Silica Nanobeads-decorated Multi-walled Carbon Nanotubes by Vapor-phase Method

Wugang Fan[†,††] and Lian Gao[*†]
[†]*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics,*
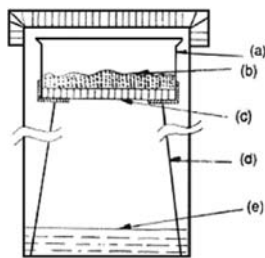*Chinese Academy of Sciences, Shanghai 200050, P. R. China*
[††]*Graduate School of the Chinese Academy of Sciences, P. R. China*

We report a new concise route to prepare carbon nanotube–silica nanobeads composites. The assembly of silica beads and nanotube by vapor-phase method make these structures an excellent platform for the development of biosensors, or for optical, magnetic and catalytic applications.

Because of fundamental interests and potential technology applications, much attention has been focused on the preparation and assembly of nanomaterials.[1] Silica nanoparticles have been widely used for biosensing and catalytic applications owing to their large surface area-to-volume ratio, straightforward manufacture, and the compatibility of silica chemistry with covalent coupling of biomolecules.[2] Carbon nanotubes (CNT) are important structural blocks for preparation of composites with unique optical,[3] electrical,[4] and mechanical properties.[5] A tremendous amount of work is being done on different aspects of CNT technology such as synthesis,[6] functionalization,[7] and applications.[8] Coating of CNT with silica has been performed by a range of methods,[9] in each case with the emphasis on the usefulness of a silica coating as a way to preventing tube–tube contacts. The assembly of silica and CNT may provide an interface between living cell and biosensors. Recently, Massimo Bottini et al.[10] prepared multi-walled CNT covalently decorated with silica nanoparticles by using microemulsion conditions. Vapor-phase method (also donated as VPT) was first reported by Xu et al.[11] in 1990 for synthesis of zeolite ZSM-5, which could reduce the organic template waste by recycling use of liquid phase and have the appealing feature of in situ synthesis.[12] It involves reaction in vapor phase containing organic and water vapor (the instrument[11] is shown in Figure 1). This novel method had not been used to functionalize or prepare CNT composites, however.

In this paper, we present the first application of the concise method to prepare multi-walled CNT decorated with silica nanoparticles. The underlying concept is captured graphically in Figure 2, which is directed to our focusing target of silica functionalized multi-walled CNT (**3**). We grew the silica nanobeads directly onto functionalized multi-walled CNT by reaction of tetraethyl orthosilicate (TEOS) with a functionalized CNT in vapor of H_2O and ethylenediamine (EDA). CNT in our experiment was prepared by the catalytic decomposition of CH_4, with diameters ranging from 15 to 40 nm nanometers and lengths ranging from five hundred nanometers to five hundred micrometers (Shenzhen nanotech Port Co., Ltd. China).

We first refluxed multi-walled CNT (**1**) in a mixed concentrated acid ($H_2SO_4/HNO_3 = 3$ v/v) at $140\,°C$ for 3 h to oxidize and remove the amorphous carbon and catalyst. Nanotube mat was obtained after centrifugation and was thoroughly washed with distilled water until the PH value was ≈ 6 (**2**). The treatment can not only shorten CNT but also make the inert surface to be active. Activated CNT (10 mg) was sonicated in 1 wt % anionic surfactant sodium dodecyl sulfate (SDS) solution (3 mL) for 2 h. Then TEOS (0.3 mL) was added into the CNT dispersion and sonicated for another 3 min. The obtained black sol was transferred as solid phase into the container with Teflon substrate (the so-called "solid phase" was inferred from dry-gel, here we still use it to mean that the materials adsorb the vapor from liquid phase). A mixture of distilled water (5 mL) and EDA (0.1 mL) was employed as liquid phase. The VPT instrument has a volume of 100 mL and there is no direct contact between the two phases.

Heat treatment on the sealed VPT instrument was conducted at $100\,°C$ for 5 h in an oven and then the solid phase was washed with distilled water and absolute alcohol for several times. Thereafter, the precipitated solid by centrifugation was dried at $60\,°C$ in vacuum oven for 6 h. Transmission electron microscopy (TEM) was conducted on a JEM-2100F. One drop of CNT nanocomposites dispersed in absolute alcohol was placed on a copper grid and sample was used after drying at room temperature.

Following above procedures, we obtained new CNT-silica nanocomposites. TEM images revealed the silica nanobeads morphologies and their distributions on CNT. The silica nanobeads have mean diameter of 12 nm and display narrow size distribution (± 2 nm). They were found attaching on the side walls and ends of the CNT (Figures 3a and 3b). Single layer coating can be seen in part of the CNT. In many cases, aggregated silica nanoparticles are observed, as expected for the high density of functional groups on CNT. The EDS spectrum of silica beads

Figure 1. VPT instrument (a) container; (b) CNT sol; (c) Teflon substrate; (d) holder; (e) EDA–H_2O.
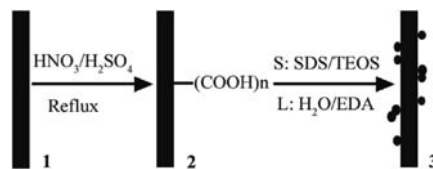
Figure 2. Scheme for preparing CNT nanocomposites. S: solid phase, L: liquid phase.
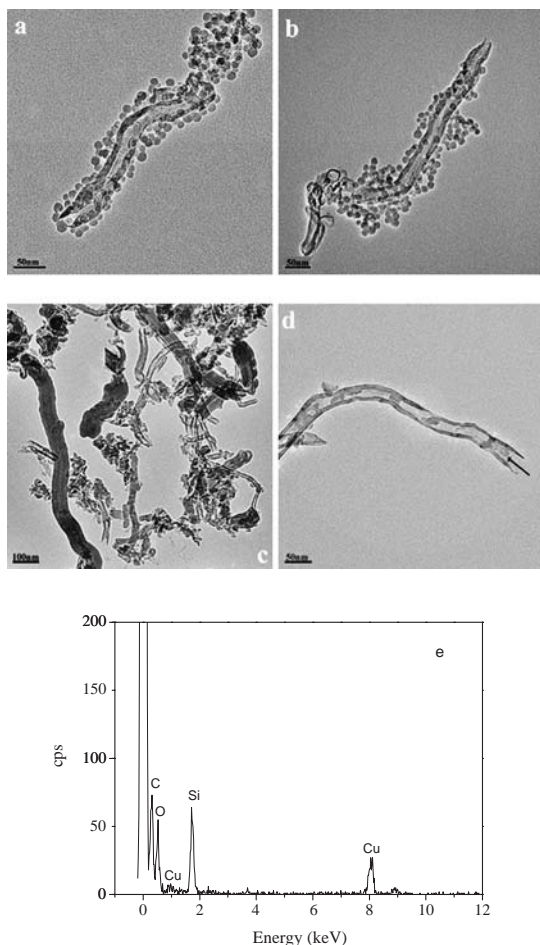
Figure 3. TEM images of CNT-silica nanocomposites prepared with (a and b) and without SDS (c and d). The arrow in panel (d) indicates polymerized silica inside a CNT (e) the corresponding EDS spectrum of (a).

is presented in Figure 3e, which confirms the presence of C, O, and Si.

CNT composite without the addition of SDS was also prepared according to the same procedures. When SDS was absent, silica nanobead was not observed and amorphous silica aggregation occurred. Some CNT had uniform silica coating around entire CNT (Figure 3c). This result is in accordance with K. Hernadi et al.[13] They coated multi-walled CNT by impregnation technique and found that SDS playing negative role for the formation of continuous coverage on CNT. We also observed that some CNT appeared to have isolated silica nanoparticles within their tubes cavities and formed pea-like structure (Figure 3d). The internal presence of silica was not observed in the presence of SDS surfactant, though SDS can decrease the water surface tension. This phenomenon can be explained by the formation of silica bead enclosed by SDS micelle.

During the heat treatment, the water and EDA will evaporate and TEOS will hydrolyze and polymerize with the catalysis of EDA, which could be adsorbed into the sol and elevate pH value. SDS plays a combinational role of dispersant and "structure-directing agent" and TEOS serves as framework source in preparation of silica nanobeads. It should be noticed that this process is relatively slow because of the limited rate of EDA dissolution

in solid phase, in contrast with hydrothermal system, which in general contains all reaction materials together in the liquid phase and tends to aggregate silica and leads to phase segregation. Further work is in process to tailor the beads size and modify them according to different demands.

In summary, we have successfully prepared covalently coated carbon nanotubes with silica nanoparticles with narrow size distribution by vapor-phase method. This work presents a simple but effective strategy to prepare the assembly of silica and CNT. The approach was also cost effective by using simple procedure and cheap reagents. Because silica can be doped with fluorescent,[14] magnetic,[15] or biological macromolecules,[16] nanostructures with a wide range of morphologies suitable for different applications can be obtained. Another feature of our work is that the reaction of CNT was in situ, it also may be used to modify CNT membrane.[17] We anticipate that further refinement of our method will allow us to combine different nanostructures and this could be useful for a variety of applications.

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