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Graphene oxide stabilized carbon nanotube-water nanofluids for direct absorption solar collectors

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Abstract. The utilization of solar thermal energy has shown remarkable growth recently. Due to the development of nanomaterials, suspensions of nanoparticles (nanofluids) have exhibited great performance in the solar thermal systems, especially in direct absorption solar collectors (DASC). The fundamental advantage of DASC by using nanofluids is the minimizing of solar energy transfer steps and reducing thermal losses in converting sunlight, as nanoparticles could harvest the solar energy directly and achieve good photothermal conversion properties. Carbon nanotube (CNT) based nanofluids showed great potential as a working fluid in DASC. Nevertheless, the stability of CNTs in suspensions is the main obstacle for the large use of CNT nanofluids. In this work, small amount of graphene oxide (GO) was introduced to stabilize CNT-water nanofluids without using any other organic surfactants. The GO stabilized CNT nanofluids exhibited long-term and high-temperature stability. The π - π interactions between the GO and CNT played a significant role for the good dispersion and stability of CNT in water. Furthermore, optical characterizations showed that the GO stabilized CNT nanofluids have widely absorbing over the solar spectrum which enabled highly efficient solar energy collections. Eventually, photothermal conversion performance of GO stabilized CNT nanofluids was tested under an irradiation of simulated solar light and the nanofluid demonstrated a high efficiency in DASC. The long-term stability coupled with broadband absorption properties of GO stabilized CNT nanofluids make them ideal candidates as photothermal conversion media for direct solar thermal collectors.

Keywords: solar thermal utilization; photothermal conversion; nanofluids; carbon nanotubes; graphene oxide; direct absorption solar collectors

1. Introduction

As a kind of clean energy source with huge reserves, solar energy has broad applications. Two most popular approaches of solar utilization, photovoltaic and photothermal utilization can meet the principal energy demands in domestic life and industrial manufacture. The solar-thermal utilization is one of the most direct and straightforward approaches in which absorbed solar radiation is converted to heat for further use, such as power generation, water heating, solar stills, and so on. Hence, the absorption of solar light and the photothermal conversion process are the key issues associated with the solar-thermal method [1].

For traditional solar thermal collectors, the solar energy is absorbed by the black painted surface and converted into thermal energy. Then, the heat is transferred to the heat transfer fluid via thermal conduction and thermal convection. There would be inevitable thermal losses from the absorber to the environments due to the high temperature at the absorption surface. Therefore, a kind of volumetric solar energy harvesting technology was developed, which was called direct absorption solar collectors



(DASC). Usually, solar light absorption media is dispersed into the fluid in a DASC to realize direct solar absorption by working fluid. By using this method, the photo-thermal conversion is achieved in the fluid media and it achieves less thermal losses and high efficient solar energy collection.

The DASC was firstly proposed by Minardi and Chaung by using a black fluid (water with 3.0 g/L, India ink) to absorb the solar radiation. Recently, nanofluids (suspensions of nanoparticles) have attracted much attentions of scientists due to its unique thermophysical properties including high thermal conductivities [2], high thermal diffusivities [3] and high heat-transfer coefficients [4]. In 2009, Tyagi et al. [5] investigated theoretically the performance of a DASC containing an Al₂O₃-water nanofluid. Otanicar et al. [6] experimentally studied the effects of three kinds of nanofluid (carbon nanotubes, graphite and silver-based) in a direct solar absorption system. Wang et al. [7] experimentally investigated the solar-collection performance of single-wall carbon-nanotube-based nanofluids for direct and volumetric solar steam generation.

Carbon based nanomaterials have great advantages in the preparing of nanofluids for DASC due to their high light absorption properties. For instance, carbon nanotubes (CNT) have extremely high capability of absorbing solar spectrum and acceptable stability. One of the major problems for CNT nanofluids applications in DASC is the suspension instability. Due to the bad dispersity of CNT, a large amount of organic surfactant was required for the dispersing of CNT into water and the method is considered as a common but easy-handling, time-saving and cost-effective choice for mass production. However, it might reduce the other thermophysical properties of CNT nanofluid, such as rheological properties. Furthermore, the stability of CNT nanofluids under long time solar irradiation is underlying.

Graphite oxide sheet, now called graphene oxide (GO), is the product of chemical exfoliation of graphite and has been known for more than a century. GO has been known to disperse well in water since its first discovery over a century ago and thus has been routinely described as hydrophilic in the literature. GO's water dispersity and hydrophilicity have been mainly attributed to the ionizable edge-COOH groups. However, its basal plane is essentially a network of hydrophobic polyaromatic islands of unoxidized benzene rings. Therefore, GO should be viewed as an amphiphile with a largely hydrophobic basal plane and hydrophilic edges. Recently, it has been investigated as a new kind of colloidal surfactant. Since GO has many π -conjugated aromatic domains in its basal plane, it should be able to strongly interact with the surface of graphite and CNTs through π - π attractions [8]. In this work, a kind of GO stabilized CNT nanofluids was prepared and the photothermal performance of CNT/GO nanofluids was investigated under concentrated solar light. In addition, the effects of solar light intensities and mass concentrations of CNT in nanofluids were discussed. Moreover, the stability of CNT/GO nanofluid for a long time and after solar light irradiation was demonstrated.

2. Experimental section

2.1. Materials

Graphite powder, CNT powder, ammonia water, NaNO₃, KMnO₄, H₂SO₄, and H₂O₂ were supplied by Aladdin Chemical Co., Ltd.. Double-deionized water (DDI water, Sartorius Water Purification System, arium® mini; 18.2 M Ω) was used in these experiments. Graphene oxide (GO) was synthesized via a chemical exfoliation of the graphite powder by a modified Hummers method [9] as follows: 46 mL concentrated H₂SO₄ was slowly added into a mixture of 2 g graphite powder and 1 g NaNO₃ at 0 °C. Then, 6 g KMnO₄ was added with stirring while the temperature of the mixture was maintained below 20 °C using an ice bath. Afterward, the ice bath was removed, and the temperature of the mixture was raised to 35 °C and stirred for 30 min. Then, 92 mL deionized water was added to the mixture with stirring for 15 min, followed by the addition of 60 mL H₂O₂ solution at 60 °C. After the suspension turned brown, it was washed with deionized water and centrifuged for several times. Finally, the GO powder was obtained by freeze-drying method and kept for further use.

2.2. Preparation of nanofluids

A two-step method was used to prepare the GO stabilized CNT nanofluids. Firstly, the GO was dispersed into DDI water with a high concentration of 8 mg/mL and stored for the further use. Then CNT powder

was added in to the GO-water dispersion at a mass ration of 1:1 (CNT/GO). The initial concentration of CNT in the solution was 100 ppm (0.1 mg/L). Subsequently, the mixture of CNT/GO-water was sonicated by a high-power tip ultrasonic oscillator for 1 hour to make sure CNTs well dispersed in GO-water. After sonication, the supernatant was carefully collected after the sample aged for 1 day to remove undispersed chunks. The well dispersed supernatant was GO stabilized CNT nanofluids. Furthermore, the CNT/GO nanofluids were diluted for the photothermal collections.

2.3. Solar thermal conversion experiments

Figure 1 shows the experimental setup for direct solar energy collections. Solar light was generated by a solar simulator (CEL HXF300, CEAULIGHT, Beijing, China). The light was generated by a 300W Xenon lamp, which could realize the exportation of collimated light with high energy. The Xenon lamp is one of the most common types of lamp for continuous solar simulators. It offers high intensities and an unfiltered spectrum matching reasonably well to sunlight. An acrylic tube filled with working fluid was placed on the electric balance and was used as a solar collector. The temperature was measured and recorded using thermocouples (TT-T-40-SLE, Omega, US) and a data-acquisition system (34972A, Agilent Technology, Santa Clara, CA, US). Due to the open system of collectors, there were evaporations due to the high temperature of the nanofluids. Therefore, the mass loss due to the evaporation was also recorded to make a better evaluation of solar thermal collection performance of the prepared nanofluids. Mass change due to evaporation was measured using an electric balance (Practum313-1CN, Sartorius, Göttingen, Germany). The inner height and diameter of the solar collector were 60 mm and 35 mm, respectively. The size and weight of the designed solar collector tube could be matched with the size of the solar light simulator and weighing range of the electric balance in the experiments. Five T-type thermocouples were inserted into the solar collector at different heights ($H = 10, 20, 30, 40,$ and 50 mm).

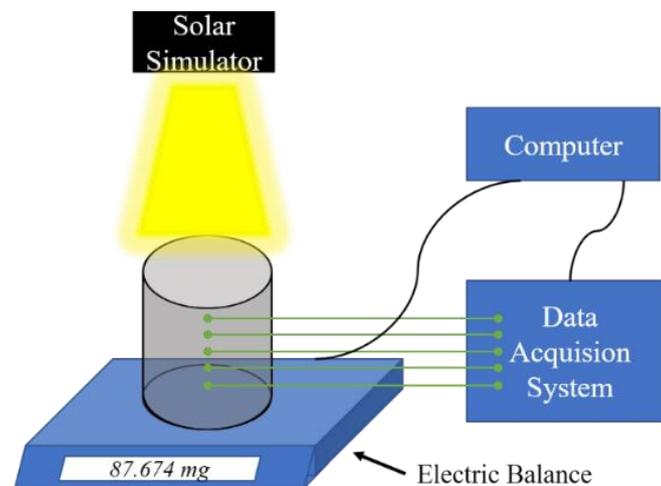


Figure 1. The diagram of experimental setup for direct solar energy.

To investigate the effect of solar illumination intensity, the solar collector was placed under different solar illumination intensities (1, 3, 5, and 7 sun, where 1 sun = 1 kW m^{-2}). The CNT/GO nanofluids with different concentrations (6.25, 12.5, 25, 50, and 100 ppm) were prepared to investigate the effect of CNT concentrations on the photothermal collection performance. Usually, the photo-thermal conversion efficiency η of water and the three nanofluids was calculated according to the following formula,

$$\eta = \frac{mc_p(T_s - T_i)}{IA\Delta t} \quad (1)$$

where m and C_p are the mass and specific heat of the nanofluids, T_i is the initial temperature, T_s is instantaneous temperature, A is the top surface area of the receiver, I is the heat flux of the incident light, and Δt is the time exposed to the light radiation. Considering the heat losses by the evaporation of the water, a modified photo-thermal conversion efficiency η model was proposed as follow,

$$\eta = \frac{(m_i - \Delta m)c_p(T_s - T_i) + \Delta mh}{I\Delta t} \quad (2)$$

where m_i is the initial mass of the nanofluids, Δm is the weight losses of the nanofluids due to evaporation, h is the latent heat of vaporization for water.

2.4. Characterization

The morphologies of the HP-Au particles were examined by field emission scanning electron microscopy (FESEM, SUPRA 55, ZEISS, Germany). High-power tip ultrasonoscope (Biosafer 900-92, 900W, Biosafer, Beijing, China) was used to disperse the GO and CNT into water for preparing nanofluids. Ultraviolet-visible (UV-Vis) spectras were recorded on a two-beam UV-Vis spectrometer (TU1901, China). During the UV-Vis spectra test, the fluids are placed in a quartz cuvette with optical length of 1 mm and the DDI water is used as blank reference. All samples were 4 times diluted for the UV-Vis spectra.

3. Results and discussion

A tremendous amount of efforts have been devoted to making CNTs water processable through wrapping by water-soluble materials. Since many surfactants for dispersing CNTs have polyaromatic components, GO should be able to adhere to CNTs and disperse them in water as well. The photograph and microstructures of the CNT/GO-water nanofluids and CNT dispersion was shown in Figure 2. The left vial in Figure 2a shows that CNTs indeed dispersed well in GO-water with a 1:1 mass ratio after sonication. While the CNT can not disperse in water alone, as shown in the right vial of Figure 2a. Microscopy analysis revealed that the initial CNTs samples were heavily entangled (Figure 2b), which remained largely unaffected by sonication in water (Figure 2c). In contrast, CNTs sonicated in GO water were completely disentangled. Extensive microscopy observations by SEM (Figure 2d) revealed that almost all the CNTs in the sample were adhered to GO (Figure 2d).

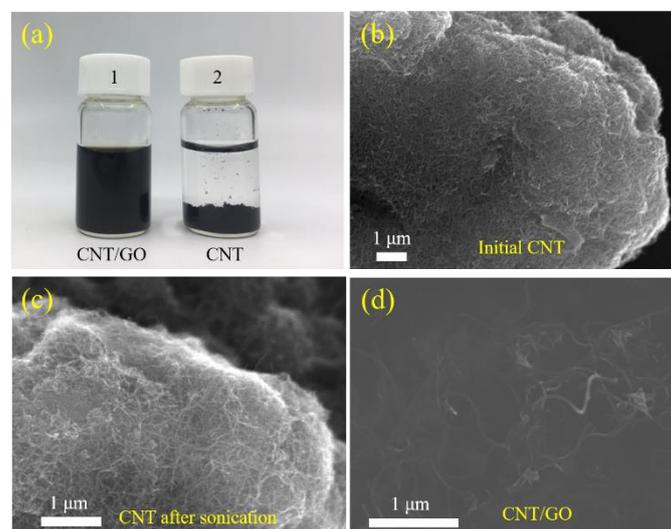


Figure 2. Dispersion of CNTs in GO-water: (a) photograph of CNT/GO dispersion and CNT dispersion. SEM images of (b) initial CNT, (c) CNT after sonication and (d) CNT dispersed in GO-water.

Furthermore, the stability of the CNT/GO nanofluids were monitored by its optical absorbance over a period of 10 hours (Figure 3), which remained nearly constant after sonication. Figure 3a shows the spectra of CNT/GO nanofluids for 10 hours and Figure 3b shows the changes of the values at the peak wavelength. The results demonstrated that CNT/GO nanofluids could keep good stability for a long time.

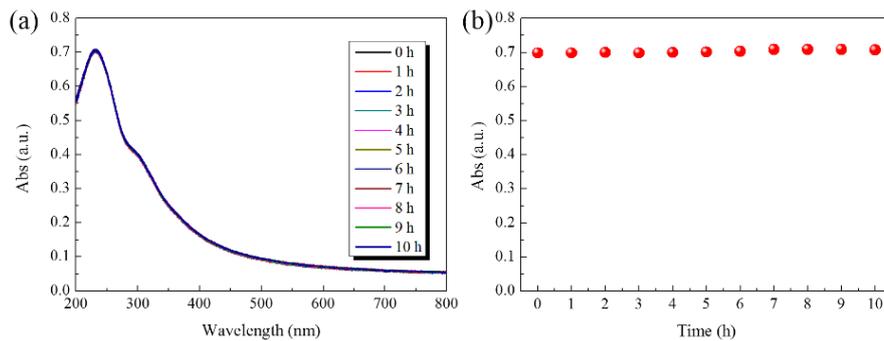


Figure 3. (a) UV-Vis spectra of CNT/GO nanofluids for 10 hours and (b) the variation of values at peak wavelength.

For the photothermal conversion test of CNT/GO nanofluids, the nanofluids with different concentrations were characterized under a solar light intensity of 7 suns ($1 \text{ sun} = 1 \text{ kW/m}^2$). Figure 4 shows the photothermal conversion performance of CNT/GO nanofluids. It can be seen from figure 4a that the mass losses due to evaporation increased as the mass concentration of CNT increased from 6.25 ppm to 100 ppm. For the concentrations above 12.5 ppm, the mass losses of water evaporation did not increase greatly. The mass losses were around 5 mg for the CNT/GO nanofluids with concentrations from 12.5 ppm to 100 ppm. The average temperatures of the bulk fluids increased as the solar light irradiation absorbed by nanofluids as show in Figure 4b. While the average temperatures of the bulk fluids decreased as the increase of CNT concentrations. It means that the nanofluids with low concentration make more contribution in sensible heat storage and the nanofluids with high concentration make more contribution in latent heat for evaporation. Furthermore, the photo-thermal conversion efficiency of CNT/GO nanofluids with different concentrations was calculated, as demonstrated in Figure 4c. The photo-thermal conversion efficiency of the nanofluids increased firstly and then decreased as the increasing of fluid temperature. The mass concentration of 12.5 ppm exhibited the best photo-thermal conversion performance and the efficiency could reach up to $\sim 90\%$ at the working temperature around 35°C . It is ascribed to the both relative high evaporation rate and average temperature increase for the CNT/GO nanofluids with concentration of 12.5 ppm.

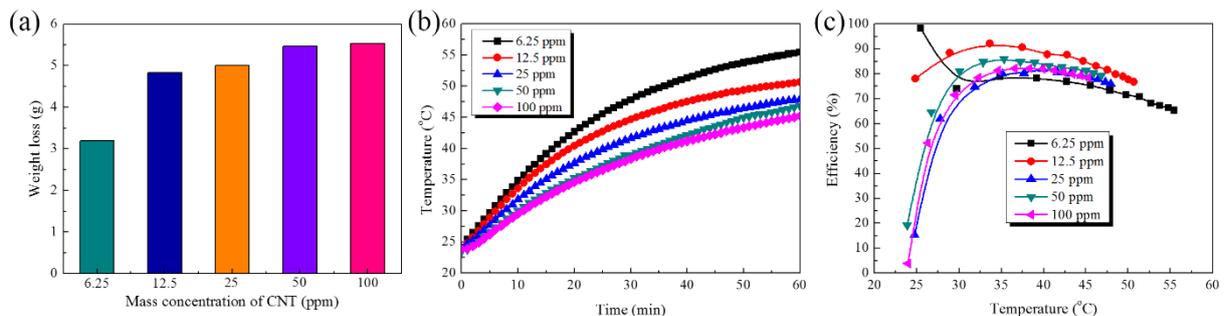


Figure 4. Solar thermal conversion performance of CNT/GO nanofluids with different concentrations: (a) weight losses Vs time, (b) average temperature Vs time, (c) photo-thermal conversion efficiency.

Eventually, the stability of the CNT/GO nanofluids before and after photothermal conversion experiments was investigated. The UV-Vis spectra of the CNT/GO nanofluids with different concentrations before and after solar light irradiation for 1 hour under 7sun is shown in Figure 5a. It can be seen that the absorption intensities slightly increased at low concentrations and increased obviously at high concentration after irradiation. In addition, the photographs of the sample before and after the solar light irradiation is shown in Figure 5b and 5c, respectively. The CNT/GO nanofluids still retained high dispersion rate and no sediment was observed. While the colour of the sample got darker after the solar irradiation, which could also be confirmed from the UV-Vis spectra in Figure 5a. The improved light absorption properties of CNT/GO nanofluids might be ascribe to the reduction of GO.

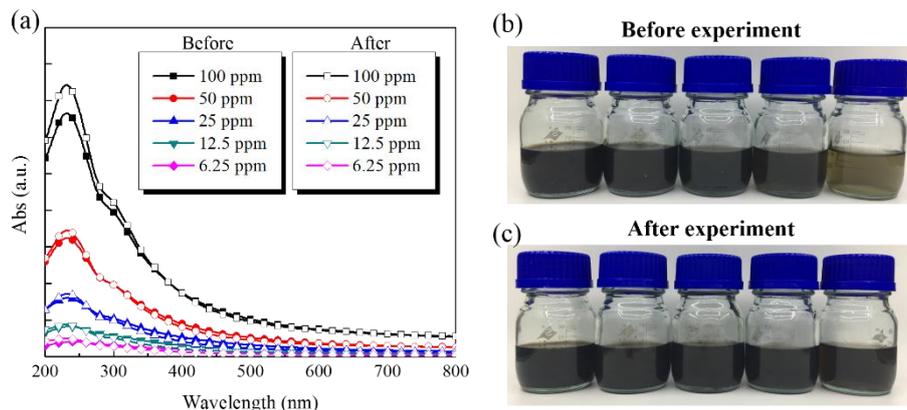


Figure 5. (a) UV-Vis spectra of CNT/GO nanofluids before and after the experiments, photographs of CNT/GO nanofluids (b) before and (c) after the experiments.

4. Conclusion

In a summary, small amount of graphene oxide (GO) was introduced to stabilize CNT-water nanofluids without using any other organic surfactants in this work. The results demonstrated that CNT/GO nanofluids could stable for over a long time. In addition, the CNT/GO nanofluids could retained high dispersivity even after a concentrated solar light irradiation (7 kw/m^2). The π - π interactions between the GO and CNT played a significant role for the good dispersion and stability of CNT in water. Eventually, the photothermal conversion properties of CNT/GO nanofluids in a DASC was characterized. The CNT/GO nanofluids exhibited excellent photothermal performance. The solar thermal collection efficiency could reach up to $\sim 80\%$. CNT/GO nanofluids is a promising alternative for the future solar thermal utilizations.

5. References

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