Surfactant-free nanofluids containing double- and single-walled carbon nanotubes functionalized by a wet-mechanochemical reaction

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) and double-walled carbon nanotubes (DWNTs) have been functionalized through the wet-mechanochemical reaction method. Results from the infrared spectrum and zeta potential measurements show that the hydroxyl groups have been introduced onto the treated SWNT and DWNT surfaces. Transmission electron microscope observations revealed that the SWNTs and DWNTs were cut short after being milled. SWNTs and DWNTs with optimized aspect ratio can be obtained by adjusting the ball milling parameters. Thermal conductivity enhancement of water-based nanofluids containing treated carbon nanotubes (CNTs) shows augmentation with the increase of temperature mainly due to the effects of an ordering liquid layer forming around the chemical surfaces of CNTs. Moreover, the thicker interfacial layer of water molecules on the surfaces of CNTs with smaller diameter, such as SWNTs, is in favor of greater thermal conductivity enhancement compared with the thinner one on the surfaces of DWNTs or MWNTs with larger diameter.

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1. Introduction

The extraordinary thermal properties [1] exhibited by carbon nanotubes (CNTs) suggest that important applications await these unique materials. One of the important applications is to prepare nanofluids. Nanofluids, a new kind of thermal transfer materials, have attracted significant attention because of their outstanding performance such as high thermal conductivity, long-term stability, and prevention of clogging in micro-channels [2]. The thermal conductivity enhancement of the nanofluid is mainly due to the additions of nanoparticles with high thermal transfer performance [3,4]. Compared with metal or metal oxide materials, CNTs have the higher thermal conductivity. For example, thermal conductivity values for single-walled carbon nanotube (SWNT), double-walled carbon nanotube (DWNT) and multi-walled carbon nanotube (MWNT) are 6000 W/mK [5], 3986 W/mK, and 3000 W/mK [6], respectively. It seems that the thermal conductivity of the CNTs shows augmentation with decrease of its tube-walled number. In view of such potential properties, there is a strong motivation to understand the thermal properties of water-based composites containing different types of CNTs. To our knowledge, to date, there is no experimental study on the thermal conductivity properties of water-based suspensions containing single- or double-walled CNTs due to their poor dispersibility in water matrix. Moreover,

the actual heat transfer mechanisms of the CNT nanofluids are still not clear. Hence, more experimental studies, especially comparing among the nanofluids containing CNTs with different tube-walled numbers, are needed for further analyzing.

Large varieties of water-soluble polymers were used to improve the poor water-soluble properties of CNTs [7–11]. However, research shows that the addition of the polymer will contaminate the matrix and increase the interfacial thermal resistance between the carbon nanotubes and the matrix [12]. The increasing interface thermal resistance will limit the heat transport in the nanotube-matrix and further confine the thermal conductivity enhancement of the nanofluids. Chemical oxidation under ultrasonication or reflux conditions using mixtures of strong acids also has been employed [13–17]. But the acid treatment holds the disadvantages including serious loss of the materials, difficulty in large scale production, and deterioration of CNT qualities. Furthermore, author's previous research shows that the acid treated CNTs are still very long. Long CNTs will aggregate seriously in the matrix [18]. The entanglements and aggregations may enlarge the viscosity of nanofluids and may cause clogging in microchannel flows. Our research group has reported a wet-mechanochemical reaction method to functionalize the MWNTs [19]. The resulted MWNTs are water-soluble and have been further cut into short ones by mechanical milling technology.

In this article, SWNTs and DWNTs were functionalized by using the wet-mechanochemical reaction method and the suitable functionalization parameters have been explored. Experimental results from the FT-IR spectra and zeta potentials show that the hydroxyl

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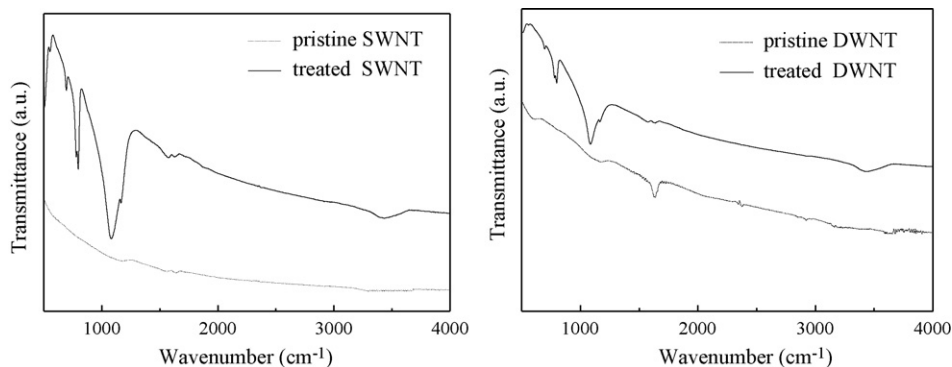*E-mail address:* hqxie@eed.sspu.cn (H. Xie).

Fig. 1. FT-IR spectra of SWNTs and DWNTs.

groups have been introduced onto the SWNT and DWNT surfaces. Heat transfer mechanism was analyzed in detail according to the thermal conductivity enhancement of water-based nanofluids containing CNTs with different tube-walled numbers.

2. Experiments

2.1. Functionalization and characterization of CNTs

SWNTs and DWNTs (purity: 90%) were purchased from Shenzhen Nanotech Port Co., Ltd., and were purified at higher temperature before being used. Potassium hydroxide is an analytical reagent.

The optimal functionalized condition has been obtained in which 0.4 g pristine SWNTs or pristine DWNTs and 8 g KOH are mixed and put into ball-milling container. The added ethanol exactly emerged the mixtures. The ball-milling container contained a total of 152 agate beads, comprising 2 pieces, 50 pieces, and 100 pieces each with diameter of 15 mm, 7 mm, and 4 mm, respectively. The mass ratio of agate beads to total reactants is 10:1. The prepared ball-milling containers were fixed on the ball-milling machine, and were rolled at a speed of 300 rpm for 15 h. During the milling procedure, the chemical reaction and mechanical action took place at the same time. The reacted mixtures were dissolved in deionized water and precipitated by centrifuge (Auegra TM 64R Centrifuge from Beckman Coulter, USA). Precipitation was repeated until the water became neutral to ensure a complete removal of KOH residues and the samples were dried in vacuum oven at 80 °C for 20 h. Pure and treated SWNTs and DWNTs with functionalization surfaces were obtained.

The treated SWNT and treated DWNT surfaces were characterized by FT-IR spectra on a spectrophotometer (Vertex 70, Germany). Zeta potentials for all the SWNTs and DWNTs were measured at a concentration of 0.01 wt.% using a Zetaplus analyzer (Nano

ZS, Malvern company, Britain) by electrophoresis light scattering method. In order to ensure constant ionic strength, 10 mmol/L NaCl solutions are used to prepare all SWNT and DWNT solutions by ultra-sonication, and the pH of the suspension was adjusted by adding either HCl or NaOH.

2.2. Preparation and thermal conductivity determination of nanofluids

The treated SWNTs and DWNTs are dispersed directly in the water by sonication. Thermal conductivities of the water-based SWNT and DWNT nanofluids are measured by using a transient short hot wire method reported elsewhere [20]. In our experiments a platinum wire with a diameter of 50.0 μm was used for the hot wire, and it served as both a heating unit and as an electrical resistance thermometer. A 7.0 μm thick insulation layer was coated on the wire surface for insulation. The uncertainty of this measurement is estimated to be within ±1.0% [20].

3. Results and discussion

The FT-IR spectra of all the SWNTs and DWNTs are depicted in Fig. 1. The FT-IR spectra of the treated SWNTs is obviously different from that of the pristine SWNTs. This difference also can be seen in the FT-IR spectrum of treated DWNTs and pristine DWNTs. The detectable transmission band at 1571 cm^{-1} in the broken line for the pristine SWNTs and DWNTs in the studied wavenumber range is assigned to the carbon skeleton [21]. In the previous study on the FT-IR spectrum of MWNTs there is a band at 1230 cm^{-1}, which is also designated to carbon skeleton. The transmission bands of the carbon skeleton turned weak in the corresponding FT-IR spectrum for the treated SWNTs and DWNTs. The signal at 1627 cm^{-1} in spectra of all the SWNTs and DWNTs is due to contaminating water [22]. The extra peaks at 800 cm^{-1} can be assigned to stretch-
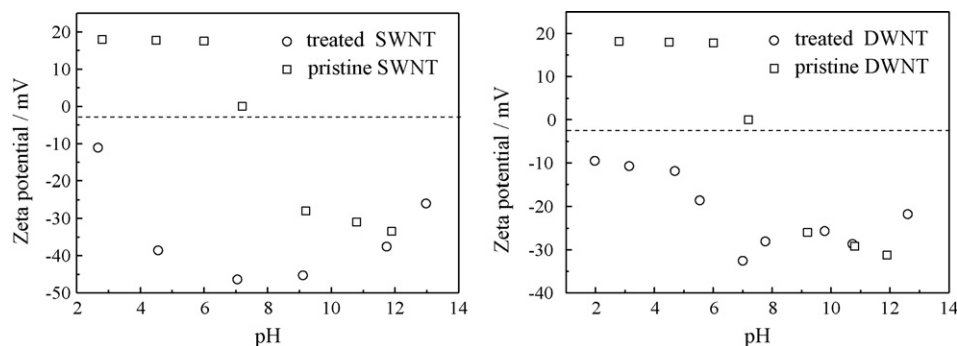

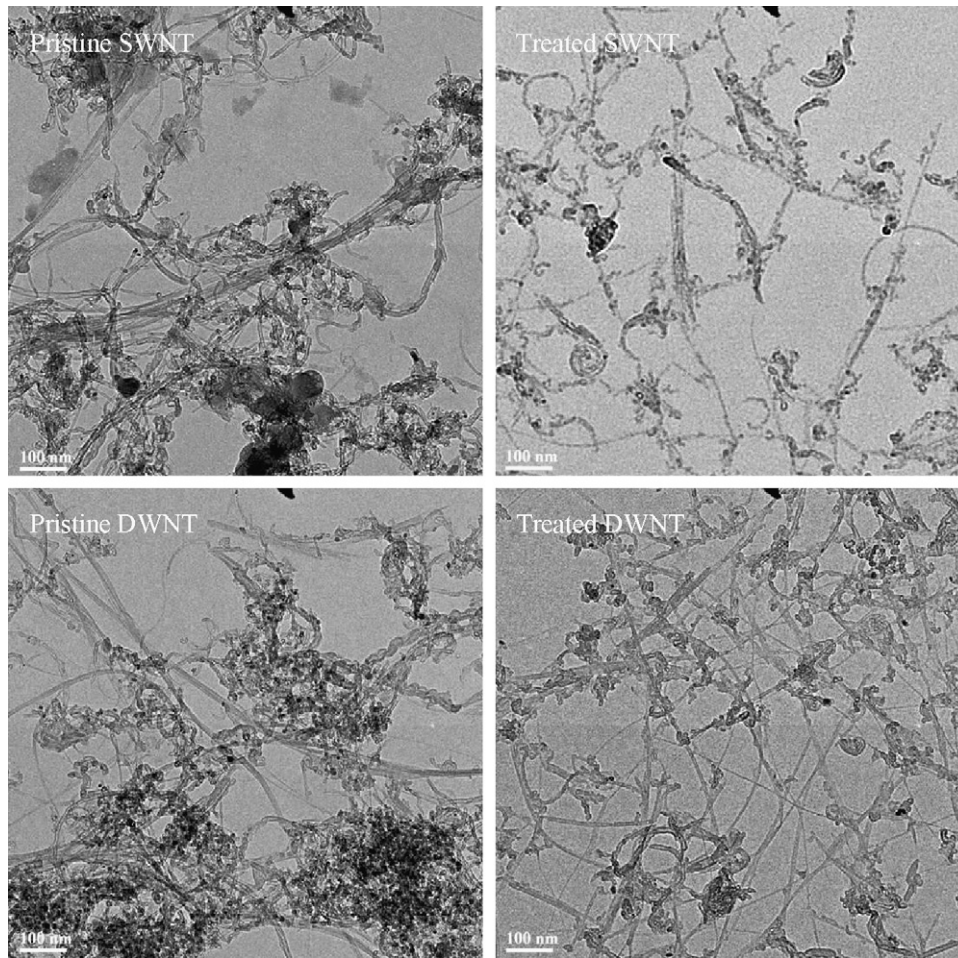**Fig. 2.** Zeta potential as a function of pH for SWNTs and DWNTs.

Fig. 3. Micrographs of SWNTs and DWNTs.

ing vibration of C–O–C groups. The strong peak at 1080 cm^{-1} can be interpreted to the characteristic of primary alcohol. It can be induced that some hydroxyls have been introduced onto the broken parts of the SWNTs and DWNTs. In addition, the very broad transmission band centered at 3443 cm^{-1} of FT-IR spectrum for the treated SWNTs and DWNTs should be attributed to the hydrogen bond –OH. The FT-IR results obviously show that the hydrophilic groups such as hydroxyls have been introduced onto the treated SWNT and DWNT surfaces. As a result, treated SWNTs and DWNTs can be dispersed directly in water and other polar solvent without the addition of water-soluble polymers.

Further evidence for hydrophilic functionalized groups of the SWNTs and DWNTs was provided by zeta potential measurements. Zeta potentials as a function of pH for all the SWNT and DWNT suspensions were determined and given in Fig. 2. As seen from Fig. 2, an isoelectric point (IEP) for pristine SWNTs and DWNTs appears at pH of 7.1. However, no IEP appears for the treated SWNTs and DWNTs, and zeta potential values of them were negative in all studied pH values. This phenomenon was usually observed from ceramic suspensions mixed with anionic dispersants [23]. The results indicate that the treated surfaces have been modified by negative groups. It was consistent with that obtained from FT-IR spectra, meaning that the treated SWNT and DWNT surfaces have been functionalized by hydroxyl groups. Furthermore, the very negative zeta potential values of treated SWNT and DWNT dispersions indicate their considerable stabilities. In fact, the obtainment of stable dispersion of the treated SWNTs and DWNTs in water is due to the formation of electrical double layer formed by the hydroxyl groups on the sur-

faces of the SWNTs and DWNTs. In the electrical double layer ionic accumulation of few angstrom thicknesses prevents the particle aggregation and thereby stabilizes the suspensions [24]. Also the hydroxyl groups increase the affinity between the treated SWNTs or the treated DWNTs and water. The increasing affinity improves the stability of the treated SWNTs and DWNTs in water.

The morphological characterization for all the SWNTs and DWNTs was obtained by using transmission electron microscope (TEM) and the results are shown in Fig. 3. In the preparation of samples for observation, SWNT and DWNT dispersions in ethanol are dropped on carbon-coated copper grid. The samples are exposed to air at room temperature for drying until suitable for the subsequent TEM analysis. Pristine SWNTs and DWNTs exhibit intensive entangles and aggregations. However, after being treated individual and short SWNTs and DWNTs are visible. The debundling of the aggregates is attributed to the functionalization from the chemical reaction. The short SWNTs and DWNTs are the results of the mechanical forces during the milling process. Therefore, the aspect ratio of the treated SWNTs or the DWNTs, the main factor in enhancing the thermal conductivity of nanofluids, can be controlled by regulating the milling parameters.

Fig. 4 depicts the thermal conductivity enhancements of the CNT nanofluids as a function of temperatures. The volume fraction of the treated CNTs in water is 0.002. In this article, k and k_0 represent the thermal conductivities of the nanofluid and the base fluid, respectively, and $(k - k_0)/k_0$ is the percentage of thermal conductivity enhancement. Fluid temperature may play an important role in enhancing the effective thermal conductivity of nanofluids. The
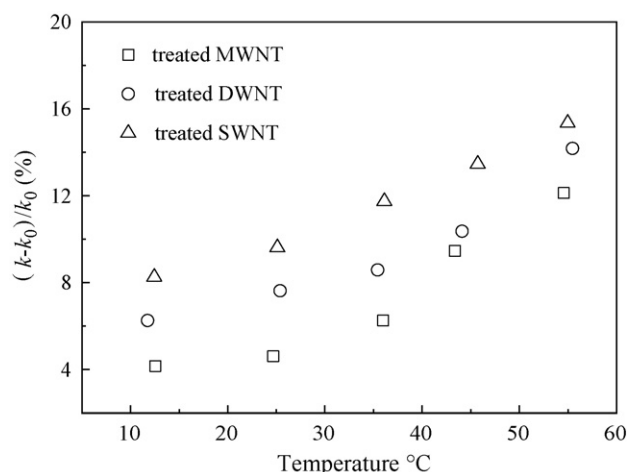
Fig. 4. Thermal conductivity enhancement of SWNT, DWNT, and MWNT nanofluids as a function of temperatures.

Fig. 5. Illustration of ordering region formation between the chemical surface and bulk liquid.

fact is that the nanofluids may be used under various temperatures. Therefore, this study was performed to investigate the temperature effect on the effective thermal conductivity of nanofluids. It was observed that thermal conductivity enhancements of water-based nanofluids containing CNTs showed augmentation with respect to temperature. At about 55 °C and the same CNT volume fraction of 0.002, the thermal conductivity enhancements are 15.6%, 14.2%, and 12.1% for SWNT, DWNT, and MWNT nanofluids in water, respectively. For the nanofluid containing sphere metal or metal oxide nanoparticles the strong temperature dependence of thermal conductivity was due to the Brownian motion of nanoparticles [25]. However, for the water-based nanofluids containing CNTs with chemical functionalization, in addition to the Brownian motion of CNTs, the chemical surface effects of CNTs should come into the main play in determining the extent of energy transfer in nanofluids with changes of temperature. The reason may be that the iceberg structure of water molecules was destroyed because the hydrogen bond turned weak with the increase of temperature. Therefore, more free water molecules are provided. It is very easy for free water molecules to form liquid layers around the surfaces of CNTs due to the affinity between the hydroxyl groups on the CNT surfaces and the water molecules. The result is that the local ordering of the atomic structure at the interface region is enhanced and the interface ordering region may be enlarged due to the van der Waals force between the water molecules. Apart from the interface region the ordering of the atomic structure turned weak due to Brownian motion of water molecules. The atomic structure of such liquid layer is much more ordered than that of the bulk liquid. This idea is also described in Fig. 5. Given those solids, which have much ordered atomic structure, exhibit much higher thermal conductivity than liquids, the liquid layer at the interface would reasonably have a higher thermal conductivity than the bulk liquid [26]. Hence, the ordering liquid layer formed due to the chemical surfaces of CNTs and van der Waals force between the water molecules should be the important factor, improving the thermal conductivity enhancements of functionalized CNT nanofluids with the increase of temperature.

It can be seen from Fig. 4 that the thermal conductivity enhancements show differences among the water-based nanofluids containing different kinds of treated CNTs as the volume fraction of CNTs is the same. The intrinsic heat transfer capacity of the CNTs should be the main factors. SWNT has the highest thermal conductivity among the three kinds of CNTs, and the thermal conductivity of the MWNT is the lowest one. The thermal conductivity enhancement of the obtained CNT nanofluids accords with that
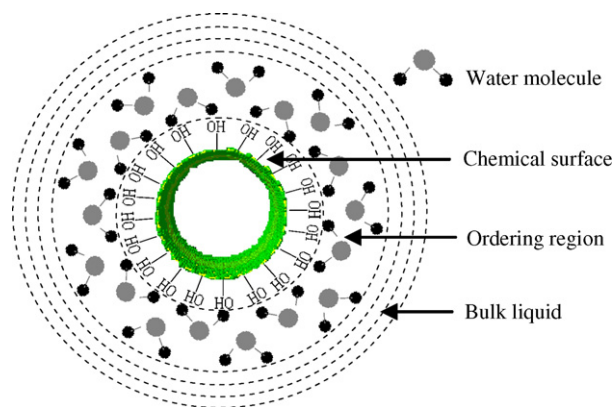
of the intrinsic heat transfer capacity of the three kinds of CNTs. Experiments showed that the effect of CNTs on thermal conductivity enhancement of nanofluid depends on the diameter and the aspect ratio of the CNTs [27–31]. The average diameters of MWNTs are much higher than those of DWNTs, and the diameters of SWNTs are the smallest ones. The smaller diameter means the larger specific surface of CNTs and the larger specific surface means more obvious Brownian movement, which is regarded as an important factor to increase the thermal conductivity of nanofluids [32,33]. Moreover, there are more water molecules close to the surface of CNTs due to the larger specific surface if the volume fractions of CNTs are the same. These water molecules can form an interfacial layer structure on the CNT surfaces, increasing the thermal conductivity of nanofluid [34,35]. Therefore, the smaller diameter means the thicker interfacial layer and the greater thermal conductivity enhancement.

Jiang et al. reported that the CNTs can build up high thermal conductivity percolation paths to enhance the thermal conductivity of the nanofluid. The longer the percolation path is, the greater the enhancement of thermal conductivity is. Higher aspect ratio means longer percolation path and the greater thermal conductivity enhancement [36]. Therefore, in future, more works will be done to obtain functionalized CNTs with optimized aspect ratio through adjusting the ball milling parameters.

4. Conclusion

In summary, a wet-mechanochemical reaction method was used to functionalize the SWNTs and DWNTs. The hydroxyl groups have been introduced onto the treated SWNT and DWNT surfaces and the dispersibility of the SWNTs and DWNTs is dramatically enhanced. The aspect ratios of the SWNTs and DWNTs could be tailored by adjusting the ball milling parameters. Chemical surface effects of CNTs play the main roles in improving the thermal conductivity enhancement with the increase of temperature. CNTs with smaller diameters offer more contribution to the thermal conductivity enhancement of CNT water-based nanofluids compared with the CNTs with larger diameters. Thermal conductivity enhancement also has close relation to the initial heat transfer performance of the CNTs.

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