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Thermo-optical properties of partially unzipped multiwalled carbon nanotubes dispersed nanofluids for direct absorption solar thermal energy systems

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ABSTRACT

Solar thermal technology has gained importance during its globalization and industrialization, due to its effective conversion of solar energy into thermal energy. Common flat black surface solar collectors generally employ selective solid coating as a solar radiation absorber; nevertheless, these collectors have several shortcomings such as low efficiency, corrosion, heating losses and cannot withstand high incident flux. Theoretical and experimental studies have shown that the nanofluids based Direct Absorber Solar Collectors (DASC) can harvest solar energy more efficiently compared to the conventional solar collectors. Present work reports the investigation of dispersion stability, optical and thermal properties of partially unzipped multiwalled carbon nanotubes (PUMWNTs) based nanofluids for DASC. PUMWNTs were prepared by modified Hummers method. Nanofluids were prepared by dispersing calculated amount of PUMWNTs in DI water and ethylene glycol (EG). Absorption and transmittance studies were conducted using UV–vis-NIR spectrophotometer. Absorption spectra confirmed the stability of nanofluids. The extinction coefficient of nanofluids shows significant improvement as compared with that of base fluids even at low concentration. Furthermore, the temperature dependent thermal conductivity study with different volume fractions carried out for DI water and EG based nanofluids reported considerable enhancement of 27% and 20.97% respectively. Based on enhanced optical and thermal properties, PUMWNTs dispersed nanofluids are found to be promising to increase the overall efficiency of DASC.

1. Introduction

Global energy consumption is estimated to increase in the present era at least by 2-fold relative to the midcentury because of population and economic growth [1]. The use of fossil fuels as the energy resources can fulfill this demand. However, the increased intake of fossil fuels is responsible for rising atmospheric carbon dioxide level, resulting in a large number of adverse environmental changes. Consequently, the cumulative nature of carbon dioxide emission in the atmosphere necessitates that maintaining atmospheric anthropogenic carbon dioxide levels to even twice their pre-industrial values requires further research, development and implementation of technologies with carbon-neutral energy production. Solar energy, the most abundant exploitable renewable resource of energy, can effectively supplement global energy demand when used efficiently. However, the major constraint to the use of solar energy is poor collection and low conversion efficiency of solar systems. Solar thermal technology captures incident solar radiations by solar collectors and converts it into thermal energy for a wide range of applications. Therefore, it can be the most promising alternative for fossil fuel power stations. Today, most of the solar collectors employ absorber surfaces to convert incident solar radiations into thermal energy. Although, these conventional absorbers are capable of converting the incident solar radiations to thermal energy, they are inefficient in transferring thermal energy to the working fluid.

Minardi and Chuang (1975) studied the performance of flat-plate solar collectors (FSC) using black liquid as solar absorber and proved that the use of black liquid in FSC increases the collector efficiency [2]. Hunt (1978) suggested the use of small particles with high surface area to volume ratio in suspension in solar collectors [3]. According to Hunt, when the size of particle is smaller than the characteristic absorption length of incident light, the entire volume of the particle absorbs light effectively thereby achieving the equivalent amount of solar absorption with less material. Recently, researchers have proposed the use of nanofluids in direct absorption solar collectors (DASC) to increase the

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efficiency of solar collectors. Tyagi et al. [4] numerically studied the effect of aluminum nanoparticles dispersed in water on the performance of direct absorption solar collector (DASC) [4]. They reported 10% higher enhancement in DASC efficiency using nanofluid compared to FSC. Otanicar et al. (2009) studied the optical properties of water, ethylene glycol, propylene glycol and therminol VP-1 and concluded that the water absorbs more incident light compared to other liquids [5]. Although water is a good absorber, it absorbs only 13% of incident solar energy. Thus, in order to improve the collector efficiency, researchers studied metal nanoparticles [5–9], metal oxide nanoparticles [10–12], graphite [6–8], and carbon nanostructures (CNS) such as carbon nanotubes (CNTs) [13–15], carbon nanohorns [16–19], hybrid carbon nanocomposite [20] and carbon-coated metal nanoparticles [21] dispersed nanofluids.

CNTs have wide-band absorption in the far-ultraviolet to far-infra-red spectrum and they act like a perfect black body [22,23]. Moreover, 1-D CNTs exhibit large surface area to volume ratio, high thermal conductivity ($\sim$6000 W/m K) [24], and low density. Hence, CNTs based nanofluids are most suitable in the application of DASC. Although CNTs based nanofluids are efficient towards the conversion of solar to thermal energy, as-grown CNTs are hydrophobic in nature and cannot be dispersed in polar solvent without surfactant. The use of surfactant changes the physical properties of base fluids. Functionalization of CNTs imparts the hydrophilic nature and helps in uniform dispersion. However, functionalization of CNTs results in agglomeration and thus affects the stability in nanofluids. The hybrid composite of 1D CNT and 2D graphene nanoribbons is predicted to have enhanced solar absorption and heat transfer properties due to prevention of agglomeration [20]. Hybrid composite is advantageous for enhancing heat transfer properties due to the intrinsic high thermal conductivity of both 1D CNTs and 2D graphene nanoribbons. Researchers have reported the multistep synthesis for such hybrid composite [25–27] is not feasible for large scale synthesis.

The present work reports the preparation of partially unzipped multiwalled carbon nanotubes (PUMWNTs) dispersed stable nanofluids. A simple modified Hummers method is used for unraveling the outer few layers of multiwalled carbon nanotubes (MWNTs) without affecting the inner core walls. This gives the hybrid composite consisting of inner 1-D MWNTs associated with 2-D graphene nanoribbons obtained due to unzipping of outer layers in MWNTs. Furthermore, during the process of unzipping, functional groups are attached over the outer walls of PUMWNTs, thus escaping the process of separate functionalization. Thermal and optical properties of PUMWNTs dispersed nanofluids are discussed in the present paper. To the best of author's knowledge, this is the first report on unique optical and thermal properties of PUMWNTs dispersed nanofluids and its application for DASC.

2. Experimental details

MWNTs were synthesized by decomposing Acetylene gas over the $MmNi_3$ catalyst in a tubular furnace. Initially, $MmNi_3$ alloy was prepared by arc melting the specific elements in a stoichiometric ratio in an inert atmosphere. The $MmNi_3$ ingot was then subjected to hydrogen decrepitation technique to obtain a fine powder with fresh surface resulted in the improving the catalytic activity for the growth of MWNTs. After that, fine powder of catalyst was directly placed in quartz boat and kept in single furnace CVD unit. Argon gas (160 sccm) was flushed for 10 min to create inert atmosphere at room temperature. Temperature of the furnace was raised to 500 °C and Hydrogen gas (50 sccm) was allowed to remove all oxygen containing functional groups from the surface of the catalyst. After 45 min, Hydrogen gas flow was stopped and furnace temperature was raised to 700 °C. At 700 °C Acetylene gas (50 sccm) was introduced into the furnace. The decomposition of Acetylene gas was carried out for 30 min after which the flow of Acetylene gas was stopped. The furnace was allowed to cool to room temperature. Argon flow was continued throughout the experiment. As-grown MWNTs contain amorphous carbon and catalytic impurities. Air oxidation at 450 °C was carried out to remove the amorphous carbon. Further, it was refluxed in conc. HNO_3 for 24 h at 60 °C to remove catalytic impurities [28].

Modified Hummers method was used to obtain PUMWNTs from purified MWNTs [29]. In brief, 500 mg of MWNTs was stirred in conc. H_2SO_4 for 5 min at ice temperature. $NaNO_3$ (250 mg) was added very slowly to the above mixture, followed by $KMNO_4$ (750 mg). The beaker was taken out from ice bath and the mixture was stirred for 1 h at room temperature. Warm water (50 °C) was added very slowly to the reaction mixture, followed by the addition of Hydrogen peroxide. $KMNO_4$ and $NaNO_3$ are responsible for the attachment of functional groups (–C=O, –COOH) at the surface which result in the opening of the outer layer in MWNTs [30]. The functional groups attached over the surface and edges make PUMWNTs hydrophilic allowing for a uniform and stable dispersion when dispersed in DI water and EG.

Nanofluids were synthesized by dispersing calculated amount of PUMWNTs in the base fluids DI water and EG with the varying concentration without surfactant. For achieving uniform dispersion, nanofluids were ultrasonicated for 20 min using a bath sonicator having frequency 40 kHz. No settlement was observed after two weeks of preparation of nanofluids, which indicates the suspension is stable.

The structural changes occurring in MWNTs after unzipping were determined by PANalytical X'pert Pro powder X-ray diffractometer using Cu-Kα radiation (λ=0.154 nm) source. Surface morphology changes in MWNTs taking place during the synthesis were investigated by scanning electron microscopy (SEM, Hitachi S4800). Transmission electron microscopy (TEM, Philips CM20, 200 KV) was used to confirm the partial unzipping of MWNTs. Thermogravimetric analysis of samples was carried out using TA instrument (SDT Q600). BET surface area analysis was carried using Micromeritic ASAP 2020 V4.01 H. A Perklin Elmer FTIR spectrometer was used to record FTIR spectrum of samples. Leica DM-IL-LED phase contrast microscope was used to take optical images of nanofluids. UV–vis-NIR spectroscopic studies were carried out using JASCO V-570 spectrophotometer. Thermal conductivity of nanofluids was measured by using TPS2500S Hot Disk Thermal Analyzer. The detailed analysis about the thermal conductivity measurement by TPS2500S Hot Disk Thermal Analyzer is already reported in our previous paper and literature [20,31].

3. Results and discussion

3.1. XRD

Sample formation was first studied by powder XRD (PANalytical X'Pert Pro) at room temperature. Fig. 1 shows the powder XRD pattern of MWNTs and PUMWNTs. MWNTs shows an intense peak at $\sim$26° corresponding to C (002) hexagonal plane of graphite with interlayer spacing of 0.34 nm (JCPDS No. 12-0212). This intense peak confirms the long-range order and crystallinity in MWNTs. In the XRD pattern of PUMWNTs a small signal is observed at $\sim$13°, corresponding to interlayer spacing of 0.6 nm. The increase in d spacing is due to inclusion of functional groups in between the unzipped outer layers of PUMWNTs. An intense peak at $\sim$26° corresponds to the C (002) plane with a d-spacing of 0.34 nm. This intense peak is due to the intact inner core of MWNTs, which did not exfoliate during the oxidation process.