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Effects of surface modification on the dispersion and thermal conductivity of CNT/water nanofluids ☆

Ahmad Ghozatloo [a,b], Ali Morad Rashidi [b,*], Mojtaba Shariaty-Niasar [a]

[a] Transport Phenomena and Nanotechnology Laboratory, Department of Chemical Engineering, College of Eng., University of Tehran, Tehran 11155/4563, Iran
[b] Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), West Blvd. Azadi Sport Complex, Tehran 14665-1998, Iran

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ABSTRACT

In the present work, effects of different surface modification methods (surfactant, acid, base, amide, sulfate) on multi walled carbon nanotubes (CNTs) are studied. The dispersion stability of CNTs in aqueous media was confirmed and the effects of the type of treatment on the thermal conductivity of CNT/water nanofluids were investigated. The surface of the CNTs was modified with acid mixtures (H_2SO_4–HNO_3), potassium persulfate (KPS), tetrahydrofuran (THF), octadecylamine and sodium dodecyl sulfate (SDS). UV–visible spectral data indicate that the CNTs treated first with the acid mixture and then with KPS show the best dispersion stability. The basic treatment and SDS treated CNT/water nanofluids (SDS-KCNT/water) showed the highest conductivity of 0.765 W/mK which increases 24.9% of water as a base fluid conductor.

1. Introduction

Carbon nanotubes (CNTs) exhibit exceptional mechanical, thermal and electrical properties due to their unique one-dimensional all-carbon structure [1,2]. Therefore, CNTs have the potential to be used in a vast range of applications. Compared with metal or metal oxide materials, CNTs have a higher thermal conductivity. For example, thermal conductivity value for MWNT is 3000 W/mK [3]. But CNTs cannot too long dispersion in polar solvent [4]. Therefore the difficulty of CNT nanofluid preparation lies in dispersing of CNT in solvent [5]. Among them, surface modification of the CNTs has been intensively studied as an efficient approach to increase their dispersion stability. Physical and chemical treatments are well known methods in material science to modify the surface of nano structures. Acid-treated CNTs contain carboxylic acid and hydroxyl groups, which are the most common functional groups on CNTs [6]. Surfactants have also been used to disperse CNTs, since they prevent them from becoming aggregated over long periods [7]. These treatments improve the dispersion of CNTs in aqueous media. The presence of a variety of functional groups was confirmed by FTIR spectra. The Raman spectra confirmed that the structure of CNTs was not ruptured after treatment. Although many papers have discussed the dispersion of CNTs by various means, none of them have explained completely the influence of surface treatment on the thermal conductivity of the nanofluids. Improving both the dispersion stability and thermal conductivity of the CNT nanofluids is an important issue for developing high-performance CNT/water nanofluids. Until now, most of the published data on CNT based nanofluid thermal conductivity have been focused on finding the mechanisms of enhancement [8–10] as well as thermal conductivity variations as a function of particle volume concentration, type of base fluid, and temperature [11–14]. However, no other studies have been found to directly point out the effects of the modified CNTs on thermal conductivity and stability of nanofluids.

2. Characterization

Transmission Electron Microscopy (TEM) was carried out using ZEISS EM900 KNL groups at 90 kV. The Fourier transform infrared (FTIR) spectra of the surface-modified CNTs were recorded on a (Thermo Scientific, Nicolet 6700) spectrometer. Typically 100 scans over the range 4000–500 cm^{-1} were taken from each sample with a resolution of 2 cm^{-1} and summed to provide the spectra. Raman spectroscopy (RENISHAW RM1000-Invia) was used to investigate the structural changes in the functionalized CNTs. The dispersion stability of the surface-modified CNTs in water was measured by UV–visible spectroscopy at ambient temperature using a UVS-2100 SCINCO spectrophotometer between 200 and 1100 nm. Samples were diluted up to the extents that were suitable for UV–vis measurements. The thermal conductivities of the CNT/water nanofluids were measured by a KD2 Pro thermal properties analyzer (Decagon Devices, Inc., USA). Each data presented is the average value of the measurements from five tested

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* Corresponding author.
E-mail address: rashidiam@ripi.ir (A.M. Rashidi).

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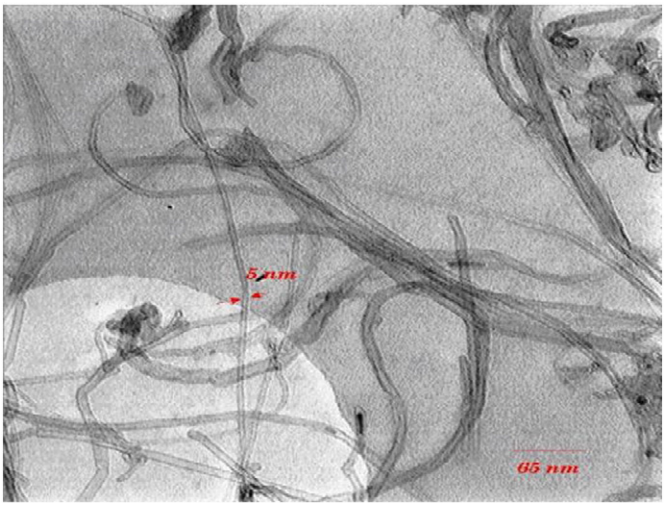

Fig. 1. TEM image of pristine CNTs.

samples. The instrument had a specified accuracy of 5% and also meets the standards of both ASTM D5334 and IEEE 442-1981.

3. Synthesis of CNT

For the present work, multi walled carbon nanotubes (MWNTs) were provided from the Research Institute of Petroleum Industry (RIPI) with 90–95% purity. The average diameter of the nanotubes varies from 10 to 15 nm and their length from 5 to 10 μm. CNTs were synthesized by catalytic decomposition of 20% methane in hydrogen over Co–Mo/MgO catalysts at 800–1000 °C [15].

In order to evaluate the morphology and diameter distribution of the CNTs, TEM images were taken for the pristine CNT of CVD as shown in Fig. 1.

4. Functionalized CNTs

4.1. Surfactant treatment

An aqueous MWNT nanofluid with sodium dodecyl sulfate (SDS) dispersants was studied [16]. Moreover, they reported the effect of particle size indirectly by increasing the homogenization time by ultrasonication, and concluded that when carbon nanotube suspensions are homogenized for long periods of time, their aspect ratio decreases, which leads to a subsequent decrease in their thermal conductivity enhancements [16]. To improve CNT dispersion in water the tubes were dispersed with the aid of sodium dodecyl sulfate (SDS) surfactant as follows [17]. The samples formed from CNTs treated with SDS were designated as SDS-CNTs. The reaction scheme for the treatment of CNTs using SDS is shown in Fig. 2.

4.2. Acid treatment

For acid treatment, the surface modification of CNTs was performed with 1:3 mixtures of concentrated HNO_3 and H_2SO_4 at 100 °C for 100 min as follows [18]. The samples formed from CNTs treated with an acid mixture were designated as A-CNTs. The reaction scheme for the treatment of CNTs using acid treatment is shown in Fig. 3.

4.3. Basic treatment

For basic treatment, pristine CNTs and deionized water were added to a flask and dispersed with the aid of an ultrasonic water bath at room temperature. Then KPS was added to the flask and the pH of the reaction system was adjusted to 13 by adding a concentrated KOH solution. The flask equipped with a reflux condenser and a magnetic stir bar was kept at 85 °C with vigorous mixing and then cooled down to room temperature naturally [19]. The samples formed from CNTs treated with the basic method were designated as K-CNTs. The reaction scheme for the treatment of CNTs using KPS is shown in Fig. 4.

4.4. Amidation

For amidation treatment, acyl-chlorinated CNTs were added to an amine compound (octadecylamine (oda) or dodecylamine (dda)). This mixture was sonicated using an ultrasound bath at 60 °C for 2 h, and then refluxed for 2 days. After cooling to room temperature the product was washed with ethanol to remove excess amine. Finally the black solid was dried at 70 °C overnight. The samples formed from CNTs treated with amidation were designated as N-CNTs. The corresponding chemical reactions are illustrated in Fig. 5 [20].

4.5. Sulfate treatment

For sulfate treatment, CNT was added to anhydrous tetrahydrofuran (THF) under vigorous mechanical stirring. To replace the terminated Na with H in CNT, sodium hydride (NaH) was added slowly to the CNT/THF mixture at 60 °C for 6 h. Propane sultone was then added dropwise to the mixture, and this mixture was reacted at 80 °C overnight with constant stirring. After the reaction, the filtered reactant was immersed into an HCl/water solution for 12 h and then washed with ethanol several times to remove the residuals. The product was dried in vacuum at 80 °C for 20 h [21]. The samples formed from CNTs treated with sulfate treatment were designated as S-CNTs. Fig. 6 gives a schematic diagram of the sulfonation process of the sulfonated CNT.

4.6. Surfactant — acid treatment

The A-CNTs were treated with SDS for 24 h at room temperature to obtain surfactant treated A-CNTs as follows [22]. The samples formed from A-CNTs treated with SDS were designated as SDS-ACNTs. Fig. 7 gives a schematic diagram of the process of the ACNTs.

4.7. Surfactant — basic treatment

The K-CNTs were treated with SDS for 24 h at room temperature to obtain surfactant treated K-CNTs as follows [22]. The samples formed from K-CNTs treated with SDS were designated as SDS-KCNTs. Fig. 8 gives a schematic diagram of the process of the SDS-KCNTs.

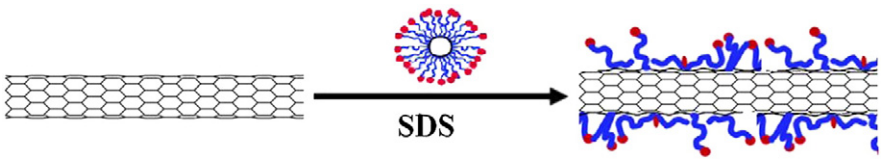

Fig. 2. Schematic representations of the mechanism by which surfactants help to disperse CNT.