Scattering and absorption properties of carbon nanohorn-based nanofluids for solar energy applications

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In this work we investigated the scattering and absorption properties of nanofluids consisting in aqueous suspensions of single wall carbon nanohorns. The characteristics of these nanofluids were evaluated in order to use them as direct sunlight absorber fluids in solar devices. The investigation was carried our for nanohorns of different morphologies and for suspensions prepared with different amounts of surfactant. The differences in optical properties induced by carbon nanoparticles compared to those of pure water lead to a considerably higher sunlight absorption with respect to the pure base fluid. Scattered light over the total attenuation of light was found to be nearly negligible at NIR wavelengths. Both these effects, together with the possible chemical functionalization of carbon nanohorns, make this new kind of nanofluids very interesting for increasing the overall efficiency of the sunlight exploiting device. [DOI: 10.2971/jeos.2011.11025]

Keywords: Carbon nanohorns, Solar Energy, Optical Scattering, Nanofluid

1 Introduction

Solar thermal collectors are heat exchangers that transform solar radiation energy to internal energy of the transport medium. Typical solar collectors use a black-surface absorber to collect solar energy [1] but this configuration entails various limitations like for example, a limited contact between absorber and fluid, with resulting non-optimal thermal energy transfer. Among the alternative concepts that have been evaluated, the use of black liquids as both solar radiation absorbers and heat transfer media has been studied [2]. It should be noticed that the efficiency enhancement in sunlight exploiting devices is a key point to decrease the cost-per-watt of generated power. Usually, black liquids are ink-based fluids containing various organic compounds and inorganic particles, but they show serious drawbacks because of their light-induced degradation and thermal degradation at the high operating temperatures. A recent development in solar thermal collectors is the use of nanofluids (i.e. fluids with suspended nanometer-sized particles) to directly absorb the light. Among the different materials that have been studied in nanofluids, carbon nanotubes appear very promising [3, 4]. However, the optical properties of the nanofluids (light extinction, light absorption, fluorescence), in general depend on the shape, size, refractive index and other optical properties of the particles, besides the properties of the fluid [5]. Therefore the characterization of fundamental optical properties of considered nanoparticles and/or nanofluids is absolutely mandatory as it is the necessary basis for any subsequent application exploiting optical properties themselves. Recently, we studied nanohorns-based aqueous suspensions in the perspective to use them as direct sunlight absorber in solar thermal collectors [6], obtaining very promising results. To assess the fundamental optical properties of single wall carbon nanohorns (SWCNHs), and in particular the relative weight of light scattering over the whole light extinction phenomenon, in this work we measured the scattering and absorption coefficients of three different SWCNH suspensions. The investigated nanofluids were prepared with dahlia and bud morphologies and with different amount of surfactant in order to understand whether the aggregation state of the nanoparticles leads to a different optical behavior.

2 Materials and Methods

SWCNHs were produced with a patented method by Carbonium Srl [7]: the method demonstrated excellent capability and, differently from other commonly used, could be easily scaled up for massive production [8]. The producer is able to differentiate the method in order to obtain different SWCNH morphologies (dahlia-like, bud-like and seeds-like). The use of some amount of dispersant was necessary to avoid

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SWCNH aggregation, and the sodium n-dodecyl sulfate (SDS, 99%, Alfa Aesar) was demonstrated to be the best dispersant for this kind of carbon nanostructure [9]. Three SWCNH suspensions were prepared, with a concentration of 0.3g/l of dahlia and bud-like nanohorns and two concentration of SDS (1.2 and 1.8 g/l), resulting in the following three investigated suspensions: dahlia+SDS 1.2g/l (D1), dahlia+SDS 1.8g/l (D2) and bud+SDS 1.8g/l (B).

The Lambert-Beer law gives the relationship for the light extinction after a path length r within a generic turbid medium:

$$\frac{I(r)}{I_0} = e^{-\varepsilon_{ext}\cdot\rho\cdot r} \tag{1}$$

where I_0 is the intensity of the input light, I(r) is the light intensity measured after the distance r and $\varepsilon_{ext}\rho$ is the extinction coefficient of the medium. In fact, if a given scattering/absorption suspension with extinction coefficient ε_{ext} is diluted in a medium (e.g. in water), the resulting suspension has an extinction coefficient $\mu_{ext} = \varepsilon_{ext}\rho$, where ρ is the concentration of the absorbing/scattering medium within the resulting medium. Thus in the following we will label in general, the scattering (or absorption) coefficient of a medium obtained from a dilution of a given suspension as μ, the respective scattering (or absorption) coefficient of the non-diluted suspension as ε and the concentration of the absorbing/scattering suspension within the resulting suspension as ρ. Therefore, the following general relationship applies: $\mu = \varepsilon \cdot \rho$.

The measurement of the ballistic radiation I(R,ρ) transmitted through a suspension inside a calibrated cell of length R as a function of the increasing concentration ρ of the absorbing/scattering medium allows to easily calculate the extinction coefficient. In fact Eq.1, once natural logarithm is applied on both sides, is a linear relation between ballistic intensity and concentration: the slope divided by the cell length is equal to ε_{ext}. As for the relationships between relevant quantities, we mention that the extinction coefficient is given by the sum of scattering and absorption coefficients. Another important quantity is the scattering albedo, that expresses the relative contribution of scattering to extinction. Relevant definitions and relationships as summarized in Table 1.

It is clear that the unique measurement of the extinction coefficient is not sufficient to uncouple scattering and absorption coefficients. The experimental measurement that leads to the separation of the two coefficients needs further definitions and the use of the diffusion equation: theory and details can be found elsewhere [10] and in this paper we will summarize only few aspects. The fluence rate Φ in an homogeneous and infinite diffusing medium at a specific distance r from a point-like CW source emitting an unit power is a function of three parameters: the distance, the effective attenuation coefficient $\mu_{eff} = (3\mu_a\mu_s')^{1/2}$ (with μ_a absorption coefficient) and the reduced scattering coefficient of the medium (this latter is defined by the relationship $\mu_s' = \mu_s(1-g)$ with g anisotropy factor of the scattering function [10]). A linear relationship between fluence rate and distance can be obtained from the expression of the fluence rate after applying the natural logarithm on both sides:

$$ln[\Phi(r)\cdot r] = -\mu_{eff}r + ln\frac{3\mu_s'}{4\pi} \tag{2}$$

Therefore, by means of multidistance fluence measurements, it is possible to obtain, with a linear fitting, the effective attenuation coefficient μ_{eff} as the slope of the relationship in Eq. 2.

A single multidistance measurement is clearly not sufficient to obtain both μ_a and μ_s' which are connected each other within the expression of μ_{eff}. To assess the values of both scattering and absorption coefficients it is necessary to repeat the measurement by changing only one of them in a controlled way, while the other remains constant. The approach we used to uncouple the two coefficients is, once again, increasing the concentration of the absorber (thus the absorption coefficient) in a calibrated diffusing medium (with high scattering and low absorption) once the scattering coefficient is maintained fixed. A suspension with a previously calibrated diffusive medium having both high scattering and small absorption, in our case Intralipid-20% (Fresnius Kabi, Uppsala, Sweden) was prepared. Then its properties were modified introducing very small quantities of SWCNH suspension that do not significantly modify the scattering properties of the resulting fluid. In fact, as nanofluid additions are lower than 0.1% vol. and the scattering coefficient of the calibrated Intralipid suspension is high (1.6 mm^{-1}), the increasing of the scattering coefficient of the resulting medium would be negligible ($<$ 1%) even if, instead of SWCNHs, the same amount of high-scattering Intralipid would be added. For each SWCNH addition, a multidistance measurement was performed and the μ_{eff} coefficient was calculated for each increased absorption.

When a known quantity of absorber is introduced in the calibrated suspension, the expression of effective attenuation coefficient as a function of the added concentration of SWCNH suspension becomes [11]:

$$\mu_{eff}^2(\rho) = 3(\mu_{a0} + \varepsilon_a\rho)\mu_{s0}' = 3\mu_{a0}\mu_{s0}' + 3\varepsilon_a\rho\mu_{s0}' \tag{3}$$

where μ_{a0} and μ_{s0}' are the calibrated absorption and reduced scattering coefficient of the Intralipid suspension, ε_a is the absorption coefficient of the original suspension of SWCNHs, before to dilute it for the present measurement and ρ the concentration of the added absorber, calculated with respect to the whole medium. Eq. 3 is a linear relationship between μ_{eff}^2 and ρ. It allows to obtain the absorption coefficient ε_a as the slope divided by $3\mu_{s0}'$. Once the absorption coefficient ε_a is determined, and the extinction coefficient ε_{ext} is independently determined as explained above (Eq. 1), the scattering coefficient and the scattering albedo of the non-diluted suspension can be calculated.

In order to assess the wavelength dependence of absorption and scattering coefficients in the vis-NIR, the fluence rate and transmittance measurements were repeated for three wave-

Definition	Symbol	Formula
Extinction coefficient of a given suspension	ε_{ext}	$\varepsilon_{ext} = \varepsilon_a + \varepsilon_s$
Scattering coefficient of a given suspension	ε_s	
Absorption coefficient of a given suspension	ε_a	
Extinction coefficient of a diluted suspension	μ_{ext}	$\mu_{ext} = \varepsilon_{ext}\rho = \mu_a + \mu_s$
Scattering coefficient of a diluted suspension	μ_s	$\mu_s = \varepsilon_s\rho$
Absorption coefficient of a diluted suspension	μ_a	$\mu_a = \varepsilon_a\rho$
Scattering albedo	ω	$\omega = \frac{\mu_s}{\mu_{ext}} = \frac{\varepsilon_s}{\varepsilon_{ext}}$
Anisotropy factor	g (ref [10])	
Reduced scattering coefficient of a diluted suspension	μ_s'	$\mu_s' = \mu_s'(1-g)$
Effective attenuation coefficient of a diluted suspension	μ_{eff}	$\mu_{eff} = (3\mu_a\mu_s')^{1/2}$

TABLE 1 Relevant names, symbols and definitions

lengths using alternatively a HeNe laser (632.8 nm) and two laser diodes (751 and 833 nm).

The setup for transmittance measurement is composed by a cell of calibrated length (Hellma, 34.51 mm) and by a chopped laser. The ballistic laser radiation transmitted through the cell is acquired using a photodiode and processed by lock-in standard techniques.

The experimental setup for fluence rate measurements in the infinite medium (i.e. a medium for which light reflections at the boundaries do not significantly affect the measurements) is composed by the chopped laser whose radiation is introduced in the medium (a large becker with nearly 3 l of solution) using an optical fiber with an end that radiates isotropically and a receiver optical fiber, identical to emitter one, mounted on a computer-controlled translation stage [11] which performs measurements for distances in the range 5-40 mm from the emitting fiber. The signal received by a photomultiplier coupled to the receiver fiber is acquired by a lock-in amplifier. The scheme of the experimental setup is shown in Figure 1.

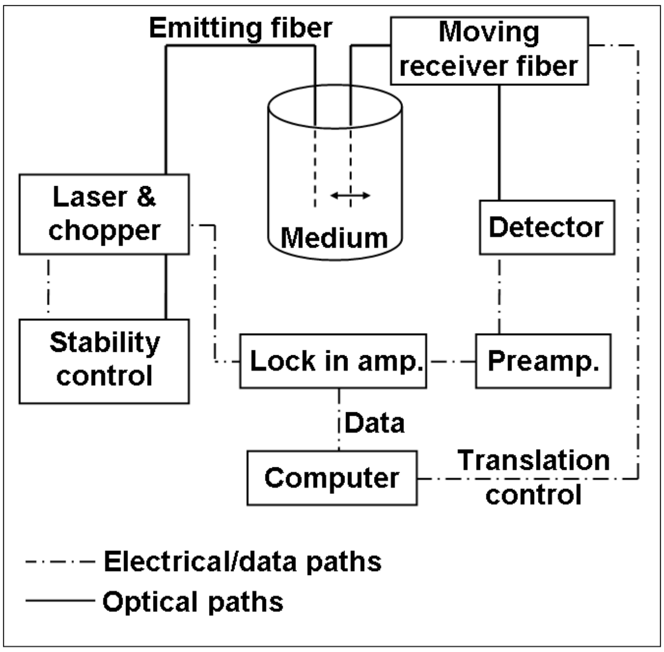

FIG. 1 Scheme of the experimental setup for fluence rate measurements in the infinite medium.

3 Results and Discussion

Transmittance measurements were repeated, for each wavelength and each suspension, for increasing SWCNH concentrations. The numeric value of ε_{eff} is given by the slope of the line that best fits the result, once divided by the cell length. Analogously, multidistance fluence rate measurements were repeated, for each wavelength and each suspension, for increasing SWCNH concentrations. This provided several values of μ_{eff}, as the slopes of the lines that best fit the measurements according to Eq. 2 (Figure 2).

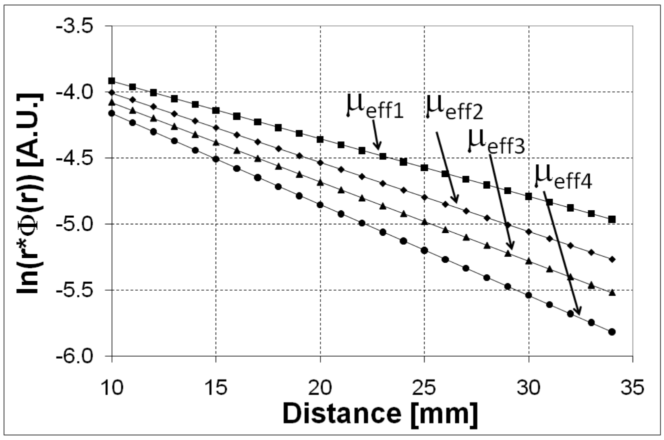

FIG. 2 Fluence rate measurements at different distances source-receiver as a function of increasing concentration of SWNHs in the medium (λ=632.8 nm, suspension D1). Effective coefficients are achieved as the slopes of the best fit lines.

The experimental values of the quadratic effective attenuation coefficient as a function of the SWCNH concentration is depicted in Figure 3: the absorption coefficient ε_a was calculated from the slope of the straight line that best fits the experimental results.

The results are summarized in Table 2 where extinction, scattering and absorption coefficients are reported together with the scattering albedo values. The amount of extinction is almost totally due to absorption. In fact extinction and absorption coefficients are very similar and scattering albedo is lower than 5%: therefore the part of scattered light is less than 5% of total extinct light. In some cases the amount of scattered light was even lower than the system sensitivity (the cases in Table 2 where the calculated values are negative) and could not be determined. The part of scattered light decreases with increasing wavelength and is negligible for NIR wavelengths (833 nm) while no differences were noticed among

D1

	$\varepsilon_{ext}[mm^{-1}g/l]$	$\varepsilon_a[mm^{-1}g/l]$	$\varepsilon'_s[mm^{-1}g/l]$	$\omega(\varepsilon'_s/\varepsilon_{ext})$
λ = 633nm	10.63	10.39	0.24	0.022
λ = 751nm	10.15	10.00	0.15	0.014
λ = 833nm	9.71	9.52	0.19	0.019

D2

	$\varepsilon_{ext}[mm^{-1}g/l]$	$\varepsilon_a[mm^{-1}g/l]$	$\varepsilon'_s[mm^{-1}g/l]$	$\omega(\varepsilon'_s/\varepsilon_{ext})$
λ = 633nm	11.59	11.07	0.52	0.045
λ = 751nm	10.54	10.53	0.01	0.001
λ = 833nm	9.98	10.06	negative	negative

B

	$\varepsilon_{ext}[mm^{-1}g/l]$	$\varepsilon_a[mm^{-1}g/l]$	$\varepsilon'_s[mm^{-1}g/l]$	$\omega(\varepsilon'_s/\varepsilon_{ext})$
λ = 633nm	10.70	10.38	0.32	0.029
λ = 751nm	9.68	9.65	0.03	0.003
λ = 833nm	9.03	9.14	negative	negative

TABLE 2 Extinction, absorption and scattering coefficient at different wavelengths for non-diluted suspension of 0.3g/l of SWCNHs. D1: dahlia+SDS 1.2g/l, D2: dahlia+SDS 1.8g/l, B: bud+SDS 1.8g/l. The scattering albedo is reported. Negative values mean that they lie under the system sensitivity

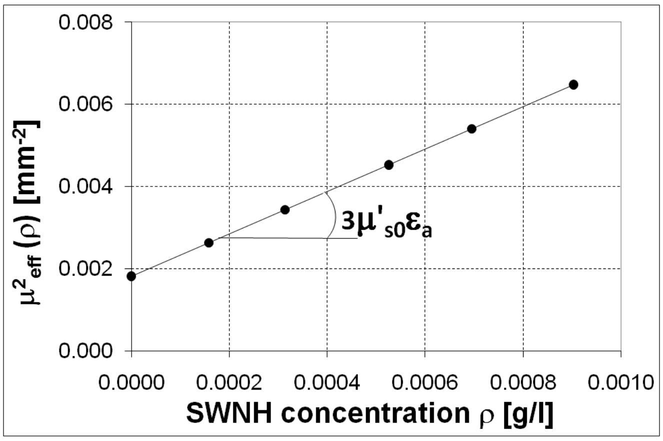

FIG. 3 Quadratic effective coefficient as a function of increasing concentration of SWCNHs (λ=632.8 nm, suspension D1). Absorption coefficient is calculated from the slope of the best fit line.

the differently-shaped SWCNH suspensions and for different concentration of dispersant.

4 Conclusions

This paper reports on the first measurements of extinction and absorption coefficients on Single Wall Carbon Nanohorn (SWCNH) suspensions as a function of the nanoparticle morphology (dahlia and bud) and with different amounts of dispersant. Scattering coefficient and scattering albedo were measured for three different wavelengths and for three different SWCNH suspensions. The obtained values of the scattering albedo were always lower than 0.05, indicating that the portion of light scattered by SWCNH suspensions was smaller than 5%. This means that an amount of light as high as 95% was directly absorbed. Moreover, we evidenced that the values of scattering albedo decreased with increasing wavelength, and therefore the value of absorbed light increased with increasing wavelength. This entails a very interesting result: i.e. that nanohorns suspensions behave as perfect absorbers for NIR wavelengths (833 nm) or for longer wavelengths. Moreover, this result is independent both on the shape of nanohorns (dahlia, bud) and on the amount of dispersant (1.2 or 1.8g/l). The obtained results open very appealing perspectives for different applications of Carbon Nanohorns, taking advantage also on their widely confirmed non-cytotoxic characteristics. Just to mention one of them, SWCNHs can be used in Solar Energy as innovative direct sunlight absorbers in new-generation solar collectors. The results reported in this work could be used in optical simulation software to optimize the use of SWCNH-based nanofluids.

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