Graphene nanofluids containing core-shell nanoparticles with plasmon resonance effect enhanced solar energy absorption

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ABSTRACT

Nanofluids are a kind of important working fluid in volumetric solar collector. Here, we presented a novel strategy to enhance the solar absorption properties of graphene nanofluids utilizing the plasmon resonance of core-shell nanoparticles. The preparation, micrograph, optical properties and thermal conductivity of nanofluid have been investigated by considering the effect of volume fractions, nanoparticles selection and temperature. Results show that the graphene-embedded Sn@SiO$_2$@Ag nanofluid exhibits a strong absorption band in the range of 250–300 nm and 380–600 nm. The solar absorption performance of graphene nanofluids is enhanced significantly by the plasmon resonance absorption and thermal conduction bridge of graphene-embedded Sn@SiO$_2$@Ag core-shell nanoparticles. The solar absorptance performance of graphene nanofluids was enhanced 2.9 times by adding 0.4 g/L Sn@SiO$_2$@Ag solutions. An enhancement in thermal conductivity of 11.3% was obtained at 20 °C and 16% enhancement at 50 °C for 0.3 g/L graphene-embedded Sn@SiO$_2$@Ag nanofluids. It is concluded that the synergic effect of Sn@SiO$_2$@Ag core-shell nanoparticles and graphene nanosheets increases both the solar absorption coefficient and thermal conductivity of the nanofluids.

1. Introduction

Nowadays, climate abnormality, environmental deterioration, and air contamination have become the most challenges in our society, especially in the developing countries. It is thought that the combustion of fossil fuel during the conventional heat supply is the main cause of aggravating global environment and climate issue (Baharoon et al., 2015; Crabtree and Lewis, 2007). In China, the achievements of local government are closely related to the reduction of smog. It is reported that the Premier Keqing Li will launch a special fund to explore more effective way of fighting against the smog pollution. Therefore, there is an urgent need to decrease the dependence on fossil fuel by developing renewable energy technology. As a clean energy source, solar energy has been developed vigorously in the past decades (Zheng and Kammen, 2014). Among various technologies of solar energy utilization, solar-thermal conversion is seen as the most direct and promising approach (Weinstein et al., 2015). It employs solar thermal collector to transform sunlight from condensing mirror into heat energy, replacing heat from combustion in power production systems (Weinstein et al., 2015; Xu et al., 2016). However, the conventional solar thermal collector usually suffers a high temperature because of its high solar absorbing surface, leading to a significant radiative heat loss ($\propto T^4$), and

consequently lowers the solar-thermal conversion efficiency, especially for applications involving concentrated solar power (CSP) (Lee et al., 2012a).

In order to decrease the heat loss at high temperature, Abdelrahman et al. (1979) proposed a black-liquid collector in the 1970s, which it is also called volumetric solar thermal collector. In contrast to the conventional solar thermal collector, solar energy is directly absorbed by the working fluid in the black-liquid collector, decreasing in turn the surface temperature of collector, and then the radiative heat loss can be also reduced. Moreover, the overall thermal resistance is also lowered since the thermal resistance from hot absorbing surface to working fluid is eliminated (Taylor et al., 2011a).

Recently, nanofluids (nano-sized particles suspended in base fluid) have been introduced to solar thermal collectors as the working fluid that directly absorbs the solar radiation. A series of explorations have been performed in order to further enhance the solar absorption of nanofluids. These explorations involve the nanoparticles material, size, shape, volume fraction, and so on (Karami et al., 2016; Saidur et al., 2012; Karami et al., 2014; Mercatelli et al., 2011; He et al., 2013; Luo et al., 2014; Han et al., 2011; Jin et al., 2016a). For example, Taylor et al. (2011a) reported that a 0.125% volume fraction of graphite resulting in approximately an 11% improvement in steady-state efficiency

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over the base fluid. Saidur et al. (2012) suggested that only 1% volume fraction, the transmittance of aluminum nanofluid is significantly reduced by 60% in average comparing with the water fluids throughout the visible light region. Karami et al. (2014) researched the transmittance spectra of functionalized carbon nanotubes (f-CNTs) nanofluid. They found that f-CNTs considerably reduce the base fluid transmittance and enhance the amount of light-capture. Luo et al. (2014) analyzed the transmittance of C, Ag, TiO_2, SiO_2, Cu, Al_2O_3 and carbontubes nanofluid. They found that the absorption of SiO_2 nanofluid is the worst, while the absorption of Cu and Al_2O_3 nanofluids are the highest.

In these previous works, a series of investigation efforts showed that nanoparticles offer a potential of improving the solar absorption of fluids. For a volumetric absorbers based on nanofluids, however, its overall conversion efficiency is still low. Further investigation on the improvement of intrinsic optical properties of nanoparticles in base fluids has to be carried out. It is reported that light absorption can be enhanced at a certain frequency by a so-called localized surface plasmon resonance effect excited in metal nanoparticles (Lee et al., 2012b). If we can design the nanoparticles in based fluid to form plasmonic nanofluid, an improvement of light absorption is foreseeable. Although numerous studies have been reported on the surface plasmon in the field of photovoltaics, the plasmonic nanofluid investigation in solar collectors has only received very limited attention (Lee et al., 2012b; Filho et al., 2014). At present, several studies on the plasmonic nanofluid have been undertaken. Lee et al. (2012b) performed the radiative heat transfer analysis in plasmonic nanofluids. Their results be greatly enhanced based on the surface plasmons effect. The photothermal conversion characteristics of silver nanofluids were reported that silver particles have excellent photothermal conversion capability even under very low concentrations (Filho et al., 2014). They found that the best photothermal conversion performance was observed at the initial radiation period mainly due to the low heat loss and strong surface plasmon resonance effect of silver nanoparticles. Jeon et al. (2014) experimentally demonstrate the spectral tunability of plasmonic nanofluids based on Au nanorod with different aspect ratios, exhibiting nearly uniform absorption characteristic from the visible to near infrared region. Jin et al. (2016b) investigated the steam generation mechanism of gold nanoparticles-based solar volumetric receivers. Their results suggested that for future solar receiver design, more solar energy should be focused and trapped in the superheated region while minimizing the temperature rise of the bulk fluid.

In this work, we prepared graphene oxide, graphene, $Sn@SiO_2@Ag$ core-shell nanoparticles, and their hybrid nanoparticles. Likewise, the corresponding nanofluids were also prepared by dispersing these nanoparticles into distilled water. The solar absorption properties and thermal conductivity of nanofluids were investigated to evaluate the potential of using the nanofluids for absorbing solar radiation in volumetric solar absorbers.

2. Experimental section

2.1. Nanofluid preparation

Graphite flakes were oxidized using the improved Hummers' method (Marcano et al., 2010). A mixture of H_2SO_4 and H_3PO_4 (270:30 mL) was added to another mixture of 3.0 g graphite flakes and 15.0 g $KMnO_4$, and then the solution was stirred for 1 h at 35 °C through a thermostat or water bath. After stirring constantly for 12 h at 50 °C, the solution was cooled to room temperature. Then the cooled solution was poured into 350 mL ice bath. When the solution becomes yellow color after adding the H_2O_2 with concentration of 30% as shown in Fig. 2(b), the filtrate was centrifuged with 6000 rpm for 2 h. The remaining solid material was then washed continuously by water, 30% HCl, and ethanol. Finally, the graphene oxide nanoparticles were obtained after drying at room temperature in vacuum ambient. The preparation process was illustrated in Fig. 1(a).

Graphene oxide can be chemically reduced to graphene with various reducing agents, such as hydrazine monohydrate (Tung et al., 2009; Compton et al., 2010; Li et al., 2008). Here, 100 mg graphene oxide was added into 100 mL water, the mixture presents a color of reddish brown. After adding 50 mL 80% hydrazine monohydrate into the mixture, the mixture quickly becomes black. The solution was heated to 100 °C for refluxing 24 h. After refluxing, the suspension was cooled to room temperature, and was filtered through filter paper. The resultant was washed successively in deionized water and ethanol for 5 times. After each washing, the mixture was filtered through filter paper. The final graphene powders were obtained by vacuum-drying the resultant deposited on the filter paper as shown in Fig. 1(b).

Tin nanoparticles were synthesized using a modified polyole wet-chemical reduction process (Cingarapu et al., 2014). 3 g poly-vinylpyrrolidone (PVP) and 50 mL tetraethylene glycol (TEG) was mixed at 140 °C by a magnetic stirrer. Then, $SnCl_2$ solution (1 g in 10 mL of TEG) was added slowly into the reaction mixture until appearing yellow-brown solutions. When the temperature was decreased to 70 °C, a freshly prepared $NaBH_4$ solution (3 g of $NaBH_4$ in 40 mL of TEG) and the $NaBH_2$ solution was added into the reaction solution to react about 90 min. After cooling to room temperature, the tin nanoparticles were obtained by in turn washing with ethanol, separating centrifugally, and ultrasonic dispersion with alcohol. Then the alcohol solution containing Sn nanoparticles was magnetic stirred at 30 °C, and 1 mL tetraethyl-ortho-silicate (TEOS) was added. After 45 min, 25 mL stronger ammonia water was added drop-wise to the reaction solution and stirred for 12 h. The schematic diagram was illustrated in Fig. 1(c). After centrifuging, the remained sediment was washed in alcohol and filtered in oily paper. Finally, the $Sn@SiO_2$ nanoparticle was obtained by drying 5 h at room temperature under vacuum condition.

The $Sn@SiO_2$ nanoparticles were dispersed to 40 mL solution consisted of 0.5 g $SnCl_2$ and 30% HCl to induce the absorption of Sn^{2+} ions on the silica sphere surface, during which HCl prohibited the hydroxylation of $SnCl_2$. After 20 min, the spheres were rinsed for 5 times with deionized water, and moved into 40 mL silver ammonia solution (1.5 g $AgNO_3$). After 10 min, the nanospheres were rinsed for three times with deionized water. Then, nanoparticles were dissolved in 70 mL ethanol, adding 0.05 mL formaldehyde and 6 mL silver ammonia solution to stirring 24 h at 70 °C. Finally, the $Sn@SiO_2@Ag$ solution was obtained. The corresponding nanofluids were also prepared by dispersing these nanoparticles into distilled water.

2.2. Characterization

Transmission electron microscopy (TEM, Tecnai 12, Philips, Netherlands) was used to conducted the observation of the micrograph of graphene oxide. The TEM images of the graphene oxide are displayed in Fig. 2(a). Its solution exhibits a yellowish-brown color giving in Fig. 2(b). It can be seen that the graphene oxide sheets are almost smooth except a tiny fold. The few-layer graphene oxide sheets are less than 10 nm by the estimation of fold. After the reduction, the resultant graphene sheets become more corrugated than the graphene oxide sheets as shown in Fig. 2(c).

Fig. 3 shows the Raman spectra of graphene and graphene oxide in the range of 200–1700 cm^{-1} collected at room temperature via Raman spectrometer made by Renishaw. It shows two characteristic peaks with the D band (1355 cm^{-1}) and the G band (1600 cm^{-1}). D band means the structure defects of graphene and G band means the in-plane vibration of sp^2 C atoms. How to judge the quality of graphene is a key problem, D band involving a process of the double resonance Raman scattering defects, so the defects of graphene will be reflected in the D band. Usually, I_D/I_G is used as important parameters of defect density in the characterization of graphene (Li et al., 2011). After chemical reduction of GO, the ratio of the intensities of the D and G bands (I_D/I_G) reduces from 1.1 to 0.8, which is caused by most of the reduction of oxygen containing functional groups.