

# High Temperature Stability of Plasma Functionalized Carbon Nanotube Nanofluids for Direct Solar Thermal Absorption

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**Abstract:** Carbon nanotubes (CNTs) directly grown from stainless steel mesh were treated using an Ar/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> glow discharge plasma in order to add oxygenated functionalities on their surface, which in turn make them dispersible in polar liquids. Stable dispersions (nanofluids) were produced for a range of CNT concentrations using ethylene and propylene glycol for high temperature solar collectors and using denatured alcohol for evacuated tube solar collectors. Quantitative analysis using absorption spectroscopy shows that all nanofluids remain stable over extended periods of time (up to 3 months) and after intense heating. Optical characterization of various concentrations of the nanofluids demonstrates that the CNTs are highly absorbing over the majority of the solar spectrum, allowing for close to 100 % solar energy absorption, even at low concentrations and small collection volumes.

**Keywords:** CNTs, nanofluids, plasma functionalization, direct solar absorption

## 1. Introduction

Solar thermal collectors, which capture the Sun's rays as heat, are currently used world-wide in applications ranging from hot water heating to large scale electricity production. As demand for cleaner energy continues to grow, solar thermal processes are expected to play a significant role in our global energy future [1]. Carbon nanotube (CNT) nanofluids (stable suspensions of CNTs in a host liquid) can be used as both volumetric solar collector and heat transfer fluid in direct solar thermal devices, as a method of improving efficiencies and reducing costs [2]. CNTs have a high spectral absorptivity over the entire solar range and consequently, these nanofluids can be tailored to absorb almost 100 % of the irradiation with relatively low CNT concentrations. As well, the CNT loading can be easily controlled such that the incident radiation is absorbed over the entire volume of fluid, instead of just at the surface, thus limiting heat losses to the surrounding [3].

The issue of suspension stability, particularly at high temperatures, must be addressed if these nanofluids are to be employed in practical applications. Typically, nanoparticles are stabilized through the use of a surfactant. However, surfactants have been shown to lose effectiveness at temperatures as low as 70 °C [4]. Given that direct solar thermal collectors could require operating temperatures as high as 400 °C, a new form of stabilization is required.

In this work we will examine the feasibility of using plasma functionalized CNTs, suspended in heat transfer fluids commonly used in high temperature solar thermal collectors (ethylene and propylene glycol) and evacuated tube collectors (denatured alcohol).

## 2. Method

The CNTs used in this study were grown directly from stainless steel 316 mesh using a thermal chemical vapor deposition (T-CVD) process [5]. The nanotubes produced are all multi-walled CNTs with an average diameter and length of approximately 30 nm and 4 μm, respectively (Fig. 1A). Following the synthesis, the CNTs are surface-functionalized through exposure to a continuous wave capacitively-coupled radio-frequency (RF, 13.56 MHz) glow discharge plasma [5]. An Ar/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> mixture was injected at flowrates of 250/5/1 sccm, respectively. The plasma pressure was 1 Torr and the treatment time was 10 min at a power of 20 W. The CNTs were removed via ultrasonication for 15 min in the base fluid. Ethylene glycol (EG) and propylene glycol (PG) were the base fluids used in the high temperature testing, while denatured alcohol (DA, 85% ethanol) was used for the evaporation/condensation experiments. The initial samples generated, with CNT concentrations up to 100 mgL<sup>-1</sup>, were used to produce dilutions corresponding to the concentrations shown in Table 1. The various nanofluids were characterized using a double-beam UV-vis spectrophotometer (Cary 5000). The samples were enclosed in Suprasil® quartz cuvette with a pathlength of

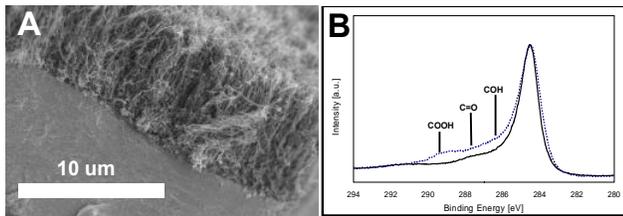


Fig 1. A) Profile image of the CNT forest covering a fractured SS wire, B) XPS C1s spectra comparing the functionalized and non-functionalized CNTs

10 mm. All trials were conducted at room temperature with the reference path left empty. To account for the difference between the refractive index of quartz and air, the acquired spectra were corrected by treating the filled cuvette as a three-slab system. The details of this procedure are described in Otanicar et al. and reference therein [6]. Measurements were taken over the range of 200-1500 nm, which account for approximately 85% of the total incident solar energy (air mass 1.5). Spectra were not taken above 1500 nm as strong absorption bands in the IR mask any change due to the addition of the CNTs. However, for direct solar collection purposes, one can assume that the base fluid would absorb the majority of the solar irradiation above 1500 nm. For all fluids the concentration of CNTs was limited to  $52 \text{ mgL}^{-1}$  as the transmitted signal for higher concentrations was below the detection limit for the spectrophotometer and pathlength used. If a higher concentration is needed, one could estimate the required concentration using Beer-Lambert law.

Table 1: CNT concentration of various nanofluids produced.

Label	CNT concentration ( $\text{mgL}^{-1}$ )
a	0
b	$5.6 \pm 0.4$
c	$11.0 \pm 1.0$
d	$17.0 \pm 1.4$
e	$27.0 \pm 2.3$
f	$53.0 \pm 5.6$

### 3. Results

#### 3.1 Stability of Plasma Functionalities

Analysis using X-ray photoelectron spectroscopy (XPS) (Fig. 1B) has shown that the plasma treatment covalently bond oxygen functionalities (COH, C=O, COOH) onto the surface of the CNTs [5]. These functionalities transform the CNTs from being superhydrophobic (contact angle  $\sim 153^\circ$ ), to superhydrophilic (no measurable contact angle) (Fig. 2A-B). As an initial test of stability of the functionalities at elevated temperatures, a plasma-

treated CNT sample was heated to  $450^\circ\text{C}$  in air for 30 min. Temperatures above this were not attempted as the CNTs themselves begin to degrade. If the functionalities were damaged upon heating, one would expect to see some hydrophobic recovery. As Fig. 2C shows the CNTs remained superhydrophilic after heating, suggesting that functionalities remain stable at high temperatures.

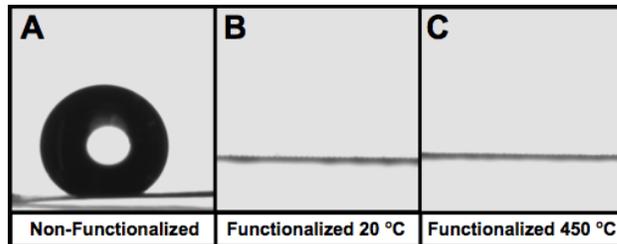


Fig. 2. Contact angle measurements of the CNTs: A) non-treated, B) treated, C) treated, then heated to  $450^\circ\text{C}$ .

#### 3.1 Long-Term Stability

CNT nanofluids (Fig. 3) of various concentrations (Table 1) were prepared using DA, EG and PG. The transmission spectra of the different nanofluids at various concentrations were acquired over a 3-month period (Fig. 4). The samples were left at room temperature without any agitation throughout this period. If agglomeration occurs, the amount of surface area available to absorb the incident radiation decreases, causing an increase in the transmittance. As Fig. 4 illustrates no increase in transmission occurs over the 3 months period for any of the nanofluids, indicating that they remain stable over extended periods of time. Suspensions produced with CNTs that are not plasma treated (not shown) experience severe agglomeration within hours of synthesis.

#### 3.2 High Temperature Stability

The previous section examined nanofluid stability at room temperature, however for a nanofluid to be used in a solar thermal application, or any heat transfer application for that matter, it must be also stable at high temperatures. To test this a second batch of nanofluids was heated for 1 hr

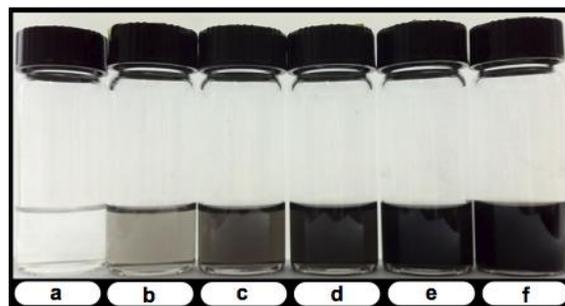


Fig. 3. Various concentrations of ethylene glycol based CNT nanofluids, 3 months after synthesis.

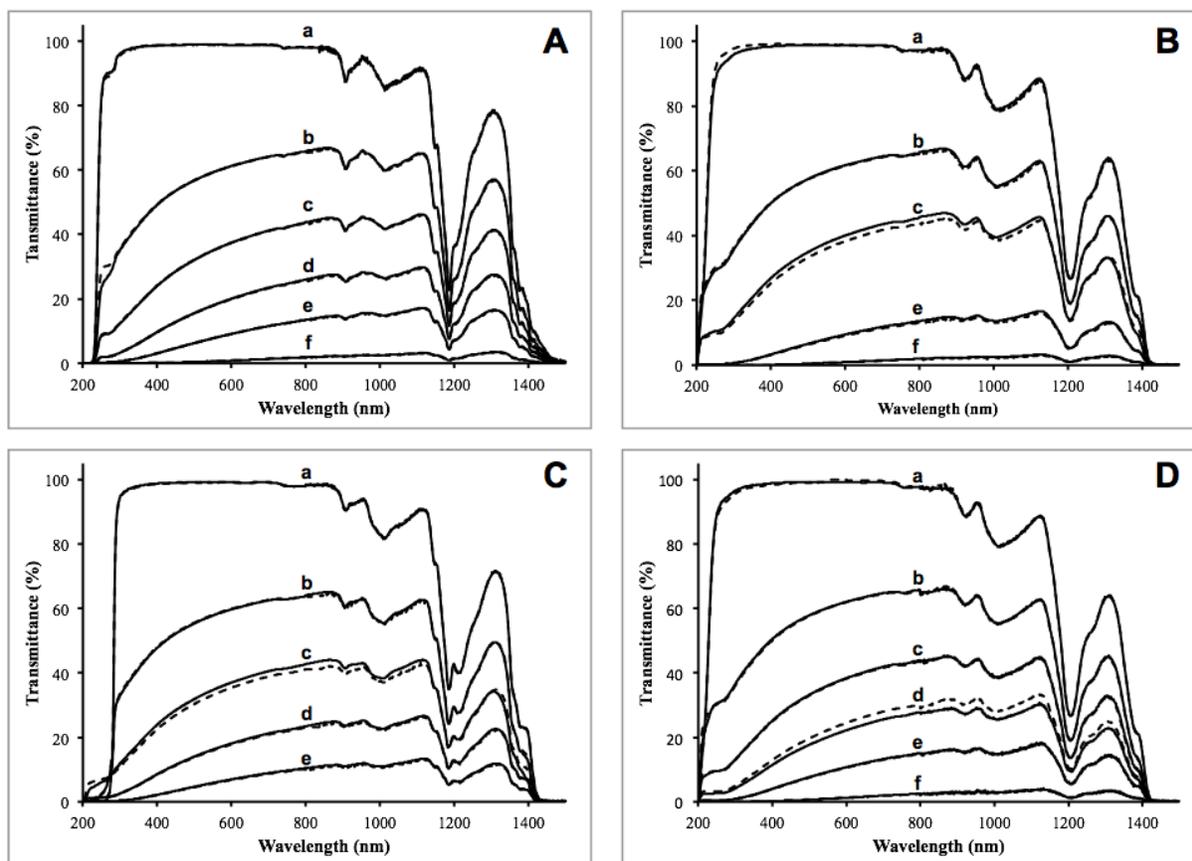


Fig. 4. Transmission spectra for various concentrations of nanofluids, after synthesis (dash) and after 3 months (solid). A: DA, B: EG, C: PG, D: EG before (dash) after heating (solid) to 170 °C for 1 h. Concentration levels (a-f) are listed in Table 1. Pathlength is 10 mm. Most of the solid/dashed curves overlap and cannot be distinguished from each other.

at approximately 85% of each base fluids respective boiling temperature (actual temperatures were 65 °C for DA and 170 °C for EG and PG). No changes in the transmittance spectra were found to occur for any of the four fluids. Only the results for the EG-based nanofluids were shown here (Fig 4D), as space is limited and no noticeable difference is seen after heating. This indicates that heating the nanofluid to high operating temperatures does not damage the functionalities, which prevent the CNTs from agglomerating.

### 3.2 Evaporation/Condensation Tests for ETC

As of 2010, over half the world's solar water heating was accomplished using evacuated tube collectors (ETC) [1]. These collectors consist of blackened metal plate attached to a heat pipe, surrounded by an evacuated glass tube. Within the heat pipe a volatile solvent (methanol, ethanol) is heated by the solar irradiation, evaporated and then condensed in a manifold, transferring the energy to produce hot water [7]. In order for a direct solar collector to be used in this type of application, the nanofluid must

remain stable throughout this continuous evaporation and condensation process. To test this, a 100 mL of a DA-based nanofluid in a volumetric flask was placed in a water bath at 78 °C (boiling temp. of DA). A cooling coil filled with cold water surrounded the top-portion of the flask to aid in the condensation process. Five evaporation/condensation cycles of 1 hour each were conducted with the transmission spectra of the nanofluid tested after each cycle. As Fig. 5 illustrates, no difference in transmission can be seen after the 5<sup>th</sup> cycle, indicating that no agglomeration occurs as a result of the evaporation and condensation process. The CNT concentration of the nanofluids, 17 mgL<sup>-1</sup>, was chosen as 100% absorption can be achieved over a fluid thickness of 5 cm, which is a typical diameter of ETCs [7].

### 3.2 Solar-Weighted Absorption

A solar-weighted absorption fraction ( $A_m$ ) can be calculated to determine what concentration of CNTs is required to obtain volumetric absorption through a solar collector (Equation 1) [8].

$$A_m(x) = \frac{\int_0^x S_m(l) (1 - e^{-\alpha(l)x}) dl}{\int_0^x S_m(l) dl} \quad (1)$$

This quantity represents the fraction of solar energy that is absorbed by the nanofluids for a particular fluid thickness ( $x$ ). The ability of the nanofluid to absorb irradiation at a given wavelength ( $\lambda$ ) is given by its extinction coefficient ( $\alpha$ ), which can be calculated from the acquired transmittance spectra (Fig. 4). A detailed description of this can be found in Drotning [8]. The spectral distribution of the solar irradiation ( $S_m$ ) was taken at an air mass of 1.5 and the integration was performed over the 200-1500 nm range. The results over a 10 cm fluid thickness for E.G. are shown in Fig. 6. Only one curve is shown as all 3 nanofluids have similar energy storage profiles. As can be seen, even the lowest concentration of CNTs had a significant effect on the absorption ability of the fluid. At 10 cm of fluid thickness, even the least concentrated nanofluids has a stored energy fraction of 1. Using these results, one could easily tailor the CNT loading in the nanofluid to obtain close to 100% absorption for any particular fluid thickness.

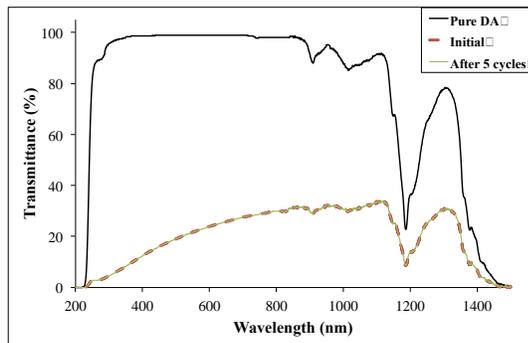


Fig. 5. Transmission spectra for DA-based nanofluid ( $17 \text{ mgL}^{-1}$ ) before and after 5 heating cycles. Pure DA given as reference. Pathlength 10 mm.

#### 4. Discussion

We are the first to quantitatively demonstrate the stability of a nanofluid over the long-term, after heating, and after repetitive evaporation/condensation cycles. The excellent stability of the produced nanofluids can be attributed to the unique CNT growth and plasma functionalization processes. Thermal-CVD growth of the CNTs directly from bulk stainless steel mesh generates a porous 3-D network of relatively short ( $\sim 4 \mu\text{m}$  in length) CNTs. This open network of CNT allows for the entire CNT surface to be treated by the plasma. A relatively short exposure (10 min) to the low-temperature plasma covalently bonds polar functionalities (COH, C=O, COOH) onto the CNT surface, allowing the CNTs to be easily suspended in

polar solvents. Upon suspension in a protonic solvent, deprotonation of the carboxylic groups leads to a negative surface charge on the CNTs, thus limiting agglomeration over time. This electrostatic repulsion is also sufficient to overcome the increased number of high velocity collisions between CNTs that occur at high temperatures [9].

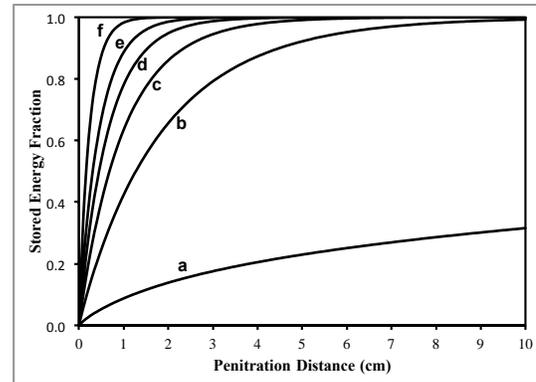


Fig. 6. Stored energy fraction as a function of penetration distance for EG-based CNT nanofluids. Concentration levels (a-f) are listed in Table 1.

#### 5. Conclusions

This study demonstrates the exceptional nanofluid stability that can be achieved by using a quick and simple glow discharge plasma process to surface treat CNTs. The plasma-generated functionalities were found to remain stable after heating in air at  $450 \text{ }^\circ\text{C}$ , after heating within the nanofluid, and over extended periods of time. The broad absorption properties of the CNTs, which allow for 100% absorption at low concentrations, coupled with the stability obtained through plasma functionalization, make them ideal candidates for direct solar collection.

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