

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 objective. 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:

$$Q = cm\Delta T = c\rho Sd\Delta T$$

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:

$$\eta = Q/E = c\rho d\Delta T/Pt$$

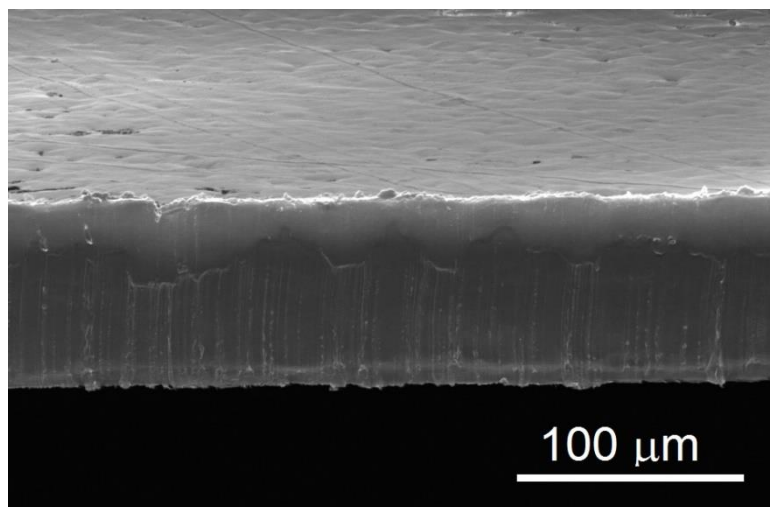


Figure S1. Typical SEM image of the as-obtained AuNC/PVDF film (cross-sectional view).

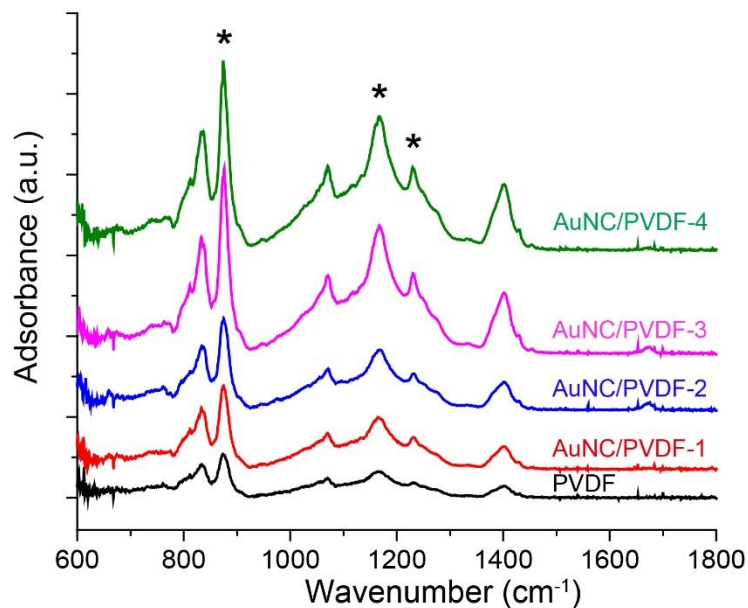


Figure S2. FTIR spectra of PVDF and AuNC/PVDF films with the mass ratios of AuNCs being controlled at 0.01, 0.02, 0.04 and 0.08% (AuNC/PVDF-1, 2, 3, and 4). The characteristic bands of the β phase of PVDF located at 839, 1176 and 1232 cm^{-1} are labeled by *. The weak peaks at 765 and 796 cm^{-1} correspond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

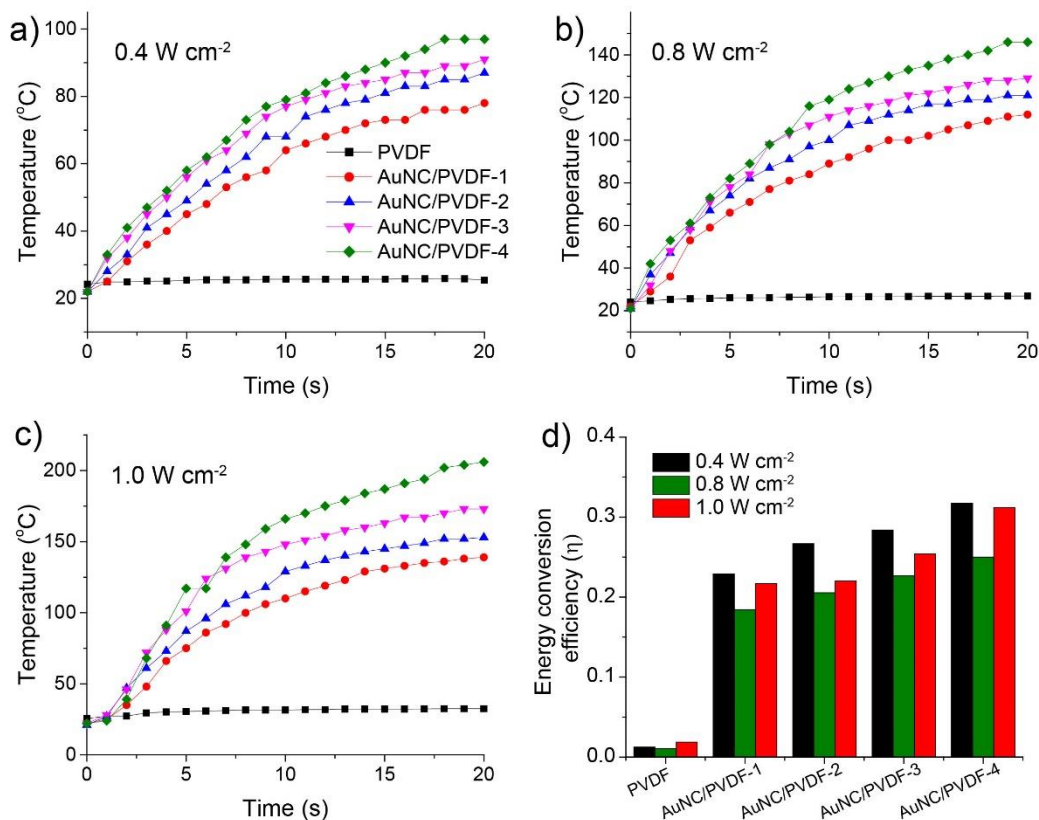


Figure S3. a-c) Temperature increase in PVDF and AuNC/PVDF films as a function of irradiation time for a 808 nm laser at different laser power densities (0.4 , 0.8 , and 1.0 W cm^{-2}). d) Energy conversion efficiencies (η) of the AuNC/PVDF films. As the mass ratios of AuNCs increased from 0 to 0.01, 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 $100 \text{ }^\circ\text{C}$ at a laser power density of 0.4 W/cm^2 . 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 $170 \text{ }^\circ\text{C}$.

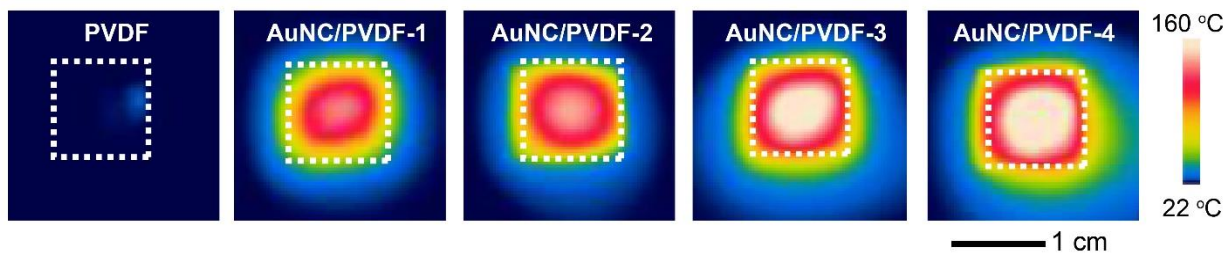


Figure S4. IR images showing the temperature rise in PVDF and AuNC/PVDF films after 20 s of irradiation with the 808 nm laser at a power density of 0.8 W cm^{-2} . The box marked by dashed lines indicates where the film was located.

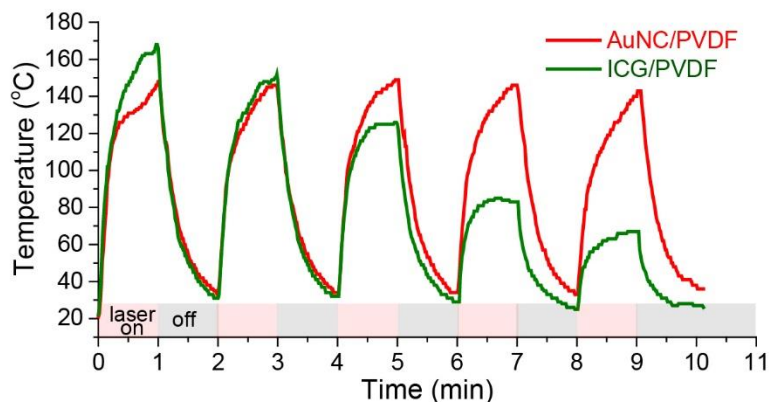


Figure S5. Plots showing the temperatures in AuNC/PVDF and ICG/PVDF films upon irradiation by a laser at 808 nm at a power density of 0.8 W cm^{-2} . AuNCs showed a higher durability under laser irradiation compared to cyanine dye indocyanine green (ICG), which also has a peak absorption around 800 nm. 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.

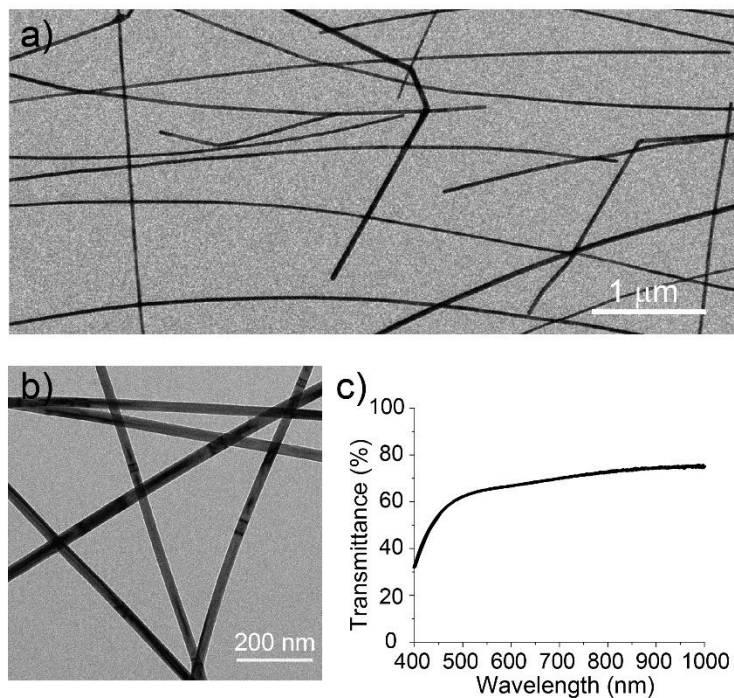


Figure S6. a, b) TEM images of the Ag nanowires used for the fabrication of transparent electrodes. The average length of the Ag nanowires was over 10 μm and the diameter was about 40 nm. c) Vis-NIR spectrum of a suspension of the Ag nanowires in ethanol (*ca.* 50 μg mL⁻¹), showing high transparency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

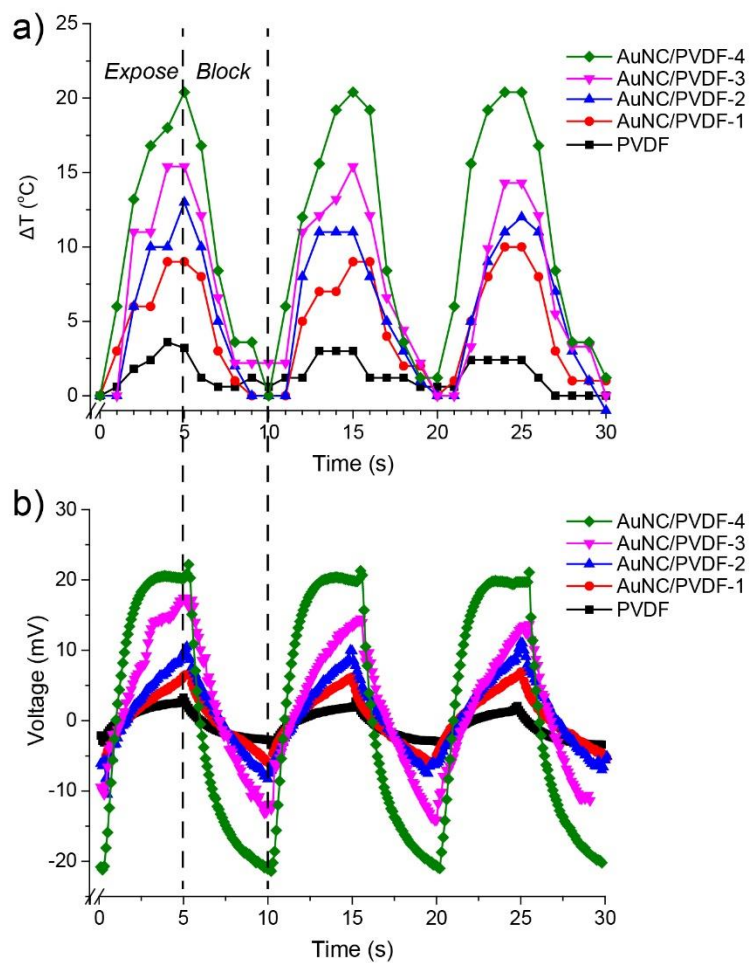


Figure S7. a) Temperature change and b) pyroelectric response of PVDF and AuNC/PVDF films ($6 \times 6 \text{ mm}^2$) when exposed to, and blocked from the NIR irradiation (0.4 W cm^{-2}).

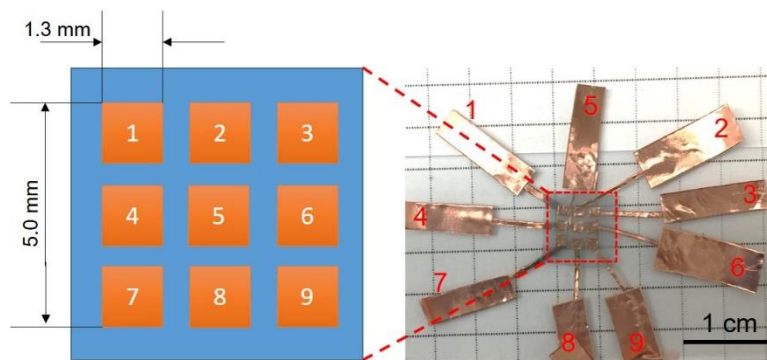


Figure S8. Layout of the proof-of-concept β -phase sensing array with 3×3 isolated pixels for IR imaging. Each pixel was covered with $1.3 \times 1.3 \text{ mm}^2$ copper electrode, which was connected to copper wires for electric measurement. The other side of the sensing array was covered by an electrode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

- [1] Q. Zhang, W. Li, L.-P. Wen, J. Chen, Y. Xia, *Chem. Eur. J.* **2010**, *16*, 10234-10239.
- [2] S. E. Skrabalak, L. Au, X. Li, Y. Xia, *Nat. Protocols* **2007**, *2*, 2182-2190.
- [3] M. Li, I. Katsouras, C. Piliago, G. Glasser, I. Lieberwirth, P. W. Blom, D. M. de Leeuw, *J. Mater. Chem. C* **2013**, *1*, 7695-7702.