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Solar energy conversion with tunable plasmonic nanostructures for thermoelectric devices†

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The photothermal effect in localized surface plasmon resonance (LSPR) should be fully utilized when integrating plasmonics into solar technologies for improved light absorption. In this communication, we demonstrate that the photothermal effect of silver nanostructures can provide a heat source for thermoelectric devices for the first time. The plasmonic band of silver nanostructures can be facilely manoeuvred by tailoring their shapes, enabling them to interact with photons in different spectral ranges for the efficient utilization of solar light. It is anticipated that this concept can be extended to design a photovoltaic–thermoelectric tandem cell structure with plasmonics as mediation for light harvesting.

Harvesting energy directly from sunlight is increasingly recognized as an essential component of future global energy production. Among the various solar conversion-based devices, thin-film photovoltaics (PV) represents a relatively low-cost solution to utilize solar energy for electricity generation. However, such a reduction in the absorber thickness generally compromises the efficiency of the device due to relatively poor light absorption (e.g., in the case of ultrathin crystalline silicon).† For this reason, plasmonics can be used as an element to localize light at the nanoscale and integrated into PV technologies for improving light absorption via a scattering mechanism.‡ In principle, the localized surface plasmon resonance (LSPR) of a metallic nanostructure can absorb incident light and release this energy through two mechanisms – either “scattering” to release photons with the same frequency or “absorption” to convert the absorbed photons into phonons or heat (i.e., the photothermal effect or so-called “damping effect”). Thus, in addition to the photons that participate in scattering, a considerable portion of photons is consumed by the photothermal effect in LSPR. As a result, the improvement of light absorption for PV via scattering alone may be significantly limited. Given this situation, it is necessary to use the photons that are consumed in the photothermal conversion for electricity generation, for the purpose of maximizing the conversion efficiency from solar light into electricity.

This demand inspired us to explore the possibility of implementing the photothermal effect in thermoelectric (TE) devices for generating electricity as a necessary supplement to use the photons involved in the photothermal conversion when integrating LSPR into thin-film PV modules. Heat generation in plasmonic nanoparticles induced by light absorption (i.e., photothermal conversion) has long been recognized and usually been considered only as a side effect when employing electromagnetic field enhancement or light scattering for various applications such as imaging techniques in biomedicine and light absorption in photovoltaics. Very recently, it has been realized and demonstrated that metallic nanoparticles can serve as efficient nanosources of heat for a new emerging set of applications that require a heat source. The potential applications include photothermal cancer therapy,§ drug delivery,¶ nanofluidics and phononics.‖ For this reason, while considerable efforts have been made to explore the function of plasmonics as light scatterers, enhancers or nanomaterials, the research community has begun to investigate the local generation of heat depending on the morphology of metallic nanostructures theoretically and experimentally.¶,§ The studies reveal that local heating by metallic nanostructures can induce an increase in the environmental temperature (e.g., by 13–40 °C for water in aqueous suspension; by 522 °C in gold), whose amplitude depends on both the incident light and the nanostructures.¶,§ In this communication, we demonstrate that the photothermal effect of metallic nanostructures can be utilized as a heat source for TE devices for the first time. In particular, the solar conversion based on photothermal and thermoelectric effects can be tailored by tuning the LSPR features of silver nanostructures. Silver is selected as the research target because the LSPR band of silver nanostructures can be readily tuned from 400 nm to the infrared region, which fully covers the solar spectrum.

The proof-of-concept experiments were performed by coating a commercial thermolectric device (p–n junction type: n, Bi₂Te₃–Bi₂S₂ solid–solution material; p, Bi₂Te₃–Sb₂Te₃ solid–solution material) with silver nanostructures. In this work, we selected two different silver nanostructures that exhibit LSPR features in visible and near-infrared (IR) regions, respectively: silver nanocubes and triangular nanoplates. The nanocubes and nanoplates were synthesized by adapting the methods in literature.¶,§ Fig. 1a shows the LSPR extinction spectra of these two nanostructures suspended in water. Clearly, the used nanocubes have a major extinction peak

located at 425 nm (in the visible region) which can be assigned to the strong dipole resonance. In contrast, the nanoplates show a strong LSPR band with the maximum at 710 nm (in the near-IR region) that can be attributed to in-plane dipole resonance, together with a relatively weak band at 400–550 nm corresponding to out-of-plane resonance. By mixing these two nanostructures with a ratio of 1 : 1, the sample can have LSPR features covering both the visible and near-IR regions. Fig. 1b and c show SEM and TEM images of the silver nanocubes and nanoplates, respectively, revealing that the edge length of the nanocubes is ca. 40 nm and the nanoplates have an average edge length of 40 nm and a thickness of ca. 5 nm. Given these dimensions of nanostructures, we have employed the discrete dipole approximation (DDA) method to simulate the LSPR properties of the silver nanocubes and nanoplates. The simulation was performed with air as the environmental media as the silver nanostructures were coated on the surface of TE devices and exposed to the air. Considering that most of the nanoparticles should lie on the device surface along their flat surface, the simulation was based on the situation that the direction of incident light was normal to one of the cubic faces of the nanocubes and the triangular face of the nanoplates, respectively. Fig. 1d–g show the extinction (i.e., the sum of scattering and absorption), scattering and absorption cross sections of these two nanostructures in various polarization directions. The LSPR features in the simulation are very consistent with those observed in our experiments, and the difference of environmental media (air versus water) does not cause much variation in the LSPR bands. Note that the out-of-plane dipole resonance of the silver nanoplates at 400–550 nm could not show up in the DDA simulation.
as the incident light was set in the normal direction to their flat faces,\textsuperscript{10} however, there is a relatively weak band at 350–400 nm under polarization in the direction normal to the edge of the nanoplates. It is worth noting that the portion of absorption (\textit{i.e.}, the photothermal effect) dominates in the LSPR features of both nanostructures, which should be very suitable for use as a photon-heat convertor for TE devices. Overall, we can conclude that the silver nanocubes and nanoplates in the dimensions that we selected for our investigations represent two typical nanostructures for covering the visible and near-IR spectral ranges, respectively.

As it is known that the photothermal heating effect is a localized event, we have also simulated the distribution of the heating power density based on the absorption cross section and incident light intensity. In our simulation, the nanocubes and nanoplates are divided into 3920 dipoles and 9320 dipoles, respectively, depending on the geometry and the convergence requirements for different nanostructures. The intensity of incident light is considered as the same value in our device characterizations (1000 W in total, 6 × 6 inch coverage). As shown in Fig. 2a–c, the heating power in a nanocube is more intensive along the front and back planes, particularly on the corners of the nanocube. Similar findings can be observed in the case of nanoplates where the edges of a nanoplate are the location for more intensive heating (see Fig. 2d–f). Regardless of the varied heating power across each nanostructure, the overall film of nanostructures should be able to contribute to the temperature increase at the interface of the TE device and the film for an enhanced TE effect since the back surface of the nanostructures can contact the TE device directly. For instance, each nanocube can generate a heat power of about 0.1 nW, according to the accumulation of the heat power density in all the dipoles, which gives a total heating power of the nanocube film at about 50 W. Estimated using the Poisson equation, the temperature increase caused by this heating power could be above 100 °C.\textsuperscript{8,13}

In the device characterizations, we used a 1000 W full-spectrum solar simulator (6 × 6 inch source diameter, 3 A standard) equipped with an AM 1.5 direct filter. Fig. 3a shows the solar spectrum of the light generated from this simulator, confirming that it matches that of the solar light form the Sun very well. In the characterizations, we coated the surfaces of commercial TE devices with silver nanostructures in three configurations and then covered them with a piece of glass slide to prevent heat dissipation from the top: (a) silver nanocubes with an LSPR band in the visible region; (b) silver nanoplates with an LSPR band in the near-IR region; (c) double layers – nanocubes as the top layer and nanoplates as the bottom layer. The device structure is illustrated in Fig. 4a. Originally, we proposed to use a mixture of silver nanocubes and nanoplates with a ratio of 1 : 1 for a single-layer coating configuration (c); however, we considered that the absorption cross sections in each spectral region may be lowered given that the surface coverage of each type of silver nanostructure is reduced to half in this mixture, although it can enable the plasmonic feature covering both the visible and near-IR regions. In contrast, the double-layer configuration ensures the full benefits of such a mixture. The device characteristics are illustrated in Fig. 4b–d. Representative current (\textit{I})–voltage (\textit{V}) characteristics of the TE devices without treatment (blank) and coated with various silver nanostructures measured (b) without an optical filter and with the (c) 435 nm and (d) 660 nm optical filters, respectively.
coverage of each nanostructure on the device surface, thus the total cross sections and spectral coverage can both be optimized. For this reason, we use the double-layer configuration in (c) instead. Fig. 4b shows representative current (I)–voltage (V) characteristics of TE devices in various plasmonics-mediated configurations measured with the solar simulator. In the absence of the plasmonic effect, the power conversion efficiency (PCE) caused by the heat effect directly from solar irradiation is as low as 2.30%. Benefitting from the photothermal effect from the silver nanocubes and nanoplates, the PCE of the devices can be enhanced to 4.70% and 6.10%, respectively. As anticipated, the double-layer configuration can further improve the PCE to 10.50%, which can be ascribed to the better spectral coverage in both the visible and near-IR regions.

To investigate the effect of various LSPR bands on the solar–TE conversion, we have used two different optical filters with maximum half-peak widths of 435 ± 100 nm and 660 ± 115 nm, respectively, to modulate the light directly from the solar simulator in the device characterizations. Fig. 3b gives the transmission spectra of the two filters, which confirms their working spectral ranges. Modulated by the optical filters, we have been able to measure the I–V characteristics of the devices in the visible and near-IR regions separately. As shown in Fig. 4c, nanocubes and nanoplates alone can provide the photothermal effect for the TE conversion (maximum power output, \( P_{\text{max}} \approx 0.218 \text{ mW} \) and 0.326 mW versus 0.192 mW for the blank devices), and the plasmonic band of nanoplates at 350–400 nm can work better than that of the nanocubes around 425 nm. This feature could be ascribed to the higher portion of absorption in the plasmonics of the nanoplates (refer to Fig. 1d and g). However, the nanocubes can still serve as a class of complementary photothermal element for more efficient power conversion. The device coated with nanocubes/nanoplates double layers has a higher open-circuit voltage \((V_{\text{oc}})\) and short-circuit current \((I_{\text{sc}})\) compared to the ones with nanocubes or nanoplates alone, generating a higher \( P_{\text{max}} \) of 0.440 mW. The performance of the devices in the near-IR region is also evaluated with the 660 nm filter (see Fig. 4d). There is no doubt that the presence of the nanoplates induces a higher \( P_{\text{max}} \) than that of the nanocubes owing to the unique strong LSPR band of the nanoplates around 710 nm. Surprisingly, we observed that the \( V_{\text{oc}} \) and \( I_{\text{sc}} \) were slightly reduced when putting a layer of nanocubes on top of the nanoplates. It is assumed that the nanocubes on the top interact with the incident light first and affect the directions of incident light and polarization on the bottom layer of nanoplates, causing a reduction of the photothermal effect and thus of the final power conversion. Near-field characterizations are underway to resolve the detailed mechanisms. Although the combination of these two nanostructures in coating causes a slight reduction of power conversion in the near-IR region, this double-layer configuration still represents a better scheme for the photothermal TE conversion (refer to Fig. 4b: PCE, 10.50% versus 4.70% and 6.10%), given that the majority of the power input in solar irradiation is located in the visible region.

Finally we have employed two methods to estimate the temperature increase and heating power induced by the photothermal effect of the silver nanostructures. First, we attempted to measure the temperature of the device surface coated by various silver nanostructures under the irradiation of a solar simulator using an infrared temperature detector (see Fig. 5a). In order to facilitate detect the surface temperature, we removed the glass slide from the surface of the devices so that the nanostructures could be exposed to the detector. In our real device application, the devices were actually covered with a piece of glass slide for preventing heat dissipation from the top. The measurements show that the temperature only increased by less than 2 °C in the absence of the silver nanostructures. In comparison, the temperature increase could be induced to about 10 °C in the presence of silver nanocubes or nanoplates. This temperature difference should be fairly sufficient for TE conversion when it is considered as a supplement for PV devices. However, it is worth noting that the actual temperature increase on the TE devices should be far above this value, given that most heat was dissipated into the surrounding air and the device below in our temperature measurements. In order to evaluate the effect of heat generation better, we have measured the temperature increase of aqueous suspensions of silver nanostructures under light irradiation. In this case, the nanostructures are kept in a symmetrical environment, and the effect of plasmonic heating can be evaluated based on the temperature of the surrounding water. As shown in Fig. 5b, the presence of \( 10^{11} \) particles per mL of silver nanocubes or nanoplates increased the temperature of water up to 13 °C, which is consistent with the previous simulation data. Based on the thermal conductivity values of water and air \((0.6 \text{ W m}^{-1} \text{ K}^{-1} \text{ versus } 0.03 \text{ W m}^{-1} \text{ K}^{-1})\), we can estimate that the temperature increase on the surface of the device may be more than 100 °C. This estimation highlights the need to further improve the power conversion efficiency by modifying the packing configuration of devices in consideration of the heat transfer in future works.
In conclusion, we demonstrate that the photothermal effect of silver nanostructures can provide a heat source for thermoelectric devices for the first time. The plasmonic band of silver nanostructures can be facilely manoeuvred by tailoring their shapes, enabling them to interact with photons in different spectral ranges for more efficient utilization of solar light. Given that the scattering in LSPR features can serve as a subwavelength element to help direct the light from the Sun into a PV absorber thin film, the implementation of the photothermal effect in TE devices makes the design of a PV–TE tandem cell structure promising, as illustrated in Fig. S1. By integrating plasmonic nanostructures into the tandem cell, the scattering portion in the LSPR can improve the light absorption in photovoltaic conversion in the top cell, while the absorption portion may be efficiently used to drive thermoelectric operation in the bottom device. In this configuration, both portions of the LSPR can be fully considered towards efficient solar conversion. It is anticipated that this concept will enable the fabrication of a mechanically flexible, high-performance solar device when down-scaling the thickness of PV and TE functional films.

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Notes and references
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