Synthesis and Characterization of Water-Soluble Multi-walled Carbon Nanotubes Functionalized with Polycystine

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Water-soluble multi-walled carbon nanotubes (MWNTs) functionalized with polycystine were prepared by solid-state polycondensation reaction under the irradiation of the infrared heat lamp, which were characterized by transmission electron microscope, X-ray powder diffractometer, and FT infrared spectroscopy. Its solubility in water was close to 7 mg/mL and no precipitates were observed after one month. This may opens the way to improve the interactions between MWNTs and polymer by the hydrogen bond, the dispersion of MWNTs in composite and the compatibility of MWNTs with biological systems.

Since carbon nanotubes (CNTs) discovered by Iijima in 1991,[1] because of their extraordinary mechanical, optical and electronic properties, they have been received great attention. However, chemical manipulation, quantitative characterization, wide application, and processing of CNTs had been limited by their insolubility in most common solvents. Recently, the solubilization of CNTs via chemically functionallized[2–4] or polymer-wrapped[5] approach has provided excellent opportunities for studying their optical properties under the condition of homogeneous dispersion at the individual nanotubes level. Therefore, considerable efforts have been devoted to chemically modify the CNTs, which might provide a way for many useful applications.[6] Some attempts have been made to attach biological molecules such as peptides,[7] enzymes,[8] antibody,[9] and DNA[10] onto the sidewalls of SWNTs to fabricate highly sensitive biosensors. But, there have been only a few reports about water-soluble functionalized MWNTs. Here we report a simple way to prepare water-soluble functionalized MWNTs through a solid-state reaction of cystine and MWNTs under the irradiation of infrared lamp. The product, polycystine-MWNTs (p-MWNTs), can be dispersed in water easily to form a homogeneous solution, and its solubility was about 7 mg/mL without the aid of ultrasonic agitation. It can be remained in aqueous solution for a long time and no precipitation could be observed after one month. This may open the way to a high number of opportunities, such as improving the interactions between MWNTs and polymer by the hydrogen bond, the dispersion of MWNTs in composite and the compatibility with biological systems.

MWNTs with 95% purity were prepared by thermal catalytic decomposition of hydrocarbon,[11] which were further purified with a mixture of H_2SO_4 and HNO_3 before used. In a typical synthesis, the 860 mg of L-cystine and 59 mg of MWNTs were mixed and ground for 10 min. Then, 570 mg of KOH was added and the mixtures were further ground for 30 min, afterward, they were ground at interval under the irradiation of infrared lamp (220 V, 250 W) with temperature at about 120 °C for 6 h. The mixtures were cooled in air and dissolved in 5-mL deionized water to form a red solution and its pH was adjusted to 7 with diluted HCl solution (ca 0.04 M). A lot of precipitate was obtained when acetone was added into the above red solution. The steps of washing with acetone and centrifuging were repeated until no chloride ions were detected. After dried at 60 °C for 4 h under vacuum, the black powder with 350.2 mg was obtained. As comparison, the similar process was applied to prepare the polycystine, and 310.4 mg of yellow powder was obtained. It is notable that the temperature is critical for the forming of polycystine.

Figure 1 shows the photographs of p-MWNTs, MWNTs and polycystine in an aqueous solution. The solution of p-MWNTs is black (Figure 1c) without the aid of sonication, whereas, the polycystine dissolved in water formed a yellow solution (Figure 1a). The original MWNTs are not dispersed in water even after sonication (Figure 1b). It revealed that the MWNTs had been modified by polycystine to form the p-MWNTs that can be dispersed in water to form a homogenous solution.

The TEM (HITACHI H-800) image shown in Figure 2a indicated that the polycystine exists in microrods without sonication. This is because the polycystine aggregated together through the interaction of hydrogen bonds between molecules. However, these interactions were destroyed by sonication and polycystine exist in nanoparticles (Figure 2b). From Figure 2c, it can be seen that polycystine has wrapped MWNTs and aggregated together. When the p-MWNTs were agitated by sonication for 5 min, polycystine would be deviated from the surface of MWNTs, as shown in Figure 2d.

The X-ray powder diffraction (XRD; Shimadzu XRD-6000 diffractometer with Cu Kα radiation, $\lambda = 1.5406$ Å) patterns shown in Figure 3 indicated that p-MWNTs have the same diffraction peaks as polycystine, when the MWNTs have been wrapped completely with the polycystine in the solid state. When MWNTs as raw materials is excess, the diffraction peak of MWNTs (Figure 3d) in p-MWNTs were observed.

The FTIR (BIO-RED FTS-40, USA) spectra of L-cystine, polycystine and p-MWNTs are shown in Figure 4. A strong

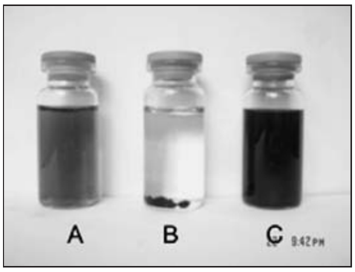


Figure 1. Photographs of vials showing polycystine in water (**A**), MWNTs in water after ultrasonication (**B**) and p-MWNTs in water without the aid of ultrasonication (**C**) (the concentration is about 7 mg/mL).

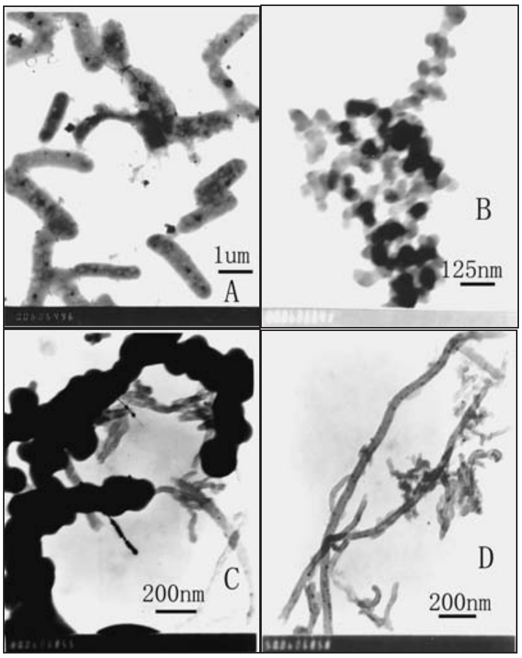


Figure 2. TEM images of polycystine without sonication (A), after sonication for 5 min (B); and p-MWNTs without ultrasonication (C) and after sonication for 5 min (D).

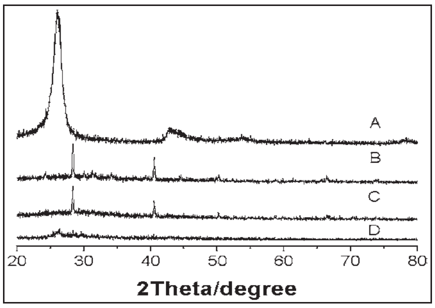


Figure 3. XRD patterns of MWNTs (A), polycystine (B), p-MWNTs (C), p-MWNTs prepared with excess MWNTs (D).

and wide peak at about 3000 $\mathrm{cm^{-1}}$ can be observed in Figure 4a, which belongs to the characteristic peak of the amino acid for cystine. In Figures 4b and 4c, the peak at 3436 $\mathrm{cm^{-1}}$ for N–H stretching vibrational absorption has disappeared, but a strong and wide peak at about 3400 $\mathrm{cm^{-1}}$ appeared, which indicated that a new amide group have been formed. The disappearance of peaks between 900 and 400 $\mathrm{cm^{-1}}$ are due to the reduction of the vibrational mode resulted from the formation of the six-group ring (as shown in Scheme 1). The IR spctra of polycystine and p-MWNTs are similar, which confirmed further that MWNTs were functionallized noncovalently with polycystine.

In summary, a solid-state reaction was applied to modify MWNTs with polycystine noncovalently under the irradiation of the infrared heat lamp. The product deliquesces very easily to form a homogenous solution without the aid of ultrasonication, which may have promising applications in biosensores. The further research is in progress.

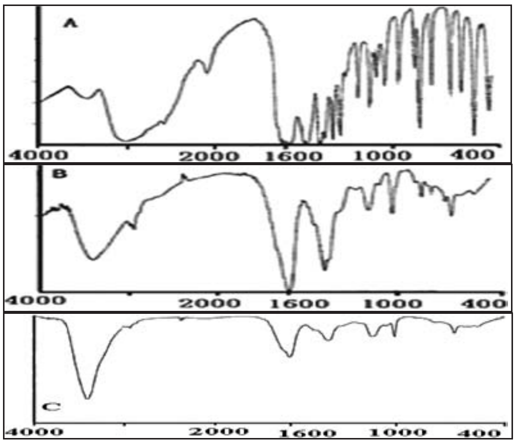
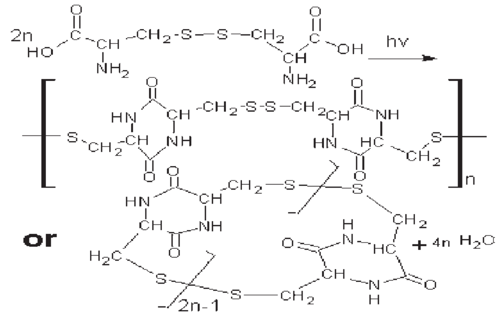


Figure 4. FTIR spectra of cystine (A), polycystine (B), and p-MWNTs (C).



Scheme 1. The proposed structures for polycystine.

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