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Plasmonic Heating from Indium Nanoparticles on a Floating Microporous Membrane for Enhanced Solar Seawater Desalination

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Lulu Zhang^a, Jun Xing^a, Xinglin Wen^a, Jianwei Chai^b, Shijie Wang^b, and Qihua Xiong^{a,c*}

Passive solar evaporation represents a promising and environmentally benign method of water purification/desalination. Plasmonic nanoparticles have been demonstrated as an effective approach for enhancing solar steam generation through plasmonic heating effect, nonetheless the efficiency is constrained by unnecessary bulk heating of the entire liquid volume, while the noble metals commonly used are not cost-effective in terms of availability and the sophisticated preparation. Herein, a paper-like plasmonic device consisting of a microporous membrane and indium nanoparticles (In NP/MPM) is fabricated through a simple thermal evaporation method. Due to the light-weight and porous nature of the device, the broad band light absorption property, and theoretically the excellent plasmonic heating effect from In NP which could be even higher than gold, silver and aluminium nanoparticle, our device can effectively enhance solar water evaporation by floating on water surface and its utility has been demonstrated in solar desalination of a real seawater sample. The durability of the device in solar seawater desalination has also been investigated over multiple cycles with stable performances. This portable device could provide a solution for individuals to do water/seawater purification in under-developed areas with limited/no access to electricity and centralized drinking water supply.

Introduction

Solar energy harvesting has drawn tremendous research attention because of its potential to provide power for a variety of processes without relying on fossil fuels which have casted sustainable and environmental concerns.¹⁻⁵ As one of the most important aspects of solar energy harvesting, conversion of solar energy to heat enables various applications in solar power and enhanced H₂ generation,^{3, 6} waste water treatment,⁷ chemical separation/purification,⁸ as well as solar steam sterilization.⁹ Since water scarcity has become one of the most serious global challenges of our time, solar seawater evaporation/desalination, which generates fresh water through the evaporation of seawater using sunlight has also been heavily investigated.¹⁰⁻¹² To enable efficient solar desalination, the first critical step is to incorporate photothermal materials which can serve as good light absorbers to further increase the absorption and conversion efficiency of solar energy in the evaporation process.

Subwavelength metallic particles which can support strong

surface plasmons as a result of the collective oscillations of their delocalized conduction electrons when shining with light, have been proven as good light-to-heat converters,¹³⁻¹⁶ in which heat can be generated through Landau damping.¹⁷ Up to now, most extensively developed plasmonic structures for solar energy conversion are noble metal-based (gold and silver) systems due to their strong visible and infrared (IR) surface plasmons which have sufficient spectral overlap with the solar spectrum.^{8, 16, 18} As gold and silver are scarce and expensive as commodities, it is desirable to explore other alternative metals to be employed for solar energy conversion, which is of crucial importance for developing low cost techniques, broadening the understanding on plasmonic heating properties from other metals as well as for fundamental research. Recently, a numerical study of quantifying the efficiency of plasmonic materials for photothermal conversion was reported, showing renewed consideration of other metals as photothermal materials.¹⁹ In consistent with this report, Zhu's group successfully designed a plasmon-enhanced solar desalination device through the 3D assembly of aluminium nanoparticles (Al NPs) in 2016,²⁰ which planted the seed of exploring plasmonic heating from metals other than Au and Ag for solar seawater evaporation experimentally.

Herein, we reported for the first time using indium nanoparticles (In NPs) for efficient and reliable plasmon enhanced solar seawater desalination which was motivated by our theoretical calculation results that In NP could exhibit even

^a Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371. E-mail: Qihua@ntu.edu.sg

^b Institute of Materials Research & Engineering, Agency for Science, Technologies and Research, 2 Fusionopolis Way, Singapore 138634

^c NOVITAS, Nanoelectronics Center of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

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better plasmonic heating ability than Au, Ag and Al NPs. In our design, we prepared In NPs on a paper like microporous membrane (MPM) through a simple one-step thermal evaporation method, while complicated procedures including chemical synthesis of the photothermal materials or specifically prepared substrates are often required in previous reports using Au,^{15, 21, 22} Ag,¹⁶ Al²⁰ and other materials.^{23–30} Taking advantage of the emergent concept which was named “solar heating at air-water interface”,^{20, 21, 24} the paper-like device with the ability to float on the water surface can avoid bulk heating of water, and thus reduce the heat loss to underlying water and improve the evaporation efficiency. In addition, the unique microporous structure of MPM can further enhance the total absorption performance due to the reduced surface reflection and increased internal light scattering.^{20, 22, 31} Moreover, the densely distributed In NPs on MPM tends to merge with each other to form larger particles with irregular shapes when increasing the deposition thickness of indium, leading to the strong and broad plasmonic absorption which is favourable in solar energy harvesting based applications. The combination of the significant plasmonic heating effect from In NPs, the simplicity in device fabrication, and the scalable production processes suggest that this portable paper like device could provide a broad prospect in the practical applications in solar seawater evaporation/desalination.

Results and discussion

Owing to the large number of free electrons, the heating effect is especially strong for a metal NP under plasmon resonance or when the light frequency resonate with the collective resonance of many metal NPs. In the case of semiconductor NPs, on the one hand, since heat dissipation occurs through an interband absorption process with the creation of a single mobile electron and hole (exciton), the heat generation rate is much weaker.³² On the other hand, it should also be noted that different from semiconductors or other light absorbing materials, light can be confined by plasmonic absorbers into deeply subwavelength volumes, which will lead to highly localized optical excitation at extremely high near field intensities, beneficial for a plasmon-enhanced liquid-vapour phase transition and local heating.⁸ Therefore, significant efforts have been devoted in designing plasmonic metal nanostructures for various photothermal conversion based applications.^{14, 21, 32} In spite of the exciting advances in noble metal based plasmonic heating effects, there are still a limited number of studies experimentally investigating the cases of poor metals. Meanwhile, according to a recent study on theoretical calculation of heat generation from different metal NPs, theoretically gold and silver may not be the best choices for the photothermal based applications.¹⁹ In this proposed theory, the ability of a plasmonic nanoparticle to produce joule heat (J_0) can be calculated using a simple close-form expression:

$$J_0 = 9 \frac{e\epsilon''}{n_s} \left| \frac{\epsilon_s}{\epsilon + 2\epsilon_s} \right|^2 \quad (\text{eq.1})$$

where e is the photon energy of the incident light radiation in eV, ϵ is the permittivity of the material while ϵ'' is its imaginary part, and ϵ_s and n_s are the dielectric constant and the refractive index of the surrounding medium, respectively. In consistency with the theoretical results in this report, Al NPs were devised experimentally for plasmon enhanced solar desalination for the first time in the following year, which inspires people to keep on searching other metals in this field.²⁰

Figure 1. (A) Calculated J_0 numbers of Ag, Au, Al, and In NP plotted as a function of the wavelength. (B) Calculated J_0 numbers of In NPs with irregular shapes plotted as a function of the wavelength based on the ellipsoid model.

Apart from aluminium, indium has been the one of the most experimentally demonstrated poor metals as plasmonic materials from visible to deep-ultraviolet (DUV) region.^{33–38} According to previous theoretical result, indium can support strong near-field enhancements as efficiently as, or even more efficiently than aluminium.³⁹ We have also calculated the J_0 of In NP and compared it with Au, Ag and Al NP using eq.1 (Figure 1A).^{19, 39} It can be seen from the as obtained curves that In NP shows the highest value of J_0 when compared with Au, Ag and Al NP at their plasmonic resonance wavelengths. To maximize the plasmonic heating performance using sunlight which has broad radiation ranges from UV to visible and IR, it is still necessary to broaden the plasmon band of In NPs. Tuning the morphology of a metal NP is the common approach to control its plasmonic resonance, through which the red shift of the plasmon resonance can be achieved by reducing the depolarization factor along certain direction.⁴⁰ Taking this

morphology induced effect into consideration, J_0 of In NPs with irregular shapes which have different plasmon resonance wavelengths can thereby be calculated (Figure 1B) based on an ellipsoid model:¹⁹

$$J_0 = \frac{e\epsilon''}{n_s} \left| \frac{\epsilon_s}{\epsilon + L_j(\epsilon - \epsilon_s)} \right|^2 \quad (\text{eq.2})$$

where

$$L_j = \frac{R_1 R_2 R_3}{2} \int_0^\infty \frac{du}{(u + R_j^2) \sqrt{(u + R_1^2)(u + R_2^2)(u + R_3^2)}}$$

where R_1 , R_2 , and R_3 denote the radii of the ellipsoid along the principal axes $j = 1, 2, 3$. Note that the depolarization factors L_j satisfy the relation $L_1 + L_2 + L_3 = 1$. L_j generally depicts the degree of a metal NP's morphology deviation from a sphere along this direction. For In NPs with different depolarization factors, namely different shapes, their plasmon bands can be red shifted and become broader with the decreasing depolarization factors. It is worth noting that the J_0 value of In NP could still remain very high when the plasmonic resonance is tuned to visible and near IR region, which implies that plasmonic device made of In NPs with broad plasmon band will be a good candidate for solar photothermal conversion based applications.

Since gold, silver and aluminium tend to form a flat film on a substrate when they are evaporated, additional treatments are

often required to obtain well defined nanostructures, such as the use of a patterned substrate or substrate annealing.⁴¹⁻⁴⁴ The situation is different for indium that well separated grains will form when indium vapour condenses on commonly used substrates such as glass and quartz (Figure S1), which could be ascribed to its natural poor wettability to the substrate surfaces.^{36, 39} Taking advantage of this unique property of indium, we successfully prepared In NPs on MPM through a simple one step vacuum thermal evaporation method without performing any treatment on the MPM substrate. Figure 2A-D shows the SEM images of the MPM substrates coated by indium with deposition thicknesses ranging from 10 to 80 nm, in which one can see the densely distributed In NPs on MPM clearly. In addition, it can be observed that In NPs tend to merge with each other to form larger particles with irregular shapes as the deposition thickness increases. As a result of the non-uniformity of the as prepared In NPs in size and shape, and their significant plasmonic effects, our devices display strong and broad light absorption which could span from visible (Figure 2E) to IR (Figure 2F) region with deposition of only tens of nanometres thickness of indium on MPM. Meanwhile, it also can be observed that the original white colour of MPM dramatically darkens with indium deposition thickness, which could be a direct indication of the efficient and broadband light absorption of the as-prepared indium-based plasmonic device (Figure 2G).

Figure 2. (A-D) SEM images of In NPs coated MPM substrates prepared through thermal evaporation of indium source in vacuum with deposition thicknesses of 10, 20, 40, and 80 nm, respectively. The scale bars are 500 nm. (E, F) Absorption spectra of the as formed In NPs on MPM substrates in visible and IR region, respectively. (G) Optical images of In NPs coated MPM substrates with different thicknesses of indium.

The outstanding light absorption property of the device offers unique opportunities for the development of highly efficient solar-thermal conversion systems. As a proof of concept, we demonstrated the use of the In NP/MPM device for solar-enabled water evaporation. Figure 3A is the schematic illustration of the solar seawater steam generation design with the floating In NP/MPM device. The microporous structure of the MPM (Figure S2) not only makes the device float on water (Figure 3B, inset), but also enables efficient water absorption and more rapid replenishment of surface water after evaporation through capillary effect. Since the In NPs are in contact with the top surface of the water, the liquid-vapour phase change occurs close to the air-water interface. Moreover, the hydrophilicity of MPM would benefit the device in water adhesion and accelerating the water transfer toward surface (Figure S3). The effect of indium thickness on the water evaporation performance was then systematically evaluated at a sunlight intensity of 3 kW/m² (3 sun). As a reference, the water evaporation experiments with and without the bare MPM were also carried out. The weight change curves of water were plotted in Figure 3B as a function of the solar irradiation time using In NP/MPM devices with different indium thicknesses. As expected, the water weight changes more dramatically with

the increasing indium deposition thickness, which is consistent with the absorption spectra that thicker indium on MPM will result in stronger and broader light absorption, and thereby leading to better evaporation performance. In contrast, bare MPM itself has insignificant effects on water evaporation, suggesting that the enhanced water evaporation performance from In NP/MPM devices should be ascribed to the plasmonic heating effects from In NPs. It is worth noting that only slight enhancements in water evaporation performance are observed by increasing the evaporated indium thickness from 20 to 80 nm, whereas 20 nm thickness of indium deposited on both sides of MPM (40 nm in total) exhibits superior water evaporation performance even much better than MPM with 80 nm thickness of indium on one side, which could be explained by the improved light absorption in the visible region (Figure 2) and theoretically the better plasmonic heating effects of In NP at shorter wavelengths (Figure 1). In NP/MPM device with 20 nm indium on both sides was thereby chosen in the following studies. IR images were also taken to confirm the surface temperature after sunlight illumination (3 sun). As shown in Figure 3C, the surface temperature of the In NP/MPM can increase from $\sim 24^\circ\text{C}$ to $\sim 50^\circ\text{C}$ in 30 minutes (III and IV), while the blank water can only reach $\sim 38^\circ\text{C}$ (I and II). As the plasmonic heating effect is highly localized at In NP/MPM on water surface, it displays distinct temperature evolutions from the top to bottom areas (IV). Subsequently, the effect of the sunlight radiation intensity on the water evaporation rate was also studied using the as designed device (20 nm indium on both sides of MPM) by monitoring the weight changes of water over time under different optical concentrations (Figure 3D). It is observed that steam generation is more efficient than pure water with the plasmonic devices under all investigated solar irradiance intensities at 1, 2, and 3 sun, which are 2.4, 2.9, and 3.1 times higher than pure water evaporation, respectively (Figure 3E). The enhancement on water evaporation by using our In NP/MPM device is even better than some recent reports of using Al NPs (best 2.4 times enhancement at 4 sun) and specifically synthesized black TiO_x NPs (1.5 times enhancement at 1 sun).^{20, 25} The corresponding solar steam efficiency η can be calculated by the following equation:^{20, 21}

$$\eta = \frac{\dot{m}h_{\text{LV}}}{I} \quad (\text{eq.3})$$

where $\dot{m}$ is the mass flux, h_{LV} is the total enthalpy of liquid-vapor phase change (sensible heat and phase-change enthalpy), and I is the power density of solar illumination. The calculated thermal efficiencies of solar steam generation under 1, 2, and 3 sun were 71.6%, 79.2%, and 84.2%, respectively.

Figure 3. (A) A schematic illustration of the floating In NP/MPM device for plasmon enhanced solar steam generation. (B) The weight changes of water, water with bare MPM, and water with different In NP/MPM devices as a function of their radiation time. The inset photo shows the floating

In NP/MPM device on water surface. (C) IR images of water before sunlight irradiation (I), water after 30 min irradiation (II), water with In NP/MPM after 30 min irradiation (III) and its side view (IV) under 3 sun. (D) The weight changes of water with and without In NP/MPM device under 1 and 3 sun irradiation as a function of irradiation time. (E) The dependence of the evaporation performance of water with and without In NP/MPM device on irradiation intensities from 1 sun to 3 sun in 30 minutes.

Figure 4. (A) The evaporation performances of a real seawater sample (from the east coast, Singapore) with In NP/MPM device under irradiation intensities at 1 and 3 sun in 30 minutes at different cycles. (B) The measured concentrations of five primary ions in the real seawater sample before and after desalination using ICP-OES. For Mg²⁺, the concentration after desalination is below the detection limit of ICP-OES (N.D.). The shaded areas refer to the overall typical salinity achieved by traditional membrane (light blue) and distillation (light green) based seawater desalination techniques. The dashed coloured lines are the regulated WHO and EPA standards of salinity for drinkable water.²⁰

To assess the utility of the In NP/MPM device in solar seawater desalination, real seawater sample collected from Singapore east coast was employed. The performances of the In NP/MPM device under fixed optical intensities (1 sun and 3 sun) were investigated. As shown in Figure 4A, the steam generation performances are stable during intensity switches between 1 sun and 3 sun irradiances, which are even comparable to the results obtained previously using pure water (Figure 3E). Meanwhile, condensed water will quickly form on the quartz cover of the evaporation chamber when In NP/MPM is used, while without this plasmonic device the amount of generated water is minimal (Figure S4). The condensed water obtained with In NP/MPM device can be easily collected by using a pipette, after which inductively coupled plasma spectroscopy (ICP-OES) measurements were carefully performed to check the concentrations of different elements (Figure 4B). For all of the five primary ions (Na⁺, Mg²⁺, Ca²⁺, K⁺ and B³⁺) naturally existed in the seawater, it is found that their concentrations are

significantly reduced, which are well below the values typically obtained through commonly used seawater desalination techniques such as distillation (1-50 ppm) and membrane (10-500 ppm), as well as the standards prescribed by World Health Organization (WHO) and the US Environmental Protection Agency (EPA).^{20, 45}

Figure 5. (A) XPS spectra of In 3d of In NPs on MPM before and after desalination processes. (B) XRD patterns of In NPs on MPM before and after desalination processes.

To evaluate the durability of the In NP/MPM device in solar desalination processes, the cycle performances were recorded under fixed optical illumination intensity (3 sun). It is observed that the performances are maintained stable for 15 cycles with each cycle for 30 minutes (Figure S5). To further confirm the robustness of the In NP/MPM device, X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical state of indium on MPM before and after the solar desalination process. As shown in the high resolution In 3d XPS spectra in Figure 5A, both of the asymmetric peak shapes and loss features which are typically found on indium metal are observed without obvious change, indicating that the chemical state of indium on MPM are stable in the desalination process. According to previous study, In 3d peaks often broaden with respect to metal peaks for compounds,⁴⁶ while in our case we

did not observe any broaden effects of the In 3d peaks after the desalination processes, which further confirms that the stability of our device. Correspondingly, high resolution O 1s XPS spectra were also recorded (Figure S6A), in which the two O 1s peaks could be ascribed to the intrinsic thin oxidation layer of In NPs that formed after preparation, and physically adsorbed or chemically contained oxygen on MPM, respectively. The negligible differences in the indium oxides peaks before and after the desalination processes imply that further oxidation of indium did not occur, which may be ascribed to the protection effect of the as formed oxidation layer on In NP surface. Our results are consistent with previous study that oxidation of indium below 145 °C in the air results in little or no oxide growth beyond the native oxide level (~4 to 5 nm).⁴⁷ X-ray diffraction (XRD) was also conducted to know the stability of the crystal structure of the as formed In NPs on MPM (Figure S5B). It is found that the diffraction peaks matches well with body-centred tetragonal crystal structure of indium (ICSD collection code: 064794), and the crystal structure also retains after the desalination processes. SEM images were taken to further confirm that there was no obvious change of the morphology and size of the In NPs on MPM after desalination (Figure S7). The In NP/MPM device developed in this work with high stability thus has the potential to be employed in practical seawater desalination in properly designed solar still (Figure S8).

Conclusion

We successfully prepared densely distributed In NPs with broad size and shape distribution on a floating MPM through a simple thermal evaporation method. As a result of the plentifully formed NPs and their non-uniformity in morphologies, In NPs on MPM show strong and broad light absorption that can span from visible to IR region. Taking advantage of the outstanding plasmonic heating effect from In NPs and the floating nature of the MPM matrix, we demonstrated for the first time the possibility of fabricating portable and efficient In NP/MPM solar photothermal device for plasmon enhanced seawater desalination, and its stability could maintain even after multiple times desalination processes. Considering the increasing efforts in exploring clean and recycle solar energy usage, our findings may be extended to many other solar energy based applications such as thermophotovoltaics and photocatalysis.

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