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Potential of carbon nanohorn-based suspensions for solar thermal collectors

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ABSTRACT

The optical characterization is reported of a new fluid consisting of single-wall carbon nanohorns and ethylene glycol for solar energy applications. Carbon nanohorns play a significant role in enhancing sunlight absorption with respect to the pure base fluid. The obtained results are compared with those obtained for fluids suspending more conventional carbon forms, i.e. carbon-black particles. We found that nanohorn spectral features are far more favorable than those of amorphous carbon for the specific application. This result shows that carbon nanohorn-based nanofluids can be useful for increasing the efficiency and compactness of thermal solar devices, reducing both environmental impact and costs.

1. Introduction

Renewable energies are gaining an increasing role in world economy because they are sustainable and safe. However, due to the expected future increased world energy demand, with a corresponding decline in oil production and a larger attention paid to global problems like climate change and pollution, renewable energies are expected to grow at an even higher rate. Therefore there is a large effort in raising their efficiency and in developing novel solutions to decrease the cost-per-watt of produced power.

The interest in so-called "nanofluids" (a conventional name indicating fluids with suspended nanometer-sized particles) has increased in the last years, due to the fact that their properties result advantageous with respect to those of the base fluid. In particular, among the physical properties, those which usually are evaluated in view of practical applications are thermal conductivity [1–7] and pool boiling heat transfer [8–10]. However, as nanofluids appear promising for thermal solar energy applications, the investigation of their optical properties allowing to assess their potential as direct sunlight absorbers should be carried out. Fluids containing black particles have already been studied in the past for applications in solar thermal collectors, because the use of a black fluid working both as light absorber and heat exchanger [11–14] is advantageous over the classical solution of a transparent fluid exchanging heat with a solid absorber (typically, a black-painted or oxidized surface in tight thermal contact with the tubes) [15]. Conventional black liquids are based on organic inks or Indian ink, but they show serious drawbacks because of light-induced degradation, thermal degradation at the operating temperatures, instability of solutions during time and fouling of inks on the internal side of exposed surfaces.

As for the particles to be used in nanofluids, single-wall carbon nanohorns (SWCNHs) [16] consist of single layers of a graphene sheet wrapped into an irregular tubule with a variable diameter of 2–5 nm and a length of 30–50 nm. The tips of the nanohorns are cone-shaped with an average angle of about 20° [16–19], corresponding to five pentagonal carbon rings at the tip of the tubule. The SWCNHs typically assemble to form roughly spherical aggregates with diameters of about 100–120 nm [19]. They exhibit both large surface area and large number of cavities [20] and therefore appear promising for a variety of applications [21–23].

When the differences between SWCNHs and carbon nanotubes are concerned, the minimum van der Waals interactions between the superstructures of SWCNH aggregates gives rise to a better dispersion of SWCNHs in liquid media [24] and a much longer time stability of their suspensions. Moreover, a very important property in view of their practical use with respect to carbon nanotubes arises from the metal-free structure of nanohorns that makes their cytotoxicity negligible, as it has been widely confirmed by experiments on mice and rats [25]. This makes SWCNHs very appealing for applications requiring nanofluid handling and in all cases where even accidental leakages into the environment are possible.

A recent preliminary work [26] discusses optical characterization studies on aqueous suspensions of SWCNHs in view of their possible use as direct sunlight absorber. However, in solar thermal collectors, water is often replaced by glycols or water/glycol mixtures, to protect

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against freeze damage and/or to increase the temperature for high temperature solar collectors.

This paper presents the comparative characterization of SWCNH and carbon-black-ethylene glycol suspensions in terms of dispersion stability and optical properties, in the perspective to evaluate their potential as a direct absorber fluid in a sunlight collecting device. We measured the SWCNH and carbon-black particles mean diameter in ethylene glycol and the dispersion stability for different particle concentrations. The light absorbing capability of the nanofluid was evaluated from the measured spectrally-resolved optical spectra. We found that SWCNHs show significantly more favorable spectral features with respect to the investigated amorphous carbon, combined with a longer time stability of the suspension and a lower ability of SWCNH than carbon-black powders to agglomerate. This demonstrates the real potential of SWCNH as innovative heat transfer fluids for solar applications. In addition, showed data provide useful information for collector and absorber design and for system integration and optimization.

2. SWCNH and nanofluid preparation

Information on the SWCNH preparation is given in detail elsewhere [27] SWCNHs were kindly supplied by Carbonium Srl-Italy and prepared by a method, based on heating of graphite rods by induction of very intense, high frequency, eddy currents, specifically tailored for mass production. A very intense specific energy supply (~60 kJ/g) was necessary to produce carbon nanostructures from the graphite solid precursors in order to obtain its vaporization/atomization. SWCNHs were then dispersed with concentrations varying from 0.005–0.12 g/l in ethylene glycol (Aldrich, ≥99%) and were prepared using the following procedure: the SWCNHs were mechanically dispersed in ethylene glycol and then a high pressure homogenizer (up to 1000 bar) was employed to optimize the dispersion. With this procedure, long term stability was assured to the dispersions, since no particle settling was detected along 6 months. The morphological characterization was performed by field emission scanning electron microscopy (FE-SEM) with a SIGMA Zeiss instrument (Carl Zeiss SMT Ltd., UK). Fig. 1 reports an example of a SEM micrograph for a dispersion of SWCNHs in glycol, dried for SEM analyses (a) and the comparative photographs showing the suspensions containing 0.005 g/l (b) and 0.12 g/l (c) of SWCNHs. We emphasize that the photos in Fig. 1(b) and (c) have been taken 6 months after the preparation of samples and without any mixing procedure in such a time. They evidence no visual nanoparticle settling or clustering occurring in the still glycol for a time as long as 6 months, even at the highest considered concentration.

The quantitative analysis on SWCNH size distribution in glycol suspensions, to investigate the possible presence of unwanted settling and clustering phenomena, was carried out using a Zetasizer Nano (Malvern). The Zetasizer works measuring the Brownian motion of particles in the sample by means of dynamic light scattering (DLS) and then calculating the size from this, according to the theory [28]. The main components of this instrument are a laser, which illuminates the sample particles within the sample cell, and a detector to acquire the intensity of the scattered light. The measured particle size is represented by the diameter of the sphere that diffuses at the same speed as the particle under investigation. Fig. 2 shows an example of the particle size distribution obtained from the Zetasizer measurements, for the glycol-SWCNH dispersions at three SWCNH concentrations, measured 6 months after the preparation. The absence of particle micrometer-sized aggregates confirmed the good stability of the obtained dispersions, indicating that even after 6 months of settling time no precipitation of aggregates was detected. The mean particle diameter, measured 3 times for each sample, was 104 ± 3 nm for the 0.005 g/l solution, 100 ± 3 nm for 0.01 g/l and 90 ± 3 nm for 0.05 g/l. The nanofluid stability under thermal cycling at high temperature was investigated performing a series of 5 cycles of quick heating and quick cooling in a sealed vessel at high pressure. During each cycle, the fluid was maintained at high temperature for an hour. We found that SWCNH-glycol suspensions were stable up to 150 °C, with only weak aggregation phenomena at higher temperatures.

For a more meaningful characterization of SWCNH suspensions, we also prepared three suspensions of amorphous carbon (Thermax Cancarb N99) in glycol. Carbon-black suspensions (labeled as CB) were prepared by the same procedure employed for the SWCNH suspensions. Size distributions of CB samples are

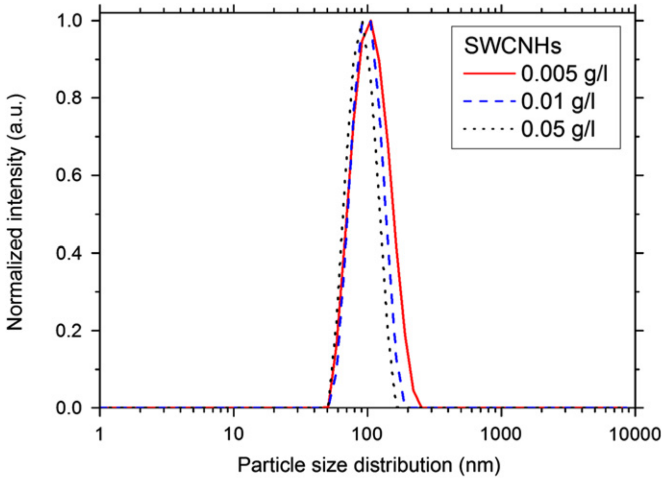

Fig. 2. Particle size distribution for glycol-SWCNH dispersions at three SWCNH concentrations, measured 6 months after the preparation.

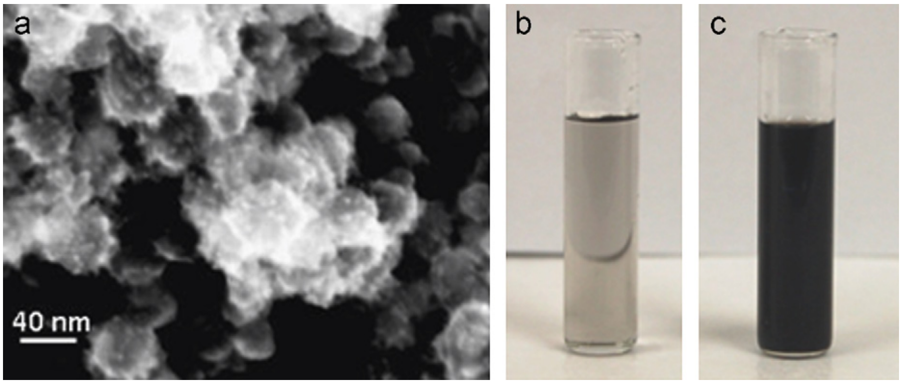

Fig. 1. (a) SEM micrograph of a dried dispersion of SWCNH in glycol; comparative photographs showing the suspensions containing 0.005 g/l (b) and 0.12 g/l (c) of SWCNHs.