Metamaterial Perfect Absorber-enhanced Plasmonic Photo-thermoelectric Conversion

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Perfect absorption is key to achieving high responsivity of a thin-film photodetector. Here, we report the effect of a metamaterial perfect absorber on the external quantum efficiency of plasmonic photo-thermoeletric conversion, which is a photodetection method based on local heating. The photodetector with a metamaterial perfect absorber shows strong absorption, resulting in external quantum efficiency about three times of that of a control device. Plasmon-induced local temperature rise contributes to the photodetection, and its amplitude is examined both experimentally and numerically.

Photodetectors are widely used in sensors, optical communications, optical imaging, and optoelectronic applications. Demands of thin-film photodetectors are growing for utilization in ultra-dense interconnects and monolithically integrated optoelectronic devices.1-7) Thin-film photodetectors that utilize thermoelectric conversion are an emerging research topic.8-13) Recently, we reported a thin-film photodetector enabled by plasmonic photo-thermoelectric conversion.14, 15) Our device consisted of an ultrathin film of a thermoelectric material embedded with plasmonic atoms, silver (Ag) nanorods that generated plasmonic local heating.16-21) Light illumination on the Ag nanorods created a thermal gradient across the thermoelectric film, resulting in the Seebeck voltage generation. Although being a new photodetection technique, the efficiency of the plasmonic photo-thermoelectric conversion is far from enough for real-world applications.

There are two potential approaches to increase the responsivity of plasmonic photo-thermoelectric sensors: to increase the Seebeck coefficient of the thermoelectric materials and to increase the light absorption of the whole device. Building on our recent work,14, 15) this work concentrates on exploring the second approach. An intuitive solution for increasing light absorption is to increase the optical length of the light absorber. However, it will increase the thickness of the device, resulting in an overall device size too large for many integrated applications. It is highly desirable to have a plasmonic photo-thermoelectric sensor that achieves the ultimate, perfect light absorption within a subwavelength thickness.

Metamaterial perfect absorber (MPA) is consequently a good candidate for increasing the responsivity of plasmonic photo-thermoelectric sensors. The most common configuration of MPAs is an ultrathin, multilayered absorber, consisting of two layers of metal structures sandwiching a thin dielectric spacer layer.22-27) This configuration supports strong electric and magnetic resonances, allowing for perfect or near-perfect light absorption within a thickness much smaller than the resonance wavelength.28-30)

Here, we report the MPA-based plasmonic photo-thermoelectric sensing for the first time. The performances of the MPA-based sensor, including both the optical property of light extinction and the electrical property of external quantum efficiency, show significant improvement over a control device that lacks perfect light absorption. Through detailed experimental and numerical exploration, this improvement is attributed to higher local temperature in the MPA-based sensor.

The MPA-based plasmonic photo-thermoelectric sensor and the control sample were fabricated on the same glass substrate. A thin film of resist (Nihonzeon, ZEP520A) was first spin-coated on top of the glass substrate, in which two identical nanorod arrays were subsequently drawn using electron beam lithography (JEOL, JBX-6300FS). Each array occupied an area of 500 × 500 m2. The resist film was then coated with an adhesive layer of chromium (5 nm in thickness) and a layer of Ag (30 nm in thickness) by thermal deposition. Two identical arrays of Ag nanorods were obtained on the glass substrate after a lift-off process. Figure 1(a) shows scanning electron microscope (SEM) images of one of the Ag nanorod arrays, obtained by using field emission SEM (Hitach-High Technologies Corporation, SU8010 FE-SEM). The resonance of the Ag nanorod was adjusted to be around 680 nm, so the results are directly comparable to our previous work.14) A thin film of poly(3,4-ethilenedioxithiophene)-poly(styrenesulfonate) (PEDOT:PSS) (Sigma Aldrich, Orgacon S315, 1.3 wt%) was spin-coated on the two Ag nanorod arrays. The thickness of the PEDOT:PSS film was 125.4±10.6 nm (measurement point number = 12). On top of one of the arrays, a 100-nm-thick Ag film was coated using thermal evaporation (see Figure S1 in the supplementary information for an SEM image of the device cross section). This Ag film was the only design difference between the MPA sample and the Ag nanorod sample as the control sample. To facilitate electrical measurement, at both ends of the PEDOT:PSS film, Ag electrodes with a thickness of 100 nm were fabricated using thermal evaporation (Fig. 1(b)).

Transmission (*T*) and reflection (*R*) of the two samples were measured using a home-built microscopic spectrometer, which consisted of an Olympus BX-51 microscope and an Ocean Optics HR4000 spectrometer. Extinction of the two samples was calculated as 1-*T*-*R*. In the characterization of photodetection performances, the samples were irradiated from the glass side by a tunable laser (Thorlabs). The laser beam was polarized and its power was maintained at 15 mW. Two orthogonal polarization states, the TE polarization and the TM polarization, were investigated. The TE polarization corresponded to the electric field of the incident light perpendicular to the short axis of the Ag nanorods, and the TM polarization was the orthogonal polarization. Photocurrent generated by the device was measured using a digital multimeter (KEITHLY 2000).

Figure 2 shows the extinction spectra of the two devices measured for the TE polarization. For the MPA device, the peak amplitude reaches 97% at 606 nm, very close to the target value of 100%. By comparison, for the control sample (i.e. the sample that contains Ag nanorods but lacks the continuous Ag film), the peak amplitude is 30%, which is at a slightly longer wavelength of 636 nm. The extinction of the MPA sensor is 3.2 times of that of the control sample. Similar level of contrast is also observed in numerically simulated extinction spectra (Fig. S2) obtained by using the commercial software COMSOL multiphysics, a simulation tool based on the finite element method (FEM).

Figure 2 also shows the external quantum efficiency (EQE) of the two samples at six different wavelengths. The EQE is calculated by dividing the number of detected electrons by the number of incident photons (Eq. (1)),

$EQE=\frac{Ihc}{ePλ}∙100$ (1)

where *I, h, c, e, P,* and ** represent the photocurrent, the Planck constant, the velocity of light in vacuum, the elementary electric charge, the power of the laser beam, and the laser wavelength, respectively. The MPA sensor shows a photocurrent and an EQE of 232 nA and 3.0×10-3%, respectively, at a wavelength of 638 nm, which is close to the extinction peak. By comparison, the photocurrent and the EQE of the control sample are 90 nA and 1.2×10-3%, respectively, at the same wavelength. This contrast indicates that, by adding a Ag film to convert a control sensor to the MPA sensor, both the photocurrent and the EQE have increased.

To assist interpreting the results, a bare PEDOT:PSS film, which did not contain any Ag nanorods or the Ag thin film, was characterized under the same conditions. It generated an electric current and an EQE of 6 nA and 8.0 × 10-5%, respectively, with the laser wavelength at 638 nm. The two samples were also characterized under TM-polarized illumination, a polarization that did not excite localized surface plasmon resonances. The electric current and the EQE at 638 nm were 29 nA and 3.9 × 10-4%, respectively, for the control sensor, and they were 127 nA and 1.7 × 10-3% for the MPA sensor. Based on these results, we concluded that the near-perfect absorption acquired by the MPA is key to increasing the electric current and the EQE of plasmonic photo-thermoelectric conversion. In plasmonic photo-thermoelectric conversion, the excitation of surface plasmon resonance leads to plasmonic local heating, which results in a thermal gradient across the PEDOT:PSS film. This thermal gradient generates an electric current flowing across the PEDOT:PSS film owing to the Seebeck effect.14)

This conclusion is further supported by the wavelength dependence observed in both the EQE and the extinction ratio (Fig. 2). For both the control sensor and the MPA sensor, the extinction is dominated by the plasmonic resonance. As the EQE traces the extinction spectra in the whole measured spectral range, we can conclude that plasmon excitation is the dominant driving force that triggers the photo-thermoelectric conversion.

Figure 2 shows that the peak intensity of the EQE of the MPA sensor is 2.6 times of that of the control sensor. This contrast is attributed to the higher absorption and higher temperature of the MPA sensor. Plasmon-induced local heating can be calculated by using the conventional heat transfer equation (Eq. (2)) and the heat power density *q* (Eq. (3)),31)

$ρ\left(r\right)c\left(r\right)\frac{δT(r)}{δt}=∇κ\left(r\right)∇T\left(r\right)+q(r)$ (2)

$q\left(r\right)= \frac{ω}{2} Im(ε\left(ω\right))ε\_{0}\left|E\left(r\right)\right|^{2}$ (3)

where $T\left(r\right)$ is the temperature, $ρ\left(r\right)$ is the mass density, $c\left(r\right)$ is the specific heat capacity, and $κ\left(r\right)$ is the thermal conductivity, ** is the angular frequency of the incident light,** is the complex relative permittivity, and **0 is the permittivity of vacuum. Equation 3 indicates that the heat power density *q* is directly related to the intensity of the electric field.

Figure 3 shows the electric and magnetic field distributions of the two samples under TE illumination. Figure 3(a) shows that, in the control sample calculated at 650 nm, the electric field enhancement is confined at the sharp edges of the Ag nanorod. By comparison, Fig. 3(b) shows that, in the MPA sample calculated at 615 nm, the electric field enhancement is stronger and occupies a large area, extending across the PEDOT:PSS film from the Ag nanorod to the Ag film. As the magnitude of plasmonic local heating increases with the intensity of the local electric field (Eq. (3)), the contrast between Figs. 3(a) and 3(b) suggests that the plasmonic local heating is more pronounced in the MPA sample. Figures 3(c) and 3(d) compare the distribution of the magnetic field in these two samples. In the control sample, the magnetic field shows weak enhancement and is localized at the interface between the nanorod and the substrate (Fig. 3(c)). By comparison, the field enhancement is much more pronounced in the MPA sample (Fig. 3(d)).

As an attempt to quantify the contribution of the plasmonic resonance to the photo-thermoelectric conversion, we further calculated the plasmon-induced local temperature increase, by using two approaches. The first approach is based on the photocurrent and a Seebeck coefficient of 42.1 nA/K for the PEDOT:PSS obtained in experiments. The local temperature increase estimated using this approach is 8.8 and 22.8 K for the control sample and the MPA sample, respectively.

The second approach is based on numerical simulation using the FEM software. It combines the simulation of electromagnetic field with that of thermal field, through the link based on Eq. (3). Although it is common practice to approximate a large array of identical nanorods by simulating a single nanorod in the simulation of electromagnetic properties, a similar approach is not viable for the simulation of thermal properties. As Govorov et al. reported in Ref.,32) because of heat accumulation and inter-particle coulombic interactions, it is not possible to derive the temperature of a large array from the temperature of a single, isolated nanorod. To address this problem, we took the approach of simulating multiple arrays, each containing a different number of identical nanorods. For the smallest array, which contains only a single nanorod, the temperature rises were 0.59 and 1.15 K for the control and MPA samples (Fig. 4). For the largest array, which contains 5 × 5 identical units, the corresponding values were 1.39 and 2.83 K for the control and the MPA samples. It is clear that, as the array becomes larger, the temperature rise (i.e. the plasmon-induced local heating) becomes less sensitive to the array size. For the two samples, the simulated temperature rises, $T\_{Control}$ for the control sample and $T\_{MPA}$ for the MPA sample, are fitted using an analytical equation. The results are shown in Fig. 4, and the fitting equations are as follows.

$T\_{Control}=0.5597x^{0.2766}$ (4)

$T\_{MPA}=1.1352x^{0.2837}$ (5)

The FWHM of the laser spot used in the experiment was 50 m, and the number of nanorods under light illumination was about 21800. By using Eqs. (4) and (5), the temperature rise is estimated to be 8.87 and 19.31 K for the control sample and MPA sample, respectively. Both values are similar to the results obtained from the first approach, which has utilized the experimental values of electric current. This similarity confirms that the EQE of plasmonic photo-thermoelectric conversion can be improved via perfect absorption. Additionally, we compare the heat propagation profile of the two samples, as such profile can provide valuable insight into the physical mechanism.33) Figure S3 shows the cross-sectional heat profile across the two samples at the moment of 30 seconds after the illumination is initiated. The thermal gradient across the MPA sample is significantly steeper than that of the control sample, a result that fits well with the analysis above.

In summary, we have fabricated and characterized a plasmonic photo-thermoelectric device that is enhanced by the MPA. The MPA consists of the Ag thin film and an array of Ag plasmonic nanorods, which are separated by a thermoelectric layer of PEDOT:PSS. The measured EQE of the sensor is 3.0×10-3% at 638 nm, 2.6 times of that of a control sample that has the same Ag nanorods. The increase in EQE is attributed to the near-perfect light absorption of the MPA, which results in effective local heat generation. The temperature rise induced by the local heat generation is calculated using two approaches, and the results are similar. This confirms that the MPA can be used to enhance the EQE of plasmonic photo-thermoelectric conversion. The principle of the plasmonic photo-thermoelectric conversion discussed here is applicable to a broad spectral range, as plasmonic resonance has been demonstrated from the visible to the THz frequency range. The responsivity of the MPA device reported here is 15.4 µA/W, significantly lower than that of commercial Si detectors. Nevertheless, this value can be increased by using a high-performance thermoelectric material such as bismuth telluride (Bi2Te3) in future works. With a Seebeck coefficient34) of 230 µV/K, Bi2Te3 is expected to increase the responsivity up to 17.5 mA/W. By combining with further optimization of device configuration, this work could pave the way to a new kind of high-sensitivity thin-film photodetector.

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**Figure Captions**

**Fig. 1.** (a) SEM image of the Ag nanorods. The inset is a zoom-in view. (b) A schematic of the measurement setup, showing the MPA-enhanced plasmonic photo-thermoelectric sensor with the control sample. (c) The cross-section of the MPA area.

**Fig. 2.** Extinction spectra (solid lines) and EQE (dots) of the MPA sensor (red) and the control (Ag nanorod) sensor (blue). The incident light has TE polarization.

**Fig. 3** Electric and magnetic field distributions of the two sensors. (a,b) Electric field distribution of (a) the control sample (Ag nanorod) calculated at 650 nm and (b) the MPA sample calculated at 615 nm. (c,d) Magnetic field distribution of (c) the control sample and (d) the MPA sample.

**Fig. 4** Dependence of plasmon-induced local temperature difference. The numerically simulated results (circles) as a function of the numbers of (a) MPA (red) and (b) Ag nanorod (blue) units. The simulated results correspond to arrays with 1 × 1, 2 × 2, 3 × 3, 4 × 4, and 5 × 5. The solid lines are exponential fits to the simulated results.



**Fig. 1** (color online)



**Fig. 2** (color online)



**Fig. 3** (color online)



**Fig. 4** (color online)