A facile method to coat mesoporous silica layer on carbon nanotubes by anionic surfactant

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ABSTRACT

This paper described a facile sol–gel method to synthesize silica-coated multi-walled carbon nanotubes (MWCNTs) using anionic surfactant sodium dodecyl sulfate (SDS) for the first time. This method is quite simple and easy to operate, the uniformly silica shell could be a readily controlled ratio of two silane agents of 3-aminopropyltriethoxysilane and tetraethoxysilane, and more suitable for large-scale production. The resulting CNTs@SiO2 composites are characterized by transmission electron microscopy, scanning electron microscopy, and Fourier transform infrared spectroscopy. It is of interest to note that the mesoporous CNTs@SiO2 materials can be obtained via the extraction or the calcination process and mesoporous property was investigated by N2 adsorption–desorption analysis.

1. Introduction

Recently, carbon nanotubes (CNTs), which were discovered by Iijima [1] in 1991, have attracted much attention in nanoscale science and technology due to their unique optical, electronic and mechanical properties [2–6]. However, due to the formation of big bundles held strongly together, CNTs are difficult to disperse homogeneously in different solvents, which greatly limit the application of CNTs. Therefore, extensive research is focused on surface modification of carbon nanotubes mainly to enhance their compatibility and dissolution properties. Silica surfaces are well-known insulating properties, biocompatible and can be easily functionalized for bioconjugation purposes. Coating CNTs with a SiO2 shell will not only solve challenges for poor solubility of CNTs, but also probably achieve the applications in cell imaging, drug and gene delivery.

Several methods have been explored to fabricate the silica-coated CNT composites [7–12] such as (1) synthesis of silica on noncovalently or covalently functionalized CNTs [2] synthesis of silica onto surface of CNTs with the aid of the cationic surfactant cetyltrimethyl ammonium bromide (CTAB). However, some of the methods require strong oxidation or covalent decoration before coating which would bring unwanted destruction of unique properties of CNTs, some of them are comparatively complicated, or some of methods are not suitable for large-scale production. To the best of our knowledge, there is no report using anionic surfactant to coat CNTs by silica. In this study, we present a simple method to synthesize CNTs@SiO2 via sol–gel process using anionic surfactant sodium dodecyl sulfate (SDS) in the large-scale production. It is of interest to note that the mesoporous CNTs@SiO2 composite can be obtained via the extraction or the calcination process.

2. Experimentals

2.1. Materials

MWCNTs (with a diameter of 60–100 nm) were provided by Shenzhen Nanotech Port Co Ltd. SDS, tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) were obtained from Alfa Aesar Chemical Company. All other materials were of analytical grade and commercially available.

2.2. Coating SiO2 on MWCNTs

In a typical synthesis, 100 mg MWCNTs, 1 g SDS were dispersed into 30 mL water, and sonicated for 1 h. The above the mixture was added to 80 mL anhydrous ethanol, and further sonicated for 1.5 h to form a stable dispersion. Immediately, 1 mL NH4OH and 0.2–0.6 mL APTES were added into the as-prepared MWCNTs dispersion. The next, a TEOS solution (0.8–0.4 mL TEOS in 40 mL ethanol) was dropped under mechanical stirring. The total volume of APTES and TEOS is 1 mL. The reaction mixture was stirred for another 12 h. Finally, the CNTs solution was centrifuged and washed with ethanol. A uniform and thick layer of silica on MWCNTs was obtained.
2.3. Mesoporous CNTs@SiO₂ materials

Mesoporous CNTs@SiO₂ materials can be obtained via the extraction or calcination method. The as-prepared products CNTs@SiO₂ were added into 100 mL 3.3 M H₂NC₂H₄OH ethanol solution, and the mixture was refluxed at 90 °C for 12 h. The solids were recovered by filtration, washed with ethanol, dried, and the above extraction procedure was repeated. The calcination process was carried out at 550 °C for 6 h with a heating rate of 2 °C/min in argon atmosphere.

2.4. Characterization

Transmission electron microscopy (TEM) and scanning electron micrographic (SEM) images of CNTs@SiO₂ composites were obtained by a Tecnai G² 20S-TWIN microscope and SS-550 scanning electron microscope respectively. The Fourier transform Infrared (FT-IR) spectra of CNTs@SiO₂ were recorded on a AVATAR 360. Thermogravimetric analysis (TGA) was performed for powder samples using a Netzsch STA 409 thermogravimetric analyzer. N₂ adsorption–desorption analysis was done at 77 K on a Micromeritics TriStar 3000 apparatus.

3. Results and discussion

The morphology of the as-prepared CNTs@SiO₂ composites is examined by TEM and SEM observation. Before coating, the average diameter of CNTs is about 60–80 nm (Fig. 1a), after coating with thin SiO₂, the diameter of the CNTs@SiO₂ increases to about 120–140 nm (Fig. 1b), corresponding to a 60 nm thick SiO₂ layer covered on CNTs. The SEM images also show the change on CNTs before (Fig. 1c) and after silica coating (Fig. 1d), which further indicates that the silica is homogeneously coated on the surface of CNTs with about 60 nm thick. These images clearly prove that silica is homogeneously deposited on CNTs to form CNTs@SiO₂ composites.

When the anionic surfactant like SDS is used, a lot of negative charge on the surface of CNTs will repulse the silicate anions catalyzed by the hydrolysis of TEOS, so the silica can’t be deposited on the CNTs and the similar result was also verified by previous work [13]. After mixing the CNTs suspension with APTES and NH₄OH, the pH of the solution was increased to 10–11, and some of the protonated APTES were attached to the surfaces of the CNTs@SDS through electrostatic attraction [14,15]. The APTES hydrolyzed and formed a layer on the surface of MWCNTs, and the CNTs@SDS modified by APTES was then used as a source of nucleation of TEOS condensation. Finally, the silica shells were formed through a sol–gel process (Scheme 1).

In order to further identify the effect of APTES and TEOS individually, a control experiment was carried out with the same amount of SDS as surfactant. It was found that the silica cannot be uniformly deposited onto CNTs’ surfaces in the absence of APTES and lots of dissociating silica particles aggregated into silica spheres (Fig. S1, Electronic supplementary information, ESI). When the volume of APTES and TEOS is fixed to 1 mL and the ratio of APTES/TEOS changed from 1:4 to 3:2, the silica can be well coated on the CNTs surface (Fig. 2). However, when the ratio of APTES/TEOS is higher than 4/1, the coating layer of silica on MWCNTs was similar to the results with only TEOS.

TGA of CNTs@SiO₂ showed two weight losses (Fig. S2, ESI). The first weight loss occurred from 310 °C to 600 °C due to decomposition of the surfactant SDS within the CNTs@SiO₂. The second case, which occurs at about 640 °C, corresponds to the oxidation of CNTs embedded in CNTs@SiO₂ and 30.7% weight loss was observed. It is proved that the thermal stability of CNTs after being coated by silica has much improved. Thus, from the TGA results, we can conclude that core-shell CNTs@SiO₂ composite was indeed obtained via this method.

FT-IR spectrum of the CNTs@SiO₂ (Fig. S3, ESI) shows an absorption peak at 2871 and 2921 cm⁻¹ assigned to the –CH₂ group from SDS, and it suggests that the SDS have been successfully encapsulated into the CNTs@SiO₂. The absorption peak at 1043 cm⁻¹
is due to the Si–O–Si stretching vibration, which confirms that silica was well coated on the CNTs.

The mesoporous CNTs@SiO₂-extraction and CNTs@SiO₂-calcination materials were obtained from the core-shell CNTs@SiO₂ in which the ratio of APTES/TEOS is fixed to 3:2 via (1) the extraction process using ethyl amine to remove SDS [16]; (2) the calcination process in which the CNTs@SDS@SiO₂ was calcinated at 550 °C for 6 h, respectively. Nitrogen adsorption/desorption isotherms of CNTs@SiO₂ show that the curve of mesoporous CNTs@SiO₂-extraction is typical type IV isotherm with one step at relative pressure between 0.15 and 0.3 due to capillary condensation of nitrogen in the mesopores, but the curve of CNTs@SiO₂-calcination becomes type I, indicating that the mesoporous structure existed in the sample of CNTs@SiO₂-calcination (Fig. 3). This is due to calcination process which resulted in the decomposition of APTS and SDS. The BET specific surface area, BJH pore sizes and pore volumes of two samples are summarized in Table 1. The pore size distribution of two samples is shown in Fig. S4. The pore size of CNTs@SiO₂-extraction is smaller than that of CNTs@SiO₂-calcination. On the contrary, the pore volume and specific surface area of CNTs@SiO₂-extraction have significant increases in comparison with CNTs@SiO₂-calcination. This feature suggests that the mesoporous CNTs@SiO₂ obtained by the extraction process is superior to calcination process.

4. Conclusion

In conclusion, we showed a simple method to coat SiO₂ on CNTs using an anionic surfactant SDS via the hydrolysis of APTES and TEOS. The mesoporous CNTs@SiO₂ composites were obtained via the
extraction or the calcination process. This method is quite simple and easy to operate, the uniformly silica shell could be a readily controlled ratio of APTES/TEOS, and more suitable for large-scale production.

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Appendix A. Supplementary data

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References