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Plasmonic multi-thorny Gold nanostructures for enhanced solar thermal conversion

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ABSTRACT

In this work, thorny Au nanoparticles (NPs) a broadband surface plasmon resonance (SPR) peak were used to enhanced the solar thermal conversion (STC) performance. The SPR peak of the thorny Au NPs can be tuned from 562 nm to 812 nm with the size ranging from 42 to 188 nm, which was controlled by the amount of Ag^+ in the growth process and the seed additive amount for optical and morphological evolution of Au NPs. Experiments indicated that the thorny Au NPs can greatly enhance the STC efficiency, the maximal increase of which was 152.0% and 18.5% compared with pure water and quasi-spherical Au NPs respectively. Then, the particle heating model was applied to further confirm that the thorny NP can enhance the solar heating process significantly. Results indicated that the thorny Au NP obtained a higher maximum temperature than that of the spherical Au NP owing to a higher heat resource from the solar radiation in the thorns. In addition, a blended nanofluid with different thorny Au NPs showed a highest STC efficiency in all experimental samples that was as high as 85.8% by broadening its absorption spectra. It indicated that tuning the NP morphology or mixing different NPs could be efficient ways to improve the STC performance.

1. Introduction

The heavy use of traditional fossil fuels has led to several environmental issues (Hill et al., 2006) such as greenhouse effect (Rodhe, 1990), acid rain (Likens et al., 1996), and haze (Huang et al., 2015). Solar radiation is the principal source of energy on earth; improving its absorption and conversion ability could effectively solve the energy crisis. Therefore, the effective utilization of solar energy has gained significant attention of researchers owing to its wide distribution and because it is a green renewable energy source (Sundström, 2009). To improve the solar energy conversion efficiency, light absorption must be enhanced, which is the primary step in various solar energy conversion applications. Solar thermal conversion (STC) serves as one of the most popular and direct conversion methods, which converts solar radiation to thermal energy directly to be utilized by the working medium in the next step. In 1975, Minardi and Chuang (1975) proposed a solar collector model called direct absorption solar collector (DASC) with black liquor as the absorption medium. The working fluid directly absorbed the solar energy in the DASCs that could avoid the occurrence of high temperature surface and reduce heat loss. Moreover, the heat transfer between the absorption surface and the working fluid resistance could be avoided, resulting in the reduction of heat losses during the conversion processes and the enhancement of the collector efficiency. However, the most common working fluids, such as water, alcohol and oil, have limited absorption ability with regard to solar energy, leading to low solar collector efficiency (Otanicar et al., 2009).

The rapid development of nanotechnology has provided various methods to enhance the solar energy absorption and conversion ability (Oelhafen and Schüler, 2005; Pospischil et al., 2014) and enhanced thermal conductivity (Qi et al., 2017). Adding nanoparticles (NPs) to the base fluid (called nanofluids) can significantly enhance the absorption ability of solar energy owing to the enhanced and tunable optical properties of the particles at the nanoscale (Chen et al., 2018a, 2018b). Therefore, NP-based DASCs have gained significant interest of researchers owing to the tunable optical properties, enhanced light absorption ability of the NPs. Various nanofluids were applied to DASCs by experiments. The collector efficiency could be improved as high as 5% in the DASCs by using nanofluids as the working fluids (Otanicar et al., 2010). Sani et al. (2011) studied the optical properties of single-layer carbon nanotube nanofluids with ethylene glycol as the base liquid in solar collectors. Results indicate that the single-layer carbon nanotube nanofluids can not only improve the efficiency of the

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collector, but also reduce the impact of the collector on the environment and the related costs. With regard to the effect of NP size and volume fraction on the solar absorption performance, the research results of Saidur et al. (2012) indicated that the NP size had negligible effect on the optical properties of the nanofluid and the extinction coefficient was linearly proportionate to the NP volume fraction. On the other hand, based on the plasmonic NPs a great improvement of the STC efficiency was obtained (Chen et al., 2017, 2016a). Localized surface plasmon resonance (LSPR) oscillation around the surface of noble metal nanostructures can significantly enhance the optical absorption and photothermal conversion (Jain et al., 2008). For example, plasmonic Au NPs were dispersed in a liquid to produce vapor without heating the fluid volume for solar vapor generation (Neumann et al., 2013). Au NPs were added to a NP fluid filter to improve the performance of a parabolic trough solar concentrator by using the heat transfer fluid as the filter itself (Dejarnette et al., 2016). Numerical simulations demonstrated that the solar collector efficiency could be enhanced significantly by using blended plasmonic NPs with an exceptionally low NP volume fraction, which was approximately 70% for a 0.05% NP volume fraction (Lee et al., 2012). In addition, Au NPs were also deposited onto heterojunctions to enhance solar cell performance exploiting the improved absorption of light by the SPR of Au NPs (Losurdo et al., 2009).

Au NP serves as one of the most important metals in the application of plasmon resonance owing to its high electrical conductivity and thermal conductivity, good stability, and strong surface plasmon resonance (SPR) over a wide wavelength range (Yuan et al., 2007; Ma and Dai, 2011). Among these plasmonic NPs supporting SPRs in the visible and near-infrared regions, Au NPs offer many advantages over Ag, Cu, Al and Li. Firstly, in terms of plasmonics, it is significant to choose a metal that can support a strong SPR at the desired resonance wavelength region. The main SPR region of Al and Cu locate in the ultraviolet and near infrared regions respectively. However, Au and Ag have a high SPR strength (or damping) in the visible and near-infrared regions (Ru and Etchegoin, 2009). On the basis of the SPR quality factor, Li should be a candidate, which supports strong SPR. However, this metal is so reactive and hard to handle that it is seldom considered and explored for plasmonic applications (Rycenga et al., 2012). Secondly, Ag and Cu are easily oxidized in the air or water and Au has a good stability. In addition, the solar thermal conversion performance of Au and Ag NPs were compared theoretically under the same conditions, and the results showed that Au NPs obtained a higher efficiency (Chen et al., 2016b). Besides, the enhancement ratio in the solar thermal conversion efficiency of Au NPs with spherical graphite NPs and carbon nanotubes were also compared. It showed that Au NPs had much higher solar thermal conversion capability than the other two materials (Zhang et al., 2017).

As discussed above, these results indicated that the plasmonic Au NP addition to the working fluid in the DASCs can significantly improve the solar absorption and conversion efficiency. Moreover, the effect of the morphology of the plasmonic Au NP on the solar absorption performance should be given more attention because the SPR peak of the plasmonic NP was significantly affected by the morphology of the plasmonic NP. However, the absorption peak of Au NPs usually locates in the visible region, it is urgent to broaden the SPR peak of Au NPs to match the solar radiation spectra. Therefore, the optical and morphological evolution of the Au NPs has been investigated first to improve its SPR peak from visible to near-infrared region. Thorny Au NPs have been prepared using a seed mediated method and added to the base fluid to enhance the STC efficiency. Moreover, the blended thorny Au NPs added to the base fluid have also been investigated.

2. Experiment section

2.1. Preparation of thorny Au NPs

Materials: Gold chloride trihydrate ($HAuCl_4{\cdot}3H_2O$), silver nitrate ($AgNO_3$), trisodium citrate dihydrate ($Na_3(C_6H_5O_7){\cdot}2H_2O$), ascorbic acid ($C_6H_8O_6$, AA) and hexadecyltrimethylammonium chloride (CTAC) were obtained from Aladdin Reagents Company (China). Prior to their use 10 mM $HAuCl_4$ aqueous solution, 2 mM $AgNO_3$ aqueous solution, fresh aqueous solutions of 5 mM trisodium citrate solution, and 40 mM AA aqueous solution were prepared.

Au Seed Preparation: Au seeds were prepared using the citrate thermal reduction method (Bastús et al., 2014). A 2.0 mL of 10 mM $HAuCl_4$ aqueous solution was dropped into 100 mL of 5 mM sodium citrate aqueous solution and mixed thoroughly. Subsequently, the mixture solution was placed in a water bath at 100 °C for 30 min for occurrence of complete reaction. After the solution turned purple-red without any further changes, it was cooled to the room temperature (~25 °C).

Thorny Au NP Preparation: A seed-mediated method was used to prepare the thorny Au NPs. In this method, 2 mL of 10 mM $HAuCl_4$, 40 mL H_2O, 0.5 g CTAC and 0.8 mL of 40 mM ascorbic acid solution were mixed into a transparent solution and added to a designated amount (0–800 μL) of 2 mM $AgNO_3$ solution. Under vigorous stirring, a designated amount (10–800 μL) of Au seeds was added to the growth solutions rapidly. Further, the color of the mixture changed from transparent to blue or red within a few minutes after the addition of the purple-red Au seed solution, indicating the generation of the Au NPs. Finally the mixture was placed for several days for the seed growth until the color of aqueous or the absorbance spectral didn't change any more.

Sample Characterization: The absorbance of the samples were measured by a UV–visible spectrophotometer (TU1901, Beijing Purkinje General Instrument Co., Ltd.). Generally, 1 mL of the sample solutions was measured with pure water as reference. The structure and morphology of the Au NPs were investigated using a scanning electron microscope (SEM, ZEISS SUPRA 55 electron microscope with a bias voltage of 30 kV). X-ray diffraction (XRD) patterns of the sample powders were measured by a Rigaku D/Max-3C equipped with a rotation anode and a Cu Kα radiation (λ = 0.15418 nm, 40 kV and 200 mA). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer using Al Kα radiation under high-vacuum conditions.

2.2. Solar thermal conversion experiments

Fig. 1 shows a diagram of STC experimental device. A polymethyl methacrylate (PMMA) beaker containing a designated amount (10 mL or 20 mL) of fluid was stirred using a magnetic stir bar (800 rpm) to reduce the fluid temperature gradients. The Au nanofluids after adding the surfactant CTAC were aged for several days to form stable nanofluids. Only heat convection with the air existed when the radiation effect was ignored due to the beaker was fixed in the air by a holder. A quartz glass covered the top of the beaker to avoid water loss and solar

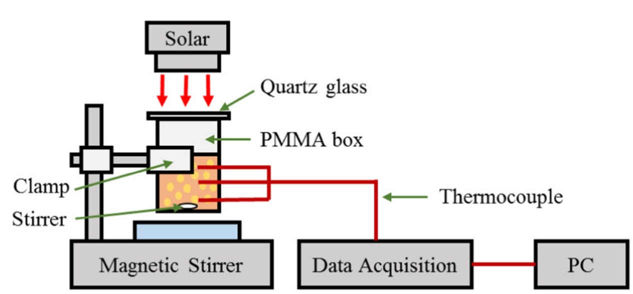

Fig. 1. Schematic of solar thermal conversion experimental device.