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Wet-grinding assisted ultrasonic dispersion of pristine multi-walled carbon nanotubes (MWCNTs) in chitosan solution

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ABSTRACT

Ultrasonication is often used to disperse nano-particles in aqueous solution. However, a good dispersion of nano-particles in aqueous solution is not always achieved, due to the fact that incoming ultrasonicwaves in liquid are usually reflected and damped at the gas/liquid interface. In this work, we report a so-called wet-grinding assisted ultrasonication (GU) method, in which wet-grinding of multi-walled carbon nanotubes (MWCNTs) in chitosan solution is carried out before ultrasonication. The dispersions of MWCNTs were characterized by visual comparison, UV/vis spectroscopy, and scanning electron microscopy (SEM). The results demonstrate that the dispersion quality of chitosan/MWCNT suspension prepared by wet-grinding assisted ultrasonication is much better than that by ultrasonication or wet-grinding alone. It was found that wet-grinding could improve the water wettability of MWCNTs and eliminate the barrier of air layer around MWCNTs to ultrasonicwaves. Meanwhile, the composite from the chitosan/MWCNTs suspension prepared by GU method has an obvious improvement in mechanical property compared to pure chitosan. This simple method for integrating MWCNTs and biocompatible chitosan into a homogeneous dispersion may have great potential application in biotechnology, such as preparing composite materials for medicine, bio-fiber, biosensor, antibacterial coating, and cell cultivation.

1. Introduction

In the past decade, carbon nanotubes (CNTs) attracted much attention from academics and industries because of their excellent mechanical, electrical, and thermal properties that make them ideal candidates for various applications ranging from nanoelectronics, sensors, nanocomposites, biomedical devices, and cellular delivery, to making novel nanoarchitectures [1–6]. However, the lack of solubility and poor dispersability of pristine CNTs in aqueous solution arising from their strong hydrophobicity and van der Waals attractions have impeded their wide applications [7,8]. To overcome these problems, much work has been done on improving the solubility and dispersibility of CNTs in aqueous solution by covalent or noncovalent modification [9,10]. The most common one is the chemical modification of the graphene surface of CNTs by oxidation in a concentrated acidic medium [11,12], which usually degrades the mechanical and electrical performance of the nanotubes. In contrast, noncovalent functionalization of CNTs by adsorption of surfactants [13,14], synthetic polymers [15,16], and biomolecules [17,18] is becoming a more promising method to disperse CNTs because it can preserve the unique properties of nanotubes. Typically, various amphiphilic molecules are designed to disperse pristine CNTs in aqueous solutions by having one component (e.g. aromatic and hydrophobic moieties) interact with CNT surface by hydrophobic and/or π–π stacking interactions and the other component (hydrophilic charged and/or noncharged moieties) interact with water [19]. Some natural biopolymers with these similar structure characteristics, such as DNA [17], protein [18], and starch [20] have also been used to disperse CNTs into aqueous solutions, which could enlarge the biomedical application of CNTs due to good biocompatibility of biopolymer. For example, the aromatic nucleotide, long chain length, and positive charge of DNA make them good dispersants for CNTs by π–π stacking, wrapping, and electrostatic repulsion simultaneously [17].

Ultrasonication is often used for dispersing pristine CNTs during non-covalent modification of CNTs, but many aggregated CNT bundles do not interact well with the modifier in aqueous solutions, which leads to relatively low yield of modified CNTs [21]. Due to the wave nature of ultrasonic, an incoming wave transporting in liquid medium is almost reflected and damped at the gas/liquid interface [22]. When the pristine CNTs are added into the water, thin air layers may cover some parts of the CNT surface and exist among the interspaces of CNT bundles due to their poor wetting by water. This prevents the ultrasonicwave from reaching CNT surface and reduces the dispersion efficiency [22]. So improving the water wettability of CNT surface plays an important role in preparation of

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CNT suspension by ultrasonication in aqueous solution. Much effort was previously made to synthesize complex molecules with special functional groups strongly interacting with CNT surface [7,19,23], however, the fundamental issues mentioned above for dispersing CNTs in solutions via ultrasonication were often neglected.

In ancient Chinese age, people had prepared homogeneous ink for calligraphy by grinding the mixture of hydrophobic carbonblack and polysaccharide (or animal bone glue) in aqueous solution. Inspired by this interesting process, our work describes a simple method for dispersing pristine multi-walled carbon nanotubes (MWCNTs) in aqueous solution containing dispersant by using grinding and ultrasonication simultaneously. Chitosan, poly-β (1, 4)-2-amino-2-deoxy-D-glusose, is a cationic polysaccharide in acid medium, which has good biocompatibility, biodegradability, anti-bacterial ability, and multiple functional groups [24]. The hydrophobic groups (–C═OCH_3) in chitosan molecules have a tendency to be adsorbed on MWCNTs, while the hydrophilic groups (–NH_2 and –OH) tend to dissolve in acetic acid aqueous solution. Here, the wettability of pristine MWCNTs in aqueous solution is significantly improved by grinding MWCNTs with chitosan solution together, which is facilitated for their further dispersion in solution by following ultrasonication. The dispersion quality of MWCNTs treated by this method is much better than those treated by grinding or ultrasonication alone. Meanwhile, the structure of MWCNTs is only very weakly destroyed by this method, keeping the original properties of MWCNTs. The mechanism of the improved solubility and dispersion of MWCNTs in aqueous solution by using wet-grinding and ultrasonication simultaneously is also discussed in this paper.

2. Materials and methods

2.1. Materials

Chitosan powder, with a deacetylation degree of 85% and a viscosity of 140 mPa s at 1% concentration in 1% acetic acid, was bought from Zhejiang Golden-Shell Biochemical Co., Ltd. (Yuhuan, China). Multi-walled carbon nanotubes (MWCNTs, purity > 98%, diameter 10–30 nm, length 5–15 μm), manufactured by CVD were purchased from Shenzhen Nanotech Port Co. (China). Glacial acetic acid was purchased from Kelong Chemical reagent plant (Chengdu, China). Distilled water was used throughout.

2.2. Preparation of chitosan/MWCNT suspensions

Firstly, a chitosan solution of 2% (w/v) was prepared by dissolving chitosan in a 2% (v/v) acetic acid aqueous solution followed by filtrating to remove the impurity. Pristine MWCNTs (20 mg) and chitosan solution (5 mL) were ground together in a ceramic mortar and pestle for 5–60 min. The inner sides of mortar were scraped down with the pestle during grinding to ensure that MWCNTs were mixed well with chitosan solution. After that, 45 mL of 2% (v/v) aqueous acetic acid solution was added into the above chitosan/MWCNTs mixture, followed by grinding for another 5 min. After the dilution, the concentrations of chitosan and MWCNTs in the mixture were 0.2% (w/v) and 0.4 mg/mL, respectively. Then, the mixture (50 mL) was transferred into a beaker and ultrasonicated for 15 min at room temperature in an ultrasonic cleaner (29 kHz, 30 W/L) to form a homogeneous suspension with an initial MWCNT concentration of 0.4 mg/mL. The above method for dispersing MWCNTs containing both grinding (G) and ultrasonication (U) procedures is termed as GU. Other control samples were prepared by grinding (G) or ultrasonication (U) alone in chitosan aqueous solution (0.2%). To confirm the interaction between chitosan and pristine MWCNTs for improving the MWCNT dispersion in aqueous solution, pristine MWCNTs were dispersed in 2% (v/v) aqueous acetic acid solution without chitosan using three methods above (GU, G, and U, respectively). For comparison, the initial concentrations of MWCNTs in these samples treated by three different methods are kept at 0.4 mg/mL.

2.3. Preparation of chitosan-coated MWCNTs

MWCNT suspensions were filtered through a cellulose membrane (0.45 μm) and washed with 2% (v/v) acetic acid aqueous solution for several times until no polymer was detected in the filtrate. Subsequently, the distilled water was used to wash the chitosan-coated MWCNTs until the pH value of filtrate got close to 7. Finally, the products were dried in a freeze-drying machine at −59 °C under high vacuum for 24 h.

2.4. Preparation of chitosan/MWCNTs nanocomposites

To compare the effect of dispersion quality of MWCNTs prepared by three methods (U, G and GU, respectively) on the mechanical properties of final chitosan/MWCNTs nanocomposites, their nanocomposites were prepared by solution-casting method. A typical process for preparing chitosan/MWCNTs nanocomposites is as follow: desired amount of chitosan was dissolved in 50 mL of chitosan/MWCNTs suspension with a MWCNT concentration of 0.4 mg/mL prepared by GU method (the same as described in Section 2.2) using a laboratory magnetic stirrer at 200 rpm for 1 h. The final chitosan concentration in solution was 2% (w/v) and the mass ratio of MWCNTs to chitosan was 2 wt%. The resulting solution was degassed for 3 h under vacuum. After that, chitosan/MWCNTs solution was poured into a hydrophobic glass plate and heated at 50 °C to remove the solvents. Other samples were also prepared by the same process.

2.5. Measurements and characterizations

2.5.1. UV/vis absorption measurements

Absorption spectra of chitosan/MWCNTs suspensions were measured by UV/vis spectrophotometer (UV-1800PC, Mapada Co., Ltd., China) in the range of 200–600 nm to examine the solubility and dispersion of MWCNTs in aqueous solution treated by three methods. The absorption of extremely dark MWCNT suspensions prepared in this experiment exceeds the upper limitation of UV/vis spectrophotometer, so all the MWCNT suspensions were further diluted with 0.2% (w/v) chitosan solution to a suspension of MWCNT concentration of 0.067 mg/mL for test. The MWCNT suspensions prepared by G or GU method were incrementally diluted with 0.2% (w/v) chitosan solution to determine the linear regions of plot of absorbance vs. MWCNT concentration.

2.5.2. Scanning electron microscopy (SEM)

MWCNT suspensions were spin-coated on the glass slide at 800 rpm for obtaining a flat surface and quickly dried at 70 °C under vacuum. Then the samples were etched by UV irradiation (provided by Hg light, 254 nm, 100 W) for 5 min to make more MWCNTs exposed for SEM observation. The distance between samples and Hg light was about 30 mm. The dispersion quality of MWCNTs in aqueous solution was examined via SEM (Inspect F, FEI Company) under an acceleration voltage of 10 kV.

2.5.3. Transmission electron microscopy (TEM)

The high-resolution TEM measurement was carried out using a Tecnai G2 F20 electron microscopy with a field emission source (FEI Company) under an accelerated voltage of 200 kV. One drop of MWCNT suspension (after removing free chitosan) was placed

on a copper grid and naturally dried at room temperature for TEM observation.

2.5.4. Rheological measurements

The rheological properties of chitosan/MWCNTs suspensions ground for different time were investigated by RH7D rheometer (Bohlin Instruments Ltd.) using 40-mm diameter cone and plate with a cone angle of 4°. The gap between the cone and the plate was 0.15 mm during measurement. The sample was allowed to equilibrate for at least 5 min at 25 °C before steady shear measurements. The relationship between viscosity and shear rate for each casting solution was obtained at a shear rate range of 0–20 s^{-1}.

2.5.5. Fourier transform infrared (FTIR)

FTIR spectra of chitosan, pristine MWCNTs, and chitosan-coated MWCNTs were measured on a nicolet560 spectrophotometer in the range of 4000–400 cm^{-1} under a transmittance mode. The samples were mixed with KBr, and the resulting mixtures were pressed into disks (about 0.3 mm in thickness) for FTIR test.

2.5.6. Thermogravimetric analysis (TGA)

TGA (WRT-2P, Shanghai Scale Factory) was performed under air flows from 30 to 700 °C at a heating rate of 10 °C/min .The weights of the samples varied from 5 to 8 mg.

2.5.7. Raman spectroscopy

Raman spectra of pristine MWCNTs and chitosan-coated MWCNTs were recorded using a micro-Raman spectrometer (Renishaw) equipped with a Leica microscope. Excitation was provided by the 136 MHe^{+} at 514.5 nm. A beam size of 2 μm was used.

2.5.8. Contact angle measurements

Contact angle goniometer (DSA100) was used to characterize the wettability of MWCNTs with aqueous solution (containing acetic acid). MWCNT suspensions were coated on a clean glass slide and dried at 80 °C. This process was repeated at least 10 times to produce a thick film on the substrates. Contact angles of samples were measured on 3 μL of aqueous solution at room temperature, and the results reported are the mean value of five replicates.

2.5.9. Mechanical property measurements

The mechanical properties of the samples were measured on an Instron universal testing machine 4302 (with a 500 N load cell and pneumatic side-action grips) at room temperature with gauge length of 20 mm and a tensile rate of 5 mm/min according to ASTM D882. The samples were cut into the strip with dimensions of 60.0 mm × 10.0 mm × 0.08 mm using a razor blade, and kept in a desiccator before test. Four parallel measurements were carried out for each sample.

3. Results and discussion

3.1. Dispersion quality of MWCNT suspensions

Due to poor wetting of MWCNTs by water, large amounts of pristine MWCNT aggregates on the surface of water instead of dispersing, even if ultrasonication (U) is applied on them (see Fig. 1a). Some portions of MWCNTs submerge below the surface of water and disperse after grinding (G). The color of the suspension treated by grinding and ultrasonication (GU) becomes darker than that treated by U or G alone, indicating that wet-grinding can improve the ultrasonic dispersion efficiency of MWCNTs in water. However, many MWCNT sediments and floccules still exist in the water. Fig. 1b shows the photograph of MWCNT suspensions with chitosan prepared by three different methods (U, G, and GU, respectively). The dispersion of MWCNTs/chitosan suspension treated by only U

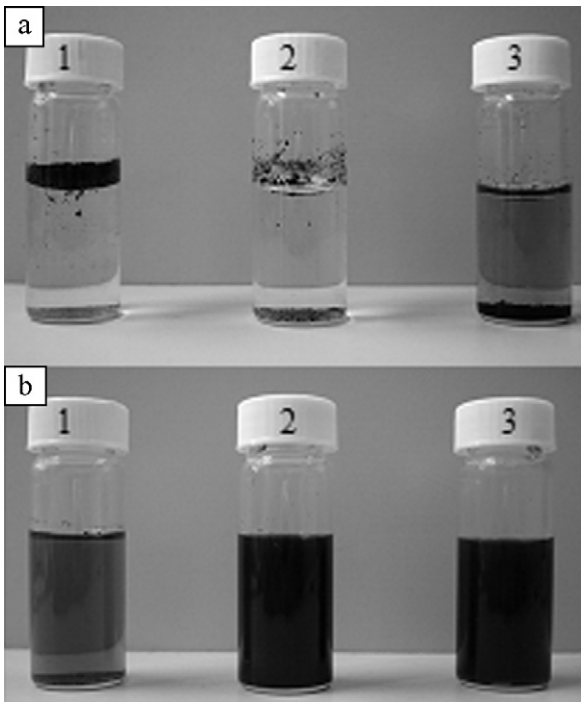

Fig. 1. Photographs of (a) MWCNT suspensions without chitosan prepared by different methods. (b) MWCNT suspensions with chitosan prepared by different methods. The number (1–3) on the vials represents different methods for preparing suspensions: (1) ultrasonication (U); (2) grinding (G); (3) grinding and ultrasonication (GU). All the suspensions are kept for one week.

is still just poor as all the suspensions without chitosan. However, no sediment was observed in chitosan/MWCNTs suspensions prepared by G or GU method alone, indicating that adding chitosan can significantly improve the solubility and dispersion of MWCNTs in solution when grinding was applied. Comparing the photographs of Fig. 1a and b, one can see that the dispersions of pristine MWCNTs in suspensions with chitosan prepared by these three methods are much better than those without chitosan prepared by counterpart methods. It demonstrates that the interaction between chitosan and MWCNTs can also improve the dispersion of MWCNTs in aqueous solutions. Noted that untreated pristine MWCNTs are generally floated and difficult to spread over on the water, which could be due to the large aspect ratio of MWCNTs and surface tension of water supporting the light MWCNTs, despite the density of the MWCNTs (1.2 g/cm^3) being slightly larger than that of water.

The dispersion qualities of MWCNTs in chitosan solution prepared by three methods (U, G, and GU, respectively) were characterized by UV/vis absorption measurements (Fig. 2). The absorption peak at about 260 nm in Fig. 2a is attributed to the characteristic absorption of MWCNTs [25]. Generally, higher absorbance of CNTs indicates better dispersion and solubility in solution [19,25,26]. The low absorbance (<0.3) in chitosan/MWCNTs suspension prepared by U method corresponds to the poor dispersion of MWCNTs as observed in Fig. 1b. After grinding, the absorbance of chitosan/MWCNTs suspension largely increases. The maximum absorbance (about 2.85) of suspension is observed when chitosan//MWCNTs suspension is treated by both grinding and ultrasonication. Fig. 2b shows the UV/vis spectra of G and GU treated chitosan/MWCNTs suspensions at different relative concentration of MWCNTs. The absorbance of chitosan/MWCNTs suspensions prepared by G method does not depend on the MWCNT concentration in a linear fashion, which is attributed to the relatively poor dispersion of MWCNTs [19,27]. However, the absorbance of suspension prepared by GU method increases

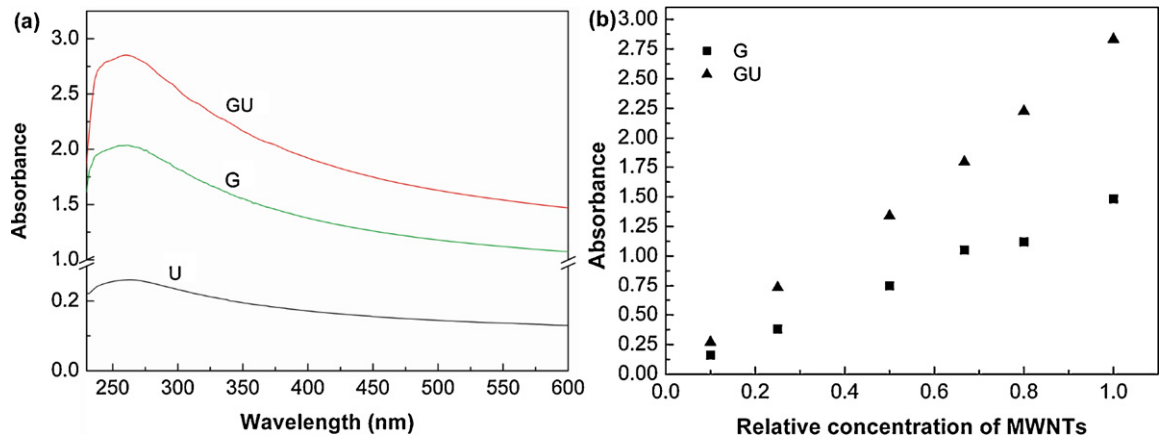

Fig. 2. (a) Absorbance spectra of MWCNT suspensions prepared by different methods (U, G, GU methods, respectively). The initial concentrations of MWCNTs in all the suspensions are 0.067 mg/mL. (b) Absorbances of MWCNT suspensions at 260 nm prepared by G and GU methods as a function of relative concentration of MWCNTs. The absorbance for each point was measured for three times and the error is ±3%.

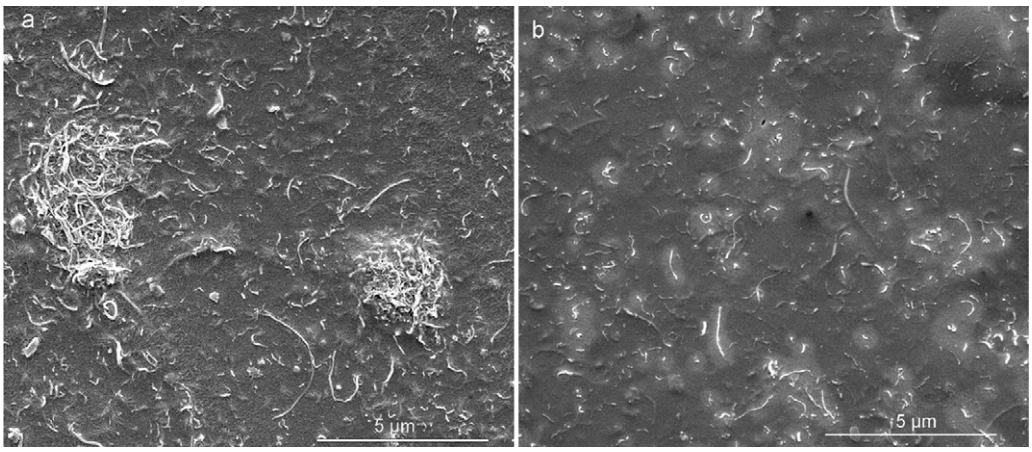

Fig. 3. SEM images of chitosan/MWCNTs suspensions after (a) grinding (G), and (b) grinding and ultrasonication (GU).

linearly with increasing MWCNT concentration in this experiment, basically obeying the Lambert–Beer's law [19]. This indicates that the best dispersion quality of MWCNTs in suspension can be obtained by combining both the grinding and ultrasonication among these methods.

The dispersion qualities of chitosan/MWCNTs suspensions were further examined by SEM. Fig. 3 shows the SEM images of suspensions, which are prepared by G and GU methods, respectively. It was found that both large MWCNT aggregates (size of several tens microns) and individual nanotubes exist in suspension after grinding. Although MWCNT bundles can be partially exfoliated by grinding, small-sized aggregates are difficult to further break up due to limited contact areas between pestle and nanoparticles, and limited power by using grinding alone. After GU treatment, fewer MWCNT aggregates and many individual MWCNTs were observed in the suspension (Fig. 3b), which is consistent with the UV/vis results (Fig. 2). Stress–strain curves for neat chitosan, chitosan/2 wt% MWCNTs nanocomposites prepared by different methods (U, G, and GU, respectively) are shown in Fig. 4. One can see that the tensile strength and elongation at break in nanocomposite prepared by U method exhibit severe deterioration compared to the neat chitosan. In contrast, the tensile strengths of chitosan nanocomposites prepared by G and GU method obviously increase after incorporation of MWCNTs. The highest mechanical property was obtained in nanocomposite prepared by GU method. In this case, tensile strength increases from 53.0 ± 2.2 to 77 ± 4.5 MPa by 45% compared to the neat chitosan. This indicates that improvement of mechanical property in chitosan nanocomposites results from the good dispersion of MWCNTs. The dispersion quality of MWCNTs in nanocomposites prepared by GU is better than that prepared by U or G method alone. It can be concluded that wet-grinding is necessary for obtaining good dispersion of MWCNT before ultrasonication based on the SEM observation, mechanical tests, and UV/vis results. Thus, the important role of wet-grinding in assisting ultrasonic dispersion of MWCNTs in aqueous solution will be discussed in detail.

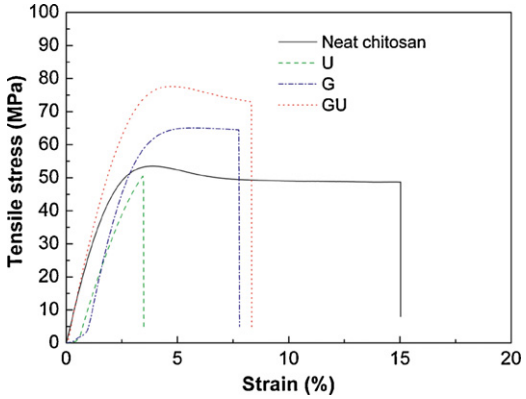

Fig. 4. Stress–strain curves for neat chitosan, chitosan/2 wt% MWCNTs nanocomposites prepared by different methods (U, G, and GU, respectively).

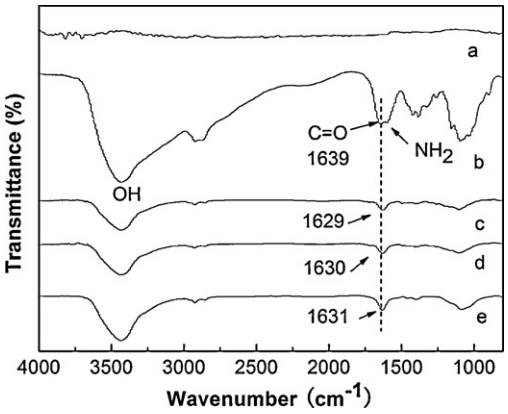

Fig. 5. FTIR spectra of (a) pristine MWCNTs, (b) chitosan, chitosan-coated MWCNTs treated by (c) ultrasonication, (d) wet-grinding, and (e) wet-grinding assisted ultrasonication.

3.2. The interaction between chitosan and MWCNTs treated by wet-grinding

Fig. 5 shows the FT-IR spectra of (a) pristine MWCNTs, (b) chitosan, chitosan-coated MWCNTs treated by (c) ultrasonication, (d) wet-grinding, and (e) wet-grinding assisted ultrasonication. For chitosan, the strong bands at 3430, 1639, and 1599 cm^{-1} are ascribed to –OH group, the amide I (C=O stretching of $–NHCOCH_3$), and amide II (N–H blending modes) absorbances [28], respectively. The MWCNTs treated by ultrasonication or grinding exhibit the characteristic peaks of chitosan, which indicates chitosan coated on pristine MWCNTs. After ultrasonication or grinding, amide I band for chitosan-coated MWCNTs shifts toward to low frequency from 1639 to 1629 cm^{-1} (or 1630 cm^{-1}). This result may be attributed to the strong interaction between hydrophobic $–COCH_3$ of chitosan and the surface of MWCNTs; or the change of hydrogen-bonding interaction of functional groups produced by the conformation change of chitosan chains on the MWCNTs. The FTIR pattern of chitosan-coated MWCNTs (Fig. 5e) prepared by grinding assisted ultrasonication is similar to that prepared by grinding alone, indicating that following ultrasonication does not affect the interaction between chitosan and MWCNTs. It seems that amide II disappears and only amide I band is observed for MWCNTs treated by ultrasonication or grinding. In fact, this is resulted from the overlap of shifted amide I band with amide II band. The FTIR could not distinguish the effects of ultrasonication and grinding on the interaction between chitosan and MWCNTs due to their similar FTIR spectra (Fig. 5c–e).

Raman spectra were used to examine the effect of wet-grinding on the structure of MWCNTs. The Raman spectra of pristine MWCNTs and their chitosan-coated MWCNTs prepared by different methods are shown in Fig. 6. As shown in Fig. 6a, pristine MWCNTs display two characteristics peak at 1345 and 1570 cm^{-1}, corresponding to D-band (C–C, the disordered graphite structure) and G-band (C=C, sp^2 carbon), respectively [7]. Fig. 6b shows that the location of the characteristic peak of MWCNTs prepared by ultrasonication alone has no obvious change as compared to that of pristine MWCNTs. However, the G-band of MWCNTs shifts to higher wavenumber from 1570 to 1577 cm^{-1} upon combination with chitosan by wet-grinding (Fig. 6c), which is indicative of strong interaction between chitosan and MWCNTs due to increase of the harmonic oscillator of polymer-coated CNTs [19,29]. The hydrophobic and π–π interactions between chitosan ($–C=OCH_3$) and graphite sheet of MWCNTs (C=C) increase the energy necessary for vibrations to occur, which leads to upshift of Raman peaks [19]. These results show that the enhancement of interaction between chitosan and MWCNTs by wet-grinding is more efficient than by ultrasonication. Meanwhile, it is found that the Raman spectrum of MWCNTs treated by grinding and ultrasonication method is similar to that treated by wet-grinding alone, indicating that the interaction between chitosan and MWCNTs is not obviously weaken by ultrasonication. This can be well used to understand the improved solubility and dispersion of MWCNTs by wet-grinding, as indicated by visual observation (Fig. 1) and UV/vis measurements (Fig. 2).

Chitosan cannot be selectively removed under nitrogen condition to calculate the polymer content of chitosan-coated MWCNTs due to formation of carboneous chitosan after 350 °C, so TGA measurements were carried out under air flow. Fig. 7 shows the TGA curves of chitosan, pristine MWCNTs and chitosan-coated MWCNTs treated by different methods under air flows. From the TGA curves, one can see that the chitosan contents of MWCNTs treated by U, G, and GU method are approximate 7, 17, and 19%, respectively. This result provides an additional evidence that wet-grinding can improve the interaction between chitosan and MWCNTs compared to ultrasonication. In addition, the chitosan wrapped on MWCNTs after grinding, does not increase very much after ultrasonication.

3.3. The effect of wet-grinding on the morphology of MWCNTs

SEM images of pristine MWCNTs and chitosan-coated MWCNTs treated by three methods are shown in Fig. 8. Compared to pristine MWCNTs, the morphology and structure of MWCNTs after these treatments have no obvious change, keeping a length of more than 5 μm (according to the manufacture's specification). It is interesting that most MWCNTs are not shortened by

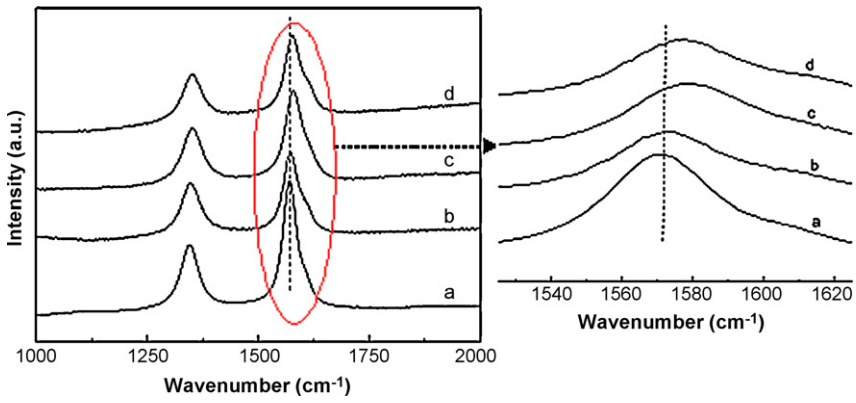

Fig. 6. Raman spectra of (a) pristine MWCNTs, (b) chitosan-coated MWCNTs treated by ultrasonication, (c) chitosan-coated MWCNTs treated by wet-grinding, (d) chitosan-coated MWCNTs treated by wet-grinding and ultrasonication. The graph on the right shows the highlighted G-bands of (a)–(d) in Raman spectra.

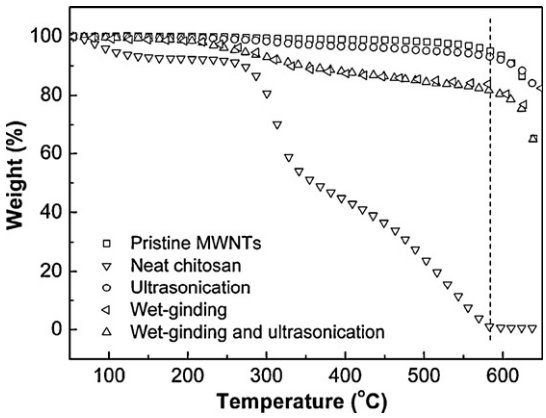

Fig. 7. TGA curves of pristine MWCNTs, chitosan, and chitosan-coated MWCNTs treated by different methods in air flow.

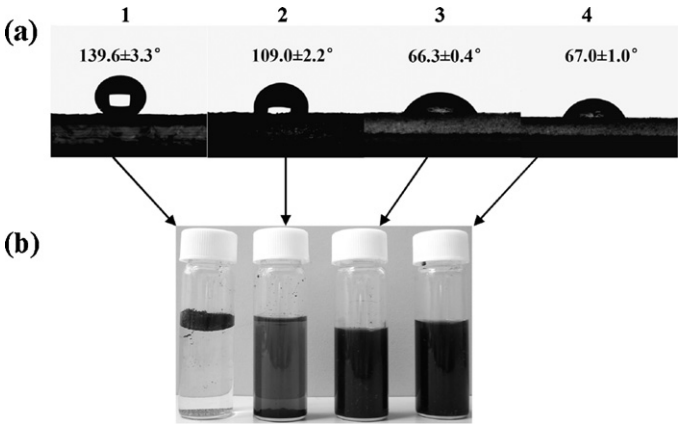

Fig. 9. (a) Contact angles of pristine MWCNTs (1), MWCNTs treated by ultrasonication (2), wet-grinding (3) and wet-grinding assisted ultrasonication (4) (from left to right); (b) pristine MWCNTs (1), MWCNTs treated by ultrasonication (2), wet-grinding (3) and wet-grinding assisted ultrasonication (4) (from left to right) were re-dispersed in acetic acid aqueous solution (2%, v/v).

wet-grinding in chitosan solution. Generally, shear and friction forces produced during grinding with extremely strong energy are used to break the inorganic fillers into micro or nanoscale particles [30]. Previous researches also showed that modification of CNTs by dry-state grinding leads to seriously shorten length of MWCNTs (below 1 μm) [31,32], which significantly damages the unique properties of CNTs (e.g. mechanical and electrical properties). Here, chitosan solution may act as a lubricating stock for MWCNTs, which protects MWCNTs from serious damage by grinding force.

3.4. The effect of wet-grinding on the wetting of MWCNTs by aqueous solution

The effect of wet-grinding on the wetting of MWCNTs by aqueous solution was characterized by water contact angle and rheological measurements. Fig. 9a shows the water contact angles of pristine MWCNTs and chitosan-coated MWCNTs treated by ultrasonication, wet-grinding and wet-grinding assisted ultrasonication. The water used for this test contains 2% (v/v) acetic acid.

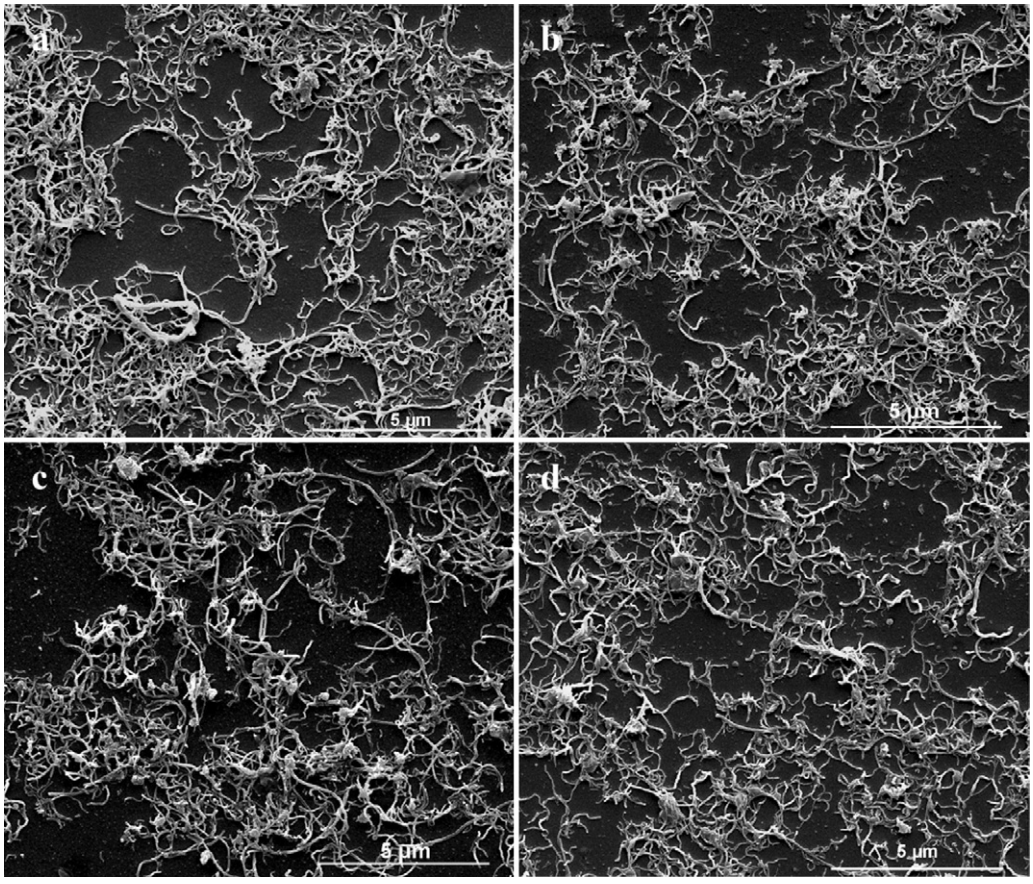

Fig. 8. SEM images of (a) pristine MWCNTs, (b) chitosan-coated MWCNTs treated by ultrasonication, (c) chitosan-coated MWCNTs treated by wet-grinding, (d) chitosan-coated MWCNTs treated by wet-grinding and ultrasonication.

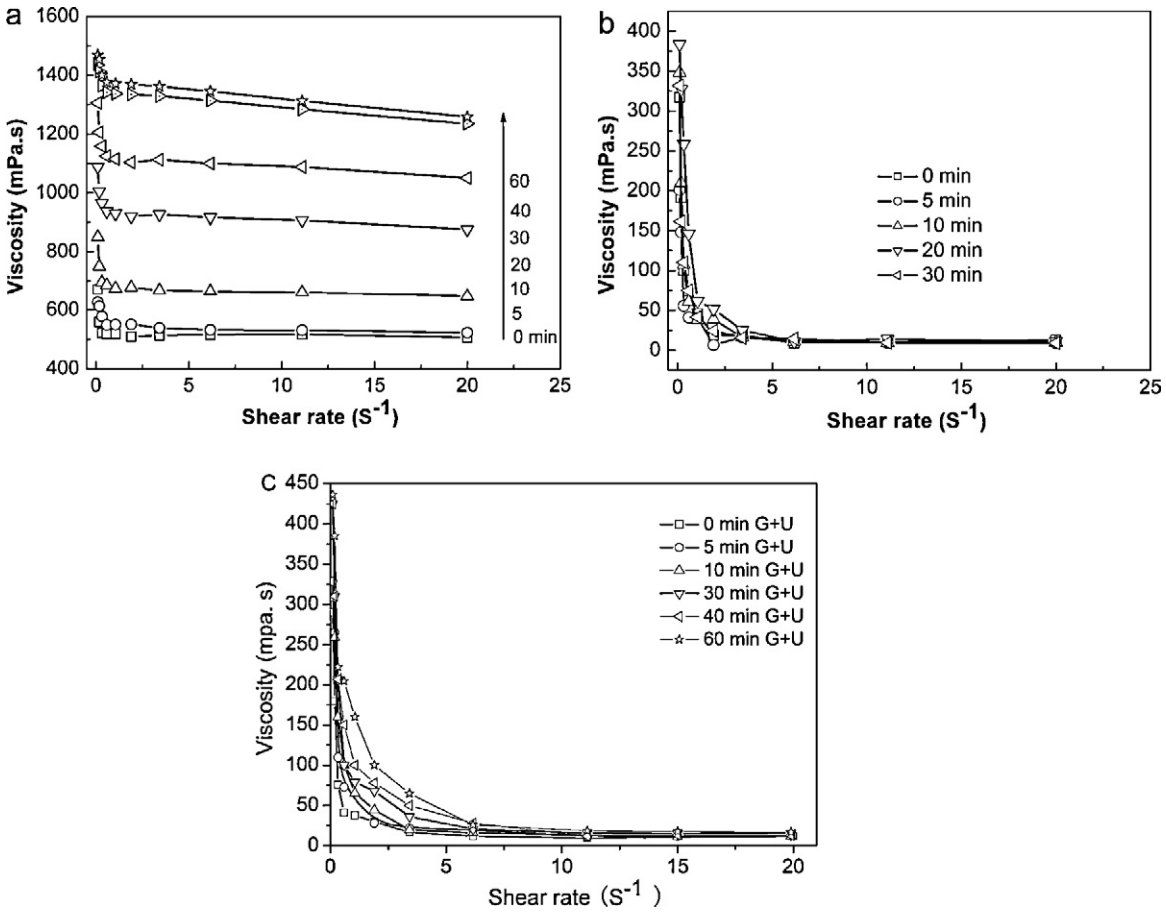

Fig. 10. The plots of shear viscosities vs. shear rate for chitosan/MWCNTs suspensions prepared by (a) wet-grinding, (b) ultrasonication, and (c) wet-grinding assisted ultrasonication with different time. The chitosan concentrations in (a–c) are 2, 0.2, and 0.2% (w/v), respectively. The ultrasonication times for all samples in (c) are constantly kept at 15 min. Being different from (a), the chitosan concentrations in (b) and (c) were diluted to 0.2% (w/v) for efficiently applying ultrasonication in suspensions because MWCNTs are difficult to be dispersed into the chitosan solution (2%) with high viscosity.

Pristine MWCNTs show high contact angle ($139.6 \pm 3.3^\circ$) due to their highly hydrophobic surface as expected, which leads to the poor water wettability of MWCNTs. After ultrasonication, the contact angle of MWCNTs decreases slightly, but it is still not wetted by water. However, for the MWCNTs treated by wet-grinding, the contact angle significantly decreases from $139.6 \pm 3.3^\circ$ to $66.3 \pm 0.4^\circ$, which indicates the improved wetting of MWCNTs by water. It can also be confirmed that only wet-grinding can largely improve the water wettability of MWCNTs by visually comparing the dispersion of MWCNTs treated by different methods in aqueous solution (Fig. 9b). MWCNTs treated by ultrasonication in chitosan solution still have poor dispersion, but those treated by wet-grinding can dissolve in solvent. The content of hydrophilic chitosan wrapped on MWCNTs treated by wet-grinding is much higher than that treated by ultrasonication as shown in TGA results (Fig. 7). Thus, the significantly increased hydrophilicity of MWCNTs treated by wet-grinding results in the improvement of wetting of MWCNTs by water, which provides a good ultrasonic wave transport condition for subsequent ultrasonication. It is noted that the contact angle and dispersion state of MWCNTs treated by wet-grinding assisted ultrasonication are almost the same as that prepared by wet-grinding alone, demonstrating that ultrasonication does not affect the water wettability of MWNTs improved by wet-grinding due to strong bond between chitosan and MWNTs.

During the dispersion of MWCNTs in aqueous solution, wet-grinding plays a very important role in enhancing the wetting of MWCNTs by solvent by wrapping the hydrophilic chitosan on them, in addition to breaking up the MWCNT aggregates. The changes in wetting of MWCNTs in aqueous solution with increasing the grinding time were characterized by rheological measurements (Fig. 10). Fig. 10a shows that the chitosan/MWCNTs suspensions with different grinding time exhibit shear-thinning behavior like most non-Newton fluids. In the first 5 min, the viscosity of suspension increases slowly, corresponding to a period of roughly mixing MWCNTs with the chitosan and the decreasing size of MWCNT aggregates. Then, the viscosity of the suspension obviously begins to increase with increasing the grinding time due to the continuously increased wetting of MWCNTs by water via wrapping hydrophilic chitosan. After 40 min, viscosity of the suspension gets saturated, which may be due to the limited ability of wet-grinding for decreasing the size of MWCNT aggregates and dispersing them into chitosan solution. The strong interaction between chitosan and MWCNTs induced by wet-grinding leads to an obvious increase in suspension viscosity. Some researchers also used rheological test to monitor the dispersion state of CNT suspensions [33–35]. Their studies showed that CNT suspensions with better dispersion exhibited a higher viscosity. In this study, the viscosity of increases with the increase of grinding time, which also demonstrates that the dispersion quality of MWNTs is enhanced as the grinding time increases. In other words, the dispersion quality of MWNTs has the dependence on grinding time. In contrary, there is no obvious increase in viscosity of the suspension treated by ultrasonication alone as shown in Fig. 10b, which is attributed to the poor wetting and dispersion of MWCNTs. The viscosities of chitosan/MWCNTs suspensions prepared by grinding with different time and ultrasonication are shown in Fig. 10c. The viscosities at low shear rate

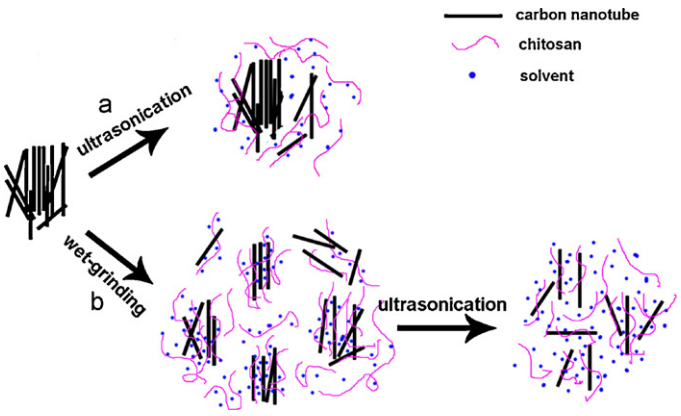

Fig. 11. Schematic illustration of preparation of chitosan/MWCNTs suspensions by two different methods: (a) ultrasonication; (b) wet-grinding and ultrasonication.

(below 7 s^{-1}) of chitosan/MWCNTs suspensions prepared by grinding assisted ultrasonication are higher than those prepared by ultrasonication. Shear viscosities in the suspensions prepared by grinding assisted ultrasonication exhibit more resistant to shear rate than those prepared by ultrasonication alone. These results provide the additional evidence that the interaction between chitosan chains and MWCNTs can be improved by grinding and it is not weakened by following ultrasonication.

3.5. The mechanism for wet-grinding assisted ultrasonic dispersion of MWCNTs in aqueous solution

Fig. 11 shows the schematic illustration of preparation of chitosan/MWCNTs suspensions by U and GU methods. Due to the poor wetting of pristine MWCNTs by solvent, the surface and interspaces of MWCNT aggregates are always covered by air layer. In the case of ultrasonicating pristine MWCNTs in aqueous solution, it is difficult for chitosan and solvent to diffuse into the interspaces of MWCNT aggregates to replace the air, as shown in Fig. 11a. Thus, the incoming ultrasonic wave in liquid is mostly reflected at the gas/liquid interface and the refractive wave also decays very quickly [22], which leads to the low ultrasonic efficiency for dispersing MWCNTs in aqueous solution. In other words, air covering on MWCNT surface acts as a barrier layer preventing ultrasonicwaves from reaching MWCNTs. The MWCNTs located on the outside of the aggregates can be wrapped by chitosan or be wettable by solvent, which can be easily peeled off by ultrasonic wave. So a lot of MWCNT aggregates with large size still keep in the suspension (Fig. 1). However, wet-grinding has two advantages for assisting ultrasonic dispersion of MWCNTs in aqueous solution. On one hand, grinding can break up MWCNTs into a number of small aggregates along with exfoliation into individual nanotubes, and make them looser as observed by SEM image (Fig. 3a). This would ease the loading of ultrasonication for dispersing MWCNTs. On the other hand, grinding can improve the interaction between MWCNTs and chitosan (as discussed in Section 3.2), and make more hydrophilic chitosan uniformly wrap MWCNTs, which is facilitated to increase the wetting of MWCNTs by water. To further examine the mechanism of the effect of grinding on the wetting of CNTs by water, the interfaces of adjacent CNTs are remarked by red arrows in Fig. 12. From the SEM image of MWCNTs treated by wet-grinding (Fig. 12b), one can see that chitosan not only wraps the surface of MWCNTs but also fills into the interspaces of MWCNT aggregates, which is not observed in MWCNTs treated by ultrasonication alone (Fig. 12a). This means that solvent can also wet the interspaces of MWCNTs to eliminate the air layer barrier for ultrasonicwaves to transport into MWCNT aggregates. Thus, the same ultrasonicwave can reach MWCNT aggregates more efficiently and further break them into individual

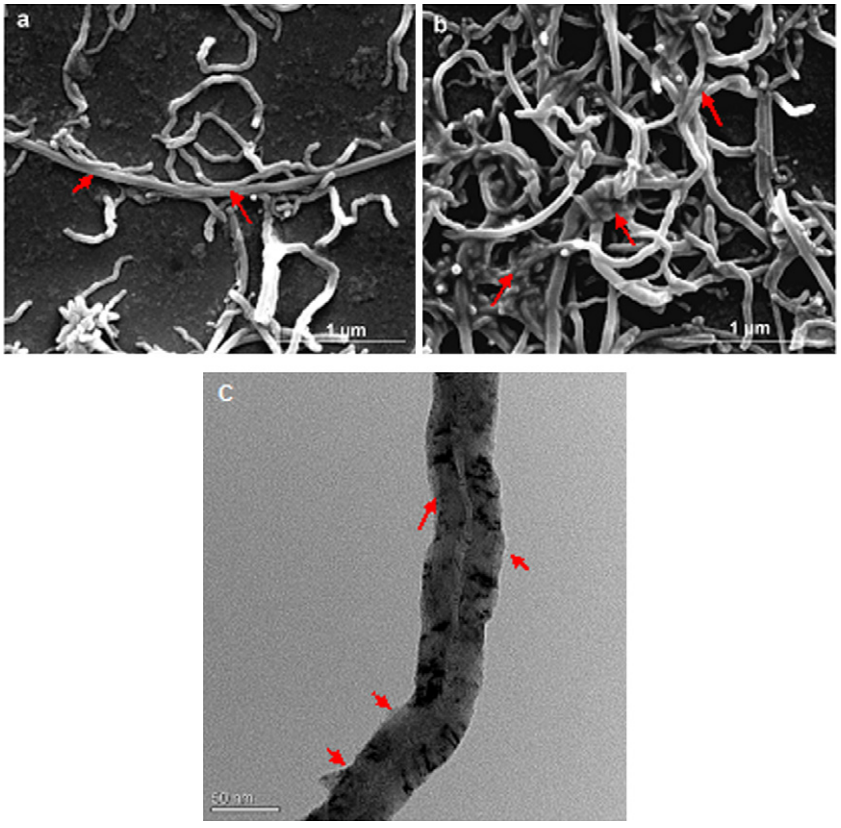

Fig. 12. SEM images of chitosan-coated MWCNTs prepared by (a) ultrasonication, and (b) wet-grinding at a high magnitude of 100,000; (c) TEM image of chitosan-coated MWCNTs prepared by wet-grinding and ultrasonication.

nanotubes. The microstructure of chitosan-coated MWCNT prepared by GU method can be further verified by TEM (Fig. 12c). It is seen that MWCNT surface is wrapped by chitosan layer with a thickness of 4–6 nm as indicated by red arrows, which could help MWCNTs dissolve in aqueous solution. It is noted that the sample is treated by ultrasonication, but chitosan still wraps closely on MWCNT surface, which indicates a strong interaction between chitosan and MWCNTs. This is consistent to the Raman results.

In this study, chitosan, an amphiphilic cationic polymer is used as a macromolecular dispersion agent for dispersing and stabilizing pristine MWCNTs. The hydrophobic acetyl group (–C═OCH_3) and backbone of chitosan can provide the binding with hydrophobic surface of MWCNTs by hydrophobic and π–π forces, while the hydrophilic part of polymer (amino with positive charges and hydroxyl groups) will greatly help MWCNTs dissolve in aqueous solution. Bedsides, chitosan can prevent the individual MWCNT from re-aggregating in suspension by electrostatic and steric repulsion.

4. Conclusion

In summary, homogeneous and stable chitosan/MWCNTs suspension has been successfully prepared by wet-grinding assisted ultrasonication (GU) method. The dispersion quality of MWCNT suspension prepared by this method is far better than that by ultrasonication or wet-grinding alone. Unlike the previous dried-grinding modified CNTs, GU method only weakly damages the MWCNTs, keeping a length of more than 5 μm (similar to original MWCNTs). Here, grinding has two advantages for assisting ultrasonic dispersion of MWCNTs in aqueous solution: (1) grinding can break up large MWCNT aggregates into a number of small aggregates along with exfoliation to individual nanotubes which can ease the work loading of ultrasonication for dispersing MWCNTs; (2) most importantly, grinding can improve the interaction between MWCNTs and chitosan and eliminate the air barrier layer around MWCNTs for the transport of ultrasonicwaves to MWCNTs by improving the wetting of MWCNTs by water. Chitosan wrapped on MWCNTs by hydrophobic and π–π forces increases the solubility of pristine MWCNTs in aqueous solution. Our work describes a simple method for integrating MWCNTs and biocompatible chitosan into a dispersion, which may have good potential application in biotechnology, such as preparing composite materials for medicine, bio-fiber, biosensor, antibacterial coating, and cell cultivation. Here we just provide a basic insight to largely improving the dispersion of CNTs by combining chitosan (dispersant) with GU method. The scalable production of CNT dispersion will be done in our future work by using well-designed automatic grinding equipment.

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