes for measuring electrical response (Figure 4a). The array was then selectively exposed to NIR radiation and the open circuit voltage from each pixel was recorded. The electric response of each pixel was then calculated and color-coded to show the difference. Figure 4b showed the illumination patterned to show the four letters of T, E, C, and H. The illuminated pixels generated a signal of 23 ± 5 mV. Negligible signal was detected from the blocked pixels, confirming that the pixels were isolated from each other by the α -phase barrier.

In conclusion, we have demonstrated the use of plasmonic nanostructures to induce ferroelectric-paraelectric phase transition in a freestanding ferroelectric polymer film. The efficient plasmon-assisted phase transition could be conveniently combined with masked exposure for the fabrication of patterned ferroelectric domains or pixels. We also demonstrated the feasibility of constructing a pixilated ferroelectric phase pattern for infrared imaging. The simple and efficient method demonstrated in this study is expected to promote both the low-cost fabrication and broader application of polymer-based flexible ferroelectronics.

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Figure 1. a) A typical TEM image of AuNCs. b) Photograph of a homogeneous mixture of AuNCs and PVDF obtained by mixing a suspension of AuNCs in ethanol with a PVDF solution in DMF. Transparent films were then cast from the mixture using a mold placed on a hot plate. c) Extinction spectra recorded from an ethanol suspension of AuNCs, PVDF film, and AuNC/PVDF film. The LSPR peak of the AuNCs red-shifted from *ca.* 733 nm in ethanol to *ca.* 800 nm in PVDF.

Figure 2. a) FTIR spectra recorded from a AuNC/PVDF film upon irradiation with 808 nm laser for different at 1 W cm^{-2} periods of time. b) Plot of phase content and temperature change in terms of laser power density.

Figure 3. a) Schematic illustration of phase patterning in a AuNC/PVDF film using direct laser writing technique. The 785 nm laser source in Raman microscope was used and the motion of the sample was driven by a software-controlled motorized stage installed in the microscope. b) Raman mapping collected over $250 \times 250 \mu\text{m}^2$ area of AuNC/PVDF film, exhibiting a patterned β phase distribution. Bar: 50 μm . Representative Raman spectra of c) non-irradiated region (β phase-dominated) and d) laser-irradiated region (α phase-dominated) in AuNC/PVDF. e) Profile of phase content from the dash line indicated in b).

Figure 4. a) Schematic showing a proof-of-concept device for IR imaging using phase-patterned AuNC/PVDF film by masking the laser irradiation with copper electrodes. b) Responses of pixels in the sensing array to the incident irradiation, which was selectively blocked to form the four letters in TECH.

Supporting Information

Experimental Section

1. Chemicals and materials

Silver trifluoroacetate (CF_3COOAg), poly(vinyl pyrrolidone) (PVP, $\text{MW} \approx 55,000$), sodium hydrosulfide (NaHS), hydrochloric acid (HCl), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), acetone, N,N-Dimethylformamide (DMF) and poly(vinylidene fluoride) (PVDF, $\text{MW} \approx 275,000$) were obtained from Sigma-Aldrich. Ethylene glycol (EG) was obtained from J. T. Baker.

2. Synthesis of gold nanocages (AuNCs)

The AuNCs were prepared using the galvanic replacement reaction between Ag nanocubes and aqueous HAuCl_4 . In a typical synthesis of Ag nanocubes,^[1] EG (50 mL) was added into a 250 mL round bottom flask and preheated under magnetic stirring in an oil bath at 150 °C. After the temperature of the oil bath had reached 150 °C, the 3 mM NaSH solution in EG (0.6 mL) and 4 min later, the 3 mM HCl in EG (5 mL) was injected, followed by the addition of the 20 mg/mL PVP solution in EG (12.5 mL). After another 2 min, the 282 mM CF_3COOAg solution in EG (4 mL) was introduced. The reaction was allowed to proceed for about 20 min and its color turned brown. The reaction solution was then quenched by placing the reaction flask in an ice-water bath. The product was collected by centrifugation and then washed with acetone once and then DI water four times.

In a typical synthesis of AuNCs,^[2] 9 mL of Ag nanocubes ($\sim 1.1 \text{ mg mL}^{-1}$) was dispersed in 200 mL water in a 1 L flask placed in the oil bath (90 °C) under magnetic stirring. Then, 0.75 mM HAuCl solution was injected into the flask by a syringe pump at a rate of 45 mL h^{-1} . The solution was heated for another 10 min before cooled down. The product was then purified by washing with saturated NaCl solution once and water twice.

3. Preparation of AuNC/PVDF films

A specific amount of a suspension of AuNCs in ethanol was added into a 10 wt% PVDF solution in DMF and sonicated to obtain a homogeneous mixture. The AuNC/PVDF composite film was obtained by casting the above mixture in a glass mold, followed by drying on a hot plate

at 80 °C for 2 h.^[3] To obtain β -phase-dominated, crystalline PVDF, the films were further annealed at 90 °C for 3 h. The AuNC/PVDF films with mass ratios of 0.01, 0.02, 0.04 and 0.08% AuNCs were noted as AuNC/PVDF-1, 2, 3 and 4, respectively.

4. Fabrication of pyroelectric phase-patterned film and sensing array

Pyroelectric phase-patterned film was prepared by irradiating the AuNC/PVDF film (0.08% AuNC content; 30 μm in thickness) with a continuous 785 nm laser source equipped in the Renishaw inVia Raman spectrometer with a 50 $\times$ object. The laser power was set at 5% (*ca.* 25 mW). The sample was driven by a software-controlled motorized stage. The moving step speed was set at 20 $\mu\text{m s}^{-1}$ and the exposure time was set at 0.2 s for each step.

The sensing array prototype was constructed using a simple photolithography technique. First, nine squared copper tapes (1.3 $\times$ 1.3 mm²) was attached to one side of the AuNC/PVDF film (*ca.* 100 μm in thickness) to form a 3 $\times$ 3 array. Then, the film with patterned electrodes was exposed under 808 nm laser at 1 W cm⁻² for 10 s to form a patterned pyroelectric array. On the other side of the film, 20 μL of a suspension of Ag nanowires ($\sim$ 1.8 mg/mL) in ethanol was spread and dried to form a thin electrode. A multimeter was used to confirm the conductivity of both electrodes.

5. Instrumentation and characterizations

Transmission electron microscopy (TEM) images were taken on a Hitachi HT7700 microscope operated at 120 kV. The sample was prepared by placing a drop of the particles (suspended in DI water) on a carbon-coated copper grid and drying under ambient conditions. The concentration of Au was determined using an inductively coupled plasma mass spectrometer (ICP-MS, NexION 300Q, PerkinElmer). Extinction spectra were recorded using a UV-vis spectrometer (Varian, Cary 50). An 808 nm diode laser coupled to a 100- μm -core fiber (Power Technology Inc.) was used to irradiate the film. In this study, the total energy output (E) of the laser within a specific period was measured using an optical power meter (Spectra-Physics 407A). A K-type thermocouple (OMEGA Inc.) with a wire diameter of 250 μm and an IR camera (FLIR E60) was used to measure and image the temperature upon laser irradiation. The FTIR spectra in ATR mode were obtained using an infrared spectrophotometer (Varian 640). The Raman spectra were recorded by a Renishaw inVia Raman spectrometer using a 20 $\times$ objective lens and 532 nm laser source (500 mW). For Raman mapping, the exposure time was set at 0.5 s, the step speed was set at 3 $\mu\text{m s}^{-1}$, and the output

power of 532 nm laser was set at 50% of its original power. The open circuit voltage was recorded using a CHI 600E electrochemical workstation in the open circuit voltage mode.

Calculation of photothermal conversion efficiency

The total heat (Q) generated in the irradiated area in the AuNC/PVDF film was calculated using the following equation:

$$Q = cm\Delta T = cpSd\Delta T$$

where c , m , ρ are the specific heat ($1.12 \text{ J g}^{-1} \text{ K}^{-1}$), mass, and density (1.78 g cm^{-3}) of the PVDF film; S is the irradiated area; d is the thickness of the film; and ΔT is the change in temperature.

The total energy output of the laser (E) was calculated from the following equation:

$$E = PSt$$

where P is the power density of the laser, S is the irradiation area and t is the irradiation time.

The light-to-heat energy conversion efficiency of AuNC/PVDF film (η) was calculated from:

$$\eta = Q/E = cpd\Delta T/Pt$$

Figure S1. Typical SEM image of the as-obtained AuNC/PVDF film (cross-sectional view).

Figure S2. FTIR spectra of PVDF and AuNC/PVDF films with the mass ratios of AuNCs being controlled at 0.01, 0.02, 0.04 and 0.08% (AuNC/PVDF-1, 2, 3, and 4). The characteristic bands of the β phase of PVDF located at 839, 1176 and 1232 cm^{-1} are labeled by *. The weak peaks at 765 and 796 cm^{-1} correspond to the vibrational modes of the α phase.

Figure S3. a-c) Temperature increase in PVDF and AuNC/PVDF films as a function of irradiation time for a 808 nm laser at different laser power densities (0.4, 0.8, and 1.0 W cm⁻²). d) Energy conversion efficiencies (η) of the AuNC/PVDF films. As the mass ratios of AuNCs increased from 0 to 0.01, 0.02, 0.04 and 0.08%, the η values increased from 1.4 to 21.0, 23.1, 25.5 and 29.3%, respectively. The composite film could only reach a maximum temperature of 100 °C at a laser power density of 0.4 W/cm². As such, the PVDF films could last for a long period of time (at least 10 min, for the duration of our test) without showing any noticeable degradation. However, when exposed to the NIR laser at a power density of 1 W cm⁻², the pyroelectric properties (PVDF/AuNC-4 sample) were lost within 10 s due to the rise of temperature close to 170 °C.

Figure S4. IR images showing the temperature rise in PVDF and AuNC/PVDF films after 20 s of irradiation with the 808 nm laser at a power density of 0.8 W cm^{-2} . The box marked by dashed lines indicates where the film was located.

Figure S5. Plots showing the temperatures in AuNC/PVDF and ICG/PVDF films upon irradiation by a laser at 808 nm at a power density of 0.8 W cm^{-2} . AuNCs showed a higher durability under laser irradiation compared to cyanine dye indocyanine green (ICG), which also has a peak absorption around 800 nm. Briefly, the PVDF/ICG film with 0.04 wt% ICG was prepared using the same procedure as for the AuNC/PVDF film with 0.04 wt% AuNC. Each cycle of irradiation lasted for 2 min (laser on for 1 min and then off for 1 min) and the cycle was repeated five times. The result indicates that there was essentially no change to the photothermal conversion efficiency of AuNCs under proper irradiation, suggesting that the irradiation brings no damage to the plasmonic nanostructures while ICG was easily photobleached.

Figure S6. a, b) TEM images of the Ag nanowires used for the fabrication of transparent electrodes. The average length of the Ag nanowires was over 10 μm and the diameter was about 40 nm. c) Vis-NIR spectrum of a suspension of the Ag nanowires in ethanol (*ca.* 50 $\mu\text{g mL}^{-1}$), showing high transparency in the NIR region.

Figure S7. a) Temperature change and b) pyroelectric response of PVDF and AuNC/PVDF films ($6 \times 6 \text{ mm}^2$) when exposed to, and blocked from the NIR irradiation (0.4 W cm^{-2}).

Figure S8. Layout of the proof-of-concept β -phase sensing array with 3×3 isolated pixels for IR imaging. Each pixel was covered with $1.3 \times 1.3 \text{ mm}^2$ copper electrode, which was connected to copper wires for electric measurement. The other side of the sensing array was covered by an electrode constructed from silver nanowires.

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