Short communication

Aqueous stability of oxidized carbon nanotubes and the precipitation by salts

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ARTICLE INFO

Article history:

Received 8 January 2008

Received in revised form 31 July 2008

Accepted 14 October 2008

Available online 19 October 2008

Keywords:

Carbon nanotube

Stability

Dispersion

Precipitation

Fate and transport

ABSTRACT

The stability of nitric acid oxidized carbon nanotubes (CNTs) and the precipitation of oxidized CNTs in water by salts were investigated. Stability investigation shows that during an aging time of 30 days, oxidized CNTs dispersion shows characteristic UV–vis absorbance peak of individual CNTs at 252 nm and CNTs concentration in the dispersion after 30 d aging is 85% of the initial concentration. The precipitation value of salts were measured and the precipitation value follows the order of $\text{NaCl} > \text{KCl} > 1/2(\text{MgCl}_2) > 1/2(\text{CaCl}_2) > 1/3(\text{FeCl}_3) > 1/3(\text{AlCl}_3)$. The nature of anions investigated has little effect on precipitation values of salts.

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1. Introduction

Nano-materials are novel promising materials which have attracted researchers' interest. Because of their unique physical and chemical properties, nano-materials have great potential use in agriculture, computer, medicine, military and many other areas. Simultaneously, it has been recognized that because of their ultra-fine particle size, nano-materials can enter cells or even cross the blood–brain carrier [1–3] and cause harm to organisms. Much research has been done to investigate the toxicity of nano-materials on organisms [4–10].

When nano-materials enter the aquatic environment, they may harm aquatic organisms or even harm human health through food chain and drinking water. Understanding their fate in natural environment is necessary for assessing their possible exposure routes to human being and the ecosystem. Up to now, only limited research has been carried out in this area. Among many kinds of nano-materials, carbon nanotubes (CNTs) are one of the most-rapidly developed. CNTs have unique mechanical, electrical, optical and thermal properties and can be used to prepare novel materials such as hydrogen storage materials, superconductors, reinforced materials, etc. [11–13]. The annually increasing production and utilization of this kind of nano-material will inevitably result in the introduction of CNTs to the environment [14]. Especially, in recent years, there is an increasing interest in preparation and application of aqueous CNT dispersions [15–20]. With the development and appli-

cation of CNT dispersions, the stabilized CNTs will inevitably be discharged in the environment. Investigation on the fate and transport of stabilized CNTs in the aquatic environment will be necessary to assess the risks they may pose to the environment and human being.

Until now, there is a lack of detailed knowledge on the fate and transport of CNTs in water. Recently, Hyung et al. [14] found that natural organic matter stabilizes carbon nanotubes in the aqueous phase. Oxidized CNT dispersion is one of the presently developed CNT dispersions. In this study, the stability of oxidized CNTs, which have potential application as supporters, field emission materials, adsorbents [21–24] and are extensively investigated for preparation of CNT dispersion [25,26] were investigated. The effect of salts on the stability was also investigated.

2. Materials and methods

2.1. Materials

CNTs used in this study were multi-walled carbon nanotubes with diameter of around 60 nm and length of several hundreds to several thousands of nanometers, which were from Tsinghua University and were prepared by catalytic pyrolysis of the propylene-hydrogen. Reagents used were all of analytical grade. Ultra-pure water was used throughout the experiments.

2.2. Preparation of oxidized CNTs dispersion

The oxidized CNTs were prepared by refluxing purified CNTs with concentrated nitric acid. For the preparation of oxidized CNTs

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dispersion, CNTs were first immersed in concentrated nitric acid and then hydrofluoric acid for 24 h each to dissolve the catalyst particles. The oxidized CNTs were prepared by adding 5.0 g CNTs into 500 mL 50% nitric acid and fluxed for 12 h. After standing for 24 h, the sample was filtered using a 0.025 μm filter, washed till the pH of the filtrate reaches 6.0 and then dispersed in water with mechanically stirring. CNTs concentration of the dispersion was analysed and the prepared dispersion was further diluted to certain concentrations using ultra-pure water for experimental investigation.

2.3. Concentration, zeta potential and UV–vis absorption spectra measurement

CNTs concentration measurement in the dispersion was analysed using total organic carbon (TOC) measurements. Before the measurement, a standard curve was established between the CNTs concentration and the dispersion TOC value. For the standard curve establishment, CNTs concentration was analysed by evaporation and drying of 50 mL dispersion at 100 °C and CNTs concentration of the dispersion was calculated according to the weight of residue CNTs after drying. Zeta potential of the dispersion was determined by microelectrophoresis using a Malvern model Zetasizer 2000 zeta potential analyzer using dispersion with CNTs concentration of 0.1 g/L. UV–vis absorbance spectra was recorded at a Hach model DR5000 UV–vis spectrophotometer using a dispersion with CNTs concentration of 0.03 g/L.

2.4. Oxidized CNTs sedimentation investigation

Sedimentation investigation was carried out in a series of 200 mL flasks. To each flask, 100 mL 0.1 g/L as-prepared oxidized CNTs dispersion was added. The flasks were set for settling for different time. After settling, the supernatants were carefully removed and collected for CNTs concentration analysis.

2.5. Determination of precipitation values

The determination of precipitation values of salts were carried out in 100 mL glass tubes according to procedures described by Zhou et al. [27]. For determination of precipitation value of each salt, certain volume of oxidized CNTs dispersion was added to each tube. Then different amount of salt solution of prescribed concentration was added to each tube to make different salt concentration. The total volume of the mixture was 50 mL and CNTs concentration of the mixture was 0.10 g/L. Then pH of the mixture was adjusted to 6.0 ± 0.2 and the mixtures were set for standing for 2 h. The minimum salt concentration at which oxidized CNTs precipitate was determined as the precipitation value.

3. Results and discussion

3.1. Stability of oxidized CNTs

Fig. 1 shows the zeta potential of oxidized CNTs in water. It can be seen that during the pH range of 2.6–6.5, oxidized CNTs have negative zeta potential and the zeta potentials range from -31.0 to -49.5 mV. This indicates that the oxidized CNTs are negatively charged. Fig. 2 shows the results of oxidized CNTs sedimentation investigation. It can be seen that CNTs concentration decreases slightly with aging time. CNTs concentration after 30 d aging is 85% of the initial CNTs concentration, which indicates that only 15% oxidized CNTs settled during 30 d aging. It was reported that individual CNTs are active in UV–vis region and exhibit characteristic bands, however bundled CNTs are hardly active [15,28–30]. Fig. 3 shows the UV–vis spectra of the prepared CNT dispersion

Fig. 1. Zeta potential of oxidized CNTs dispersion.

Fig. 2. CNTs concentration versus aging time in oxidized CNTs dispersion (initial CNTs concentration: 0.10 g/L).

at different aging time. During the aging time investigated, the oxidized CNTs dispersion has characteristic absorption peak at wavelength of 252 nm. This indicates that during the aging in 30 days, a substantial part of CNTs are stably dispersed in water individually.

The stability of oxidized CNTs in water maybe is due to the fact that, the oxidation process introduces oxygen-containing groups on the CNTs surface. These groups ionize in water and the oxygen-containing groups are negatively charged. In aqueous phase, the electrostatic repulsive forces between negative surface charges of the oxygen-containing groups may lead to stability of oxidized CNTs and the oxidized CNTs can form stable dispersion in water. The sta-

Fig. 3. UV–vis spectra of the prepared CNT dispersion at different aging time.

Fig. 4. Visual examination of oxidized CNTs in after quiescent settling for 2 h with different salt concentration: (A1) 400 mmol/L NaCl, (A2) 300 mmol/L NaCl, (A3) 150 mmol/L NaCl, (B1) 0.80 mmol/L CaCl_2 , (B2) 0.60 mmol/L CaCl_2 , (B3) 0.40 mmol/L CaCl_2 , (C1) 0.10 mmol/L AlCl_3 , (C2) 0.05 mmol/L AlCl_3 , (C3) 0.025 mmol/L AlCl_3 .

ble dispersion of oxidized CNTs makes potential pollutants when discharged into water bodies.

3.2. Effect of salts on the stability of oxidized CNTs

Fig. 4 shows the visual examination of oxidized CNTs in NaCl, CaCl_2 and AlCl_3 solutions after quiescent settling for 2 h. It can be seen that, NaCl, CaCl_2 and AlCl_3 precipitate dispersed oxidized CNTs when their concentration is high enough. Zeta potential of the dispersion at various salts concentrations was shown in Fig. 5. It can be seen that, after the precipitation, zeta potential increases.

The above results indicate that, in oxidized CNTs dispersion containing NaCl, CaCl_2 and AlCl_3 , the salts increase zeta potential of negatively charged oxidized CNTs and precipitate the dispersed CNTs. These results suggest that the mechanism of the precipitation is that the electrolyte neutralized the surface charge on the oxidized CNTs, compressed the electrical double layer and thus decreased the electrostatic repulsive forces between dispersed CNTs particles. According to zeta potential measurements, the oxidized CNTs were negatively charged in aqueous phase, which is due to the ionization of the oxygen-containing groups. These oxygen-containing groups are effective adsorption sites for metal cations. The adsorption of cations neutralized the negative surface charge. On the other hand, according to the electrical double layer theory, there is an electrical double layer surrounding the dispersed CNTs. The electrolyte in the solution contracts the double layer by a compression of the out layer surrounding the dispersed particles. This decreases the distance between the two layers of opposite charge and a lowering of the zeta potential follows [31]. The lowering of the zeta potential facilitates the precipitation.

3.3. Precipitation values of salts and critical zeta potential of oxidized CNTs

It can be seen from Fig. 4 that, NaCl precipitates oxidized CNTs at a concentration in the range of 125–205 mmol/L. CaCl_2 precipitates oxidized CNTs at a much lower concentration in the range of 0.35–0.58 mmol/L. While AlCl_3 precipitates oxidized CNTs at the lowest concentration in the range of 0.030–0.045 mmol/L. The minimum concentration of electrolyte required to precipitate dispersed oxidized CNTs depends on the nature of electrolyte. The efficiencies of various salts in destabilizing the oxidized CNTs dispersion can be expressed by precipitation value, the minimum concentration of a particular electrolyte required to just produce the precipitation. The precipitation values of NaCl, KCl, CaCl_2 , MgCl_2 , AlCl_3 and FeCl_3 for oxidized CNTs dispersion were determined in this investigation and the results were shown in Table 1.

The effective entity in precipitation of oxidized CNTs is cation which has opposite charge to that of the negatively charged oxidized CNTs. The precipitation values of electrolytes for oxidized

Table 1

Precipitation values of NaCl, KCl, CaCl_2 , MgCl_2 , AlCl_3 and FeCl_3 for oxidized CNTs dispersion.

Salt	Precipitation value (mmol/L)
NaCl	185
KCl	125
MgCl_2	1.05
CaCl_2	0.55
FeCl_3	0.150
AlCl_3	0.036

Fig. 5. Zeta potential of the oxidized CNTs dispersion at various electrolytes concentrations.

CNTs are in the following order:

The precipitation value decreases with the increase in charge on the cations. The precipitation values of univalent cations NaCl and KCl are 185 and 125 mmol/L, respectively. Bivalent cations have much lower precipitation values and precipitation values for CaCl_2 and MgCl_2 are 1.05 and 0.55 mmol/L, respectively. The precipitation values of AlCl_3 and FeCl_3 are 0.036 and 0.150 mmol/L, respectively. Trivalent cations have the lowest precipitation values, which indicates that trivalent cations have the highest precipitation efficiency. For univalent and bivalent cations, precipitation value of cations with the same charge seems to be related to cation radii and the larger the cation radius is, the lower precipitation value the cation will have. K^+ and Ca^{2+} have larger radii than Na^+ and Mg^{2+} , respectively. And K^+ and Ca^{2+} have lower precipitation values than Na^+ and Mg^{2+} , respectively. This maybe is due to the fact that cations with larger radius have smaller hydrated radius. The existence of hydrated shell around the metal cations decreases the electrostatic attraction between cations and oxidized CNTs. For cations of the same charge, the smaller the hydrated radius of the cation is, the easier the cation will be adsorbed to the oppositely charged particles and cations with smaller hydrated radii have higher precipitation efficiency. For trivalent cations Fe^{3+} and Al^{3+} , Fe^{3+} has larger cation radius than Al^{3+} . However, precipitation value of FeCl_3 is higher than AlCl_3 and the precipitation value does not decrease with the increase in cation radius. This is mainly due to the fact that, Fe^{3+} and Al^{3+} tend to hydrolyze and the hydrolyzation has effect on cation precipitation capacity.

In order to investigate the effect of anions nature on the stability, the precipitation value of NaCl, NaNO_3 , Na_2SO_4 and $\text{Na}_2\text{C}_2\text{O}_4$ have been determined. The results (data not shown) showed that the nature of anions has little effect on the precipitation value, which indicates that anions have little effect on the stability of oxidized CNTs dispersion.

4. Conclusions

- (1) During an aging time of 30 days, oxidized CNTs dispersion shows characteristic UV–vis absorbance peak of individual CNTs at 252 nm and CNTs concentration in the dispersion after 30 d aging is 85% of the initial concentration.
- (2) The precipitation value of NaCl, KCl, MgCl_2 , CaCl_2 , FeCl_3 and AlCl_3 were determined to be 185, 125, 1.05, 0.55, 0.15 and 0.036 mmol/L, respectively. For univalent and bivalent cations, precipitation value of cations with the same charge seems to be related to cation radius and the larger the cation radius is, the lower precipitation value the cation will have. For trivalent cations Fe^{3+} and Al^{3+} , precipitation value does not decrease with the increase in cation radius.
- (3) The nature of anions investigated has little effect on oxidized CNTs stability.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant Nos. 20607027 and 50538090) and Research Start-up Fund for Dean's Scholarship Winner from Chinese Academy of Sciences.

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