Research Article

Surface Chemical Modification of Multiwalled Carbon Nanotubes by a Wet-Mechanochemical Reaction

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A wet-mechanochemical reaction for surface modification of multiwalled carbon nanotubes (CNTs) has been developed. In the treatment, CNTs reacted with potassium hydroxide in alcohol solvent at room temperature under mechanical milling. The results from Fourier transmission infrared spectroscopy demonstrate that the nonreactive surfaces of CNTs have been modified successfully by multiple hydroxyl groups. Functionalized carbon nanotubes exhibit higher zeta potential values indicating their high dispersibility in polar solvents. XRD studies corroborate that the surface functionalization does not affect the basic crystal domain size of CNTs. TEM observations reveal that CNTs have been cut into shorter ones by the milling. Shortened CNTs with functionalized surfaces show good dispersion properties.

1. INTRODUCTION

Carbon nanotubes (CNTs) possess unique electronic, chemical, and mechanical properties that make them leading materials for a variety of applications [1–3]. While many potential applications often need them to be prior purified and functionalized, because the bundling nature of CNTs originating from huge van der Waals binding energy [4] makes them difficult to be soluble in solvents either aqueous or nonaqueous even with dispersing materials. The lack of solubility and the difficult manipulation of CNTs in solvents impose great limitations to the practical applications of CNTs. Therefore, surface functionalization of CNTs has become the subject of research in recent years in order to improve their compatibility with matrix. A variety of methods, including covalent or noncovalent functionalization, have been developed to achieve effective deaggregation and dispersion [5–9]. Covalent reactions, such as cycloadditions [10], and addition reactions with nitrenes and diazonium salts [11, 12] were employed by many researchers in functionalizing the CNTs. However, the covalent functionalization has been found to deteriorate the intrinsic properties of single-walled carbon nanotubes (SWNTs) [13, 14]. Noncovalent approaches, that is, supramolecule formation using amphiphilic surfactants, have been proved to be capable of debundling SWNTs

ropes and stabilizing individual tubes while maintaining the SWNT integrity and intrinsic properties [15, 16]. However, the addition of surfactants may contaminate the matrix. A generally known method to functionalize CNTs is chemical oxidation under ultrasonication or reflux conditions using mixtures of strong acids [17–21]. But the acid treatment results in serious loss of the materials as well as deterioration of CNT qualities. This method also holds the disadvantage of the difficulty in large-scale production. Recently, direct introduction of reactive monomers on CNT surfaces by organic chemical reactions has been reported [22, 23]. Another reported method to functionalize SWNTs is solid-phase mechanochemical reaction in which potassium hydroxide (KOH) reacted with SWNTs and hydroxyl groups were added directly onto the surfaces of SWNTs at room temperature [24]. However, when this technique was applied in treating multiwalled CNTs (MWNTs), the reactants (KOH and CNTs) agglomerated severely and could not mix equably.

In this study, we present a new way to modify the surfaces of pristine multiwalled carbon nanotubes (PCNTs) in a large-scale production with no damage of CNT sidewalls. We name this method as wet-mechanochemical reaction, in which PCNTs react with KOH in ethanol solvent at room temperature under mechanical milling. Compared with solid-phase mechanochemical reaction, the

wet-mechanochemical reaction, in addition to involving highly reactive centers generated by the mechanical energy imparted to the reaction system [24], makes materials contact effectively. The effects of milling time on surface functionalization of MWNTs have been studied in detail. The treated CNTs (TCNTs) are analyzed by Fourier transmission infrared spectroscopy (FT-IR), thermal gravimetric ananlysis (TGA), zeta potential measurements, X-ray powder diffraction (XRD), and transmission electron microscope (TEM).

2. EXPERIMENTAL

MWNTs (purity: 95%) were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, and were used as received without further purification. KOH is analytical reagent.

Typically, mixtures of 0.4 g PCNTs and 8 g KOH, and ethanol were milled intensively using a ball-milling machine. Chemical reaction and mechanical action took place during the milling procedure. The mass ratio of agate balls to total reactants was 5 : 1. The treated time were selected as 4 hours, 15 hours, and 30 hours. The obtained mixtures were dissolved in deionized water and precipitated by centrifuge (Auegra TM 64R Centrifuge, Beckman Coulter, Calif, USA). Precipitation was repeated until the water became neutral to ensure a complete removal of KOH residues and the samples were dried at 80°C for 20 hours. Pure and functionalized TCNTs were obtained.

FT-IR spectra of TCNTs were measured on a spectrophotometer (Vertex 70, Germany). TGA measurements were carried out on a series thermal analysis system (NETZSCH STA449C, Germany) under a flowing nitrogen atmosphere in the temperature range 50–900°C at a scan rate of 10°C/min. Zeta potentials of PCNTs and TCNTs were measured at a concentration of 0.01 wt% using a zetaplus analyzer (Nano ZS, Malvern company, UK) by electrophoresis light scattering method. PCNTs and TCNTs were dispersed in 10 mmol/L NaCl solutions by ultrasonication to ensure constant ionic strength, and the pH of the suspension was adjusted by adding either HCl or NaOH. However, XRD measurements were recorded using an X-ray diffractometer (D8-Advance, Germany) equipped with a back monochromator operating at 40 kV, and a copper cathode was used as X-ray source (λ = 0.154 nm). XRD patterns were recorded from 10 to 80° (2θ) with a scanning step of 0.01°. Morphological characterization of carbon nanotubes was performed using transmission electron microscope (JEOL 2010, Japan).

3. RESULTS AND DISCUSSION

The nature of surface groups of PCNTs and TCNTs was studied by FT-IR and the results are shown in Figure 1. The FT-IR spectrum of TCNTs is obviously different from that of PCNTs. The detectable transmission band at 1230 cm^{-1} and 1574 cm^{-1} observed for the PCNTs in the studied wavenumber range (Figure 1(a)) are assigned to the carbon skeleton [25]. The transmission bands turned weak in the corresponding FT-IR spectrum (Figure 1(b)) for TCNTs. The signal at 1630 cm^{-1} in spectra of TCNTs and PCNTs
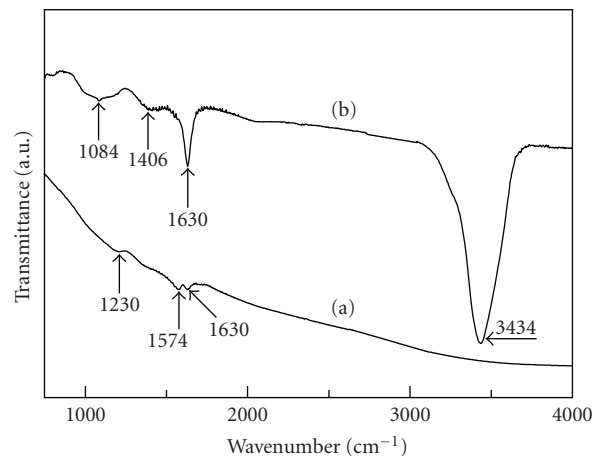
(a) PCNTs
(b) TCNTs
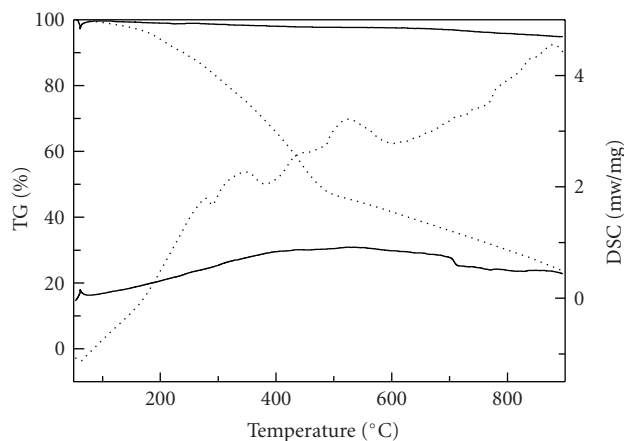
Figure 1: FT-IR spectra of (a) PCNTs and (b) TCNTs.

Figure 2: TG-DSC curves of PCNTs (solid line) and TCNTs (broken line).

is due to contaminating water [26]. The TCNTs presented extra peaks at 1084 cm^{-1}, which can be assigned to C–O–C stretching group. The peak at 1406 cm^{-1} can be interpreted to the characteristic of hydroxyl bond (O–H). In addition, the very broad transmission band centered at 3434 cm^{-1} with high intensity of FTIR spectrum for TCNTs should be attributed to the hydrogen bond –OH. The FT-IR results obviously show that the hydroxyl groups have been introduced onto the surfaces of TCNTs. As a result, TCNTs can be dispersed in water and other polar solvent without surfactants.

Further evidence for functionalization of PCNTs by hydroxyl groups was provided by TGA. TGA provided useful information about functionalized CNTs because most functional moieties on CNTs are thermally unstable [27], that is, most of the organic functional groups are decomposed before the onset of CNTs weight loss [28, 29]. Figure 2 shows the thermograms of PCNTs and TCNTs in the range 40–900°C. The weight loss also includes degassing and solvent
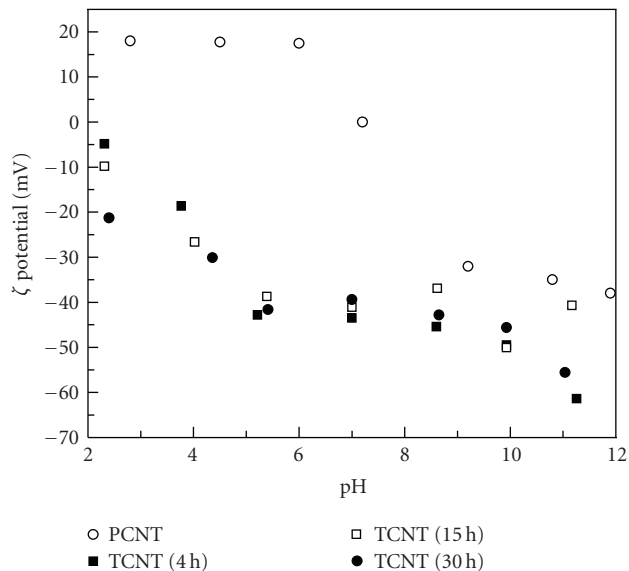
Figure 3: Zeta potential as a function of pH for PCNTs and TCNTs with different treated times.

Figure 4: XRD patterns of PCNTs and TCNTs with different treated times.

evaporation at low temperatures [27]. The weight loss at 40–200°C accounted for approximately 10%. The weight loss in the range of 200–480°C should be attributed to the decomposition between the functional groups and the CNTs. There is little weight loss of PCNTs as shown in Figure 2. The appearance of only two peaks at about 340 and 520°C in DSC curve also confirmed that there was little disordered carbon material in the TCNT sample, as the characteristic combustion temperature of disordered carbon usually emerges at around 400°C [30].

Zeta potentials as a function of pH for PCNT and TCNT suspension were determined and given in Figure 3. As seen in Figure 3(a), PCNTs have an isoelectric point (IEP) at pH 7.1. In TCNT suspensions, the IEP moves to a much acidic value at pH 3.7 when the treated time was 4 hours. Zeta potential values of TCNT suspension were negative in all studied pH values and more negative with increase of treated time. This tendency was usually observed on ceramic suspensions mixed with anionic dispersants [31]. The changes in zeta potential values might be attributed to the surface chemical modification of CNTs, which introduces the hydroxyl groups onto the surfaces of CNTs. The result was consistent with that obtained from FT-IR. Furthermore, the more negative zeta potential values of TCNT dispersions indicate their considerable stabilities. Earlier reports on acid functionalized SWNTs reveal that the obtainment of stable dispersion of CNTs in water is due to the formation of electrical double layer in which ionic accumulation of few angstrom thicknesses prevents the particle aggregation and thereby stabilizes the suspension [32]. In the present case, the hydroxyl groups on the surfaces of TCNTs lead to the formation of electrical double layer around the TCNTs, preventing their aggregation. Also, the hydroxyl groups increase the affinity between TCNTs and water and thereby increase the stability of TCNTs in water.
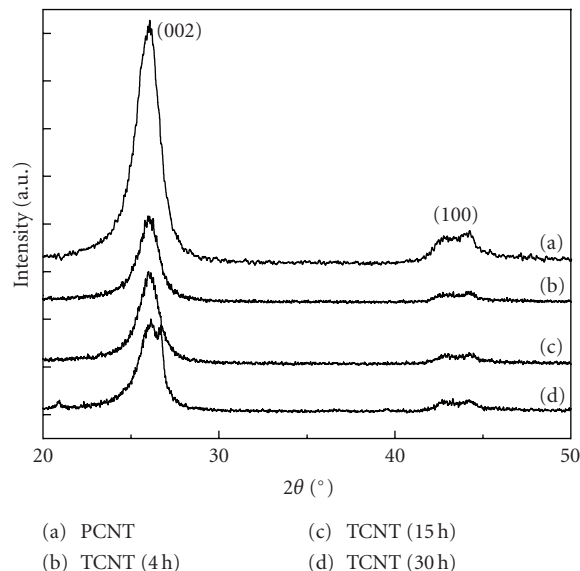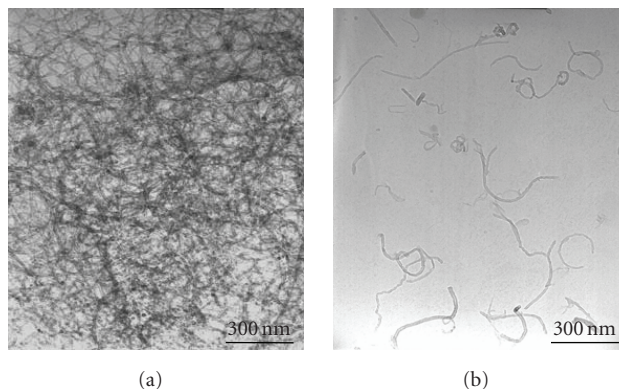

Figure 5: TEM micrographs of (a) PCNTs and (b) TCNTs.

The XRD patterns of PCNTs and TCNTs with different treated times of 4 hours, 15 hours, and 30 hours are presented in Figure 4. The average interlayer spacing decided from (002) peak is 3.509 Å. The (002) peak is broaden because of the finite number of layers and of the curvature of each tube. The broaden (10) bands indicate the curved sheet of the materials [33]. The average coherence length (L_c) of CNTs can be deduced from the width of the (002) Bragg peaks [34]. L_c of PCNTs and TCNTs with different treated times are 5.2 nm, 5.4 nm, 5.4 nm, and 5.4 nm, respectively. The values are very similar and show that the crystalline organization remains almost the same for all the samples. The results confirm that the wet-mechanochemical treatment does not damage the graphene layer organization. It indicates that the wet-mechanochemical reaction is feasible and facile to functionalize the surfaces of MWNTs. Furthermore, the intensity of (002) peak of PCNTs is much larger than TCNTs. This might be caused by the much lower packing density in

TCNTs or some defects introduced in the process of wet-mechanochemical treatment.

The morphological characterization was obtained using transmission electron microscope and the results are shown in Figure 5. PCNT and TCNT dispersions in ethanol dropped on copper grid covered with an amorphous carbon film, respectively. The samples are exposed to air at room temperature for drying until being suitable for the subsequent TEM analysis. PCNTs exhibit aggregation as observed by earlier researchers [35]. However, individual fibers are visible in the case of TCNTs. The debundling of the aggregates is attributed to the functionalization. Furthermore, TCNTs have been cut into short ones. It indicates that TCNTs with suitable length can be obtained by regulating the milling parameters.

4. CONCLUSIONS

Surface chemical functionalization of MWNTs was carried out by reaction of MWNTs with potassium hydroxide in ethanol solvent at room temperature under mechanical milling. FT-IR studies reveal that the hydroxyl groups have been introduced onto the surface of TCNTs. Thermogravimetric analysis of TCNTs exhibits degradation supporting the chemical functionalization. Higher zeta potential values for TCNTs indicate their excellent dispersing ability in solvents compared to PCNTs. Results of DSC and XRD show that the introduction of hydroxyl groups on TCNT surfaces has no effect on the crystallite species in the carbon nanotube bundles. TEM micrographs show that the carbon nanotubes have been cut during the mechanical milling. Preliminary studies on the influence of dispersion and aspect ratio of functionalized carbon nanotube reveal that it significantly affects the thermal conductivity of the nanofluids. The detailed study is underway in our laboratory and the results will be communicated shortly.

ACKNOWLEDGMENTS

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