Preparation of multi-walled carbon nanotubes/SiO$_2$ core–shell nanocomposites by a two-step Stöber process

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The surface modification and functionalisation of multi-walled carbon nanotubes (MWNTs) could provide enhanced properties to MWNTs for highly specific applications which often require solubilisation and dispersion, promotion of functionality, biocompatibility or lower toxicity of MWNTs. Herein, a novel nanocomposite consisting of MWNTs as a core and amorphous silica (SiO$_2$) as a shell is developed. First, the functionalisation of MWNTs with carboxylic functional group (MWNTs-COOH) was obtained via oxidation using the concentrated sulphuric acid/nitric acid mixture (3:1 v/v) treatment. Second, a silica uniform layer was grown on MWNTs-COOH by a two-step Stöber process. The core–shell nanostructure is characterised by Fourier-transform infrared spectroscopy, X-ray powder diffraction, transmission electron microscopy, and energy dispersive spectrometer. Experimental results show that a SiO$_2$ shell was uniformly coated on the surface of MWNTs with a thickness of 5–10 nm. The results can have important implications for the preparation of carbon nanotube core–shell nanocomposites in general.

1. Introduction: Core–shell nanocomposites integrating multiphase materials at the nanometre scale have received much attention because they can be tailored to collective or novel material properties from individual components. They are opening new avenues for applications in catalysis [1], magnetics [2], biological labels [3], optical devices [4], and ceramics and so on [5]. By coating or encapsulating the core particle within a shell of preferred materials, the surface properties of particles can be designed to meet some required specifications [6]. For instance, the shell can alter the charge, functionality, reactivity of the surface, and enhance the stability, flowability, wettability, electrostatic properties, magnetic and electromagnetic properties, catalysis, and optical properties [7]. Herewith, core–shell composites have higher physical and chemical properties compared to that of their single-component counterparts [8]. There are many methods to prepare core–shell nanocomposites, such as reverse micellars, sonochemical deposition, elecroless plating, precipitation, layer-by-layer, and sol–gel [9].

Carbon nanotubes (CNTs), the most ubiquitous material in the world, have been intensely studied since their discovery in 1991 [10], because of their exceptional electrical, magnetic, mechanical, and thermal properties compared with conventional carbon fibres [11, 12]. This molecular scale wires have a large number of applications, such as energy or hydrogen storage materials; field emissive displays and radiation sources; semiconductor apparatus, scanning probes, and multilevel interconnects; molecular computers; and high-strength, absorbing and conductive composites [13–21]. To enhance their properties for highly specific applications which often require solubilisation and dispersion, promotion of functionality, biocompatibility or lower toxicity of CNTs, some methods including tuning their diameter, arrangement, helicity, and the introduction of defects, have been used [22]. Recently, several novel strategies have been investigated to introduce new properties to CNTs such as surface modification with inorganic, organic, and biological species [23, 24]. These functionalised cell–shell composites show eminent opportunities and prospects to extend the range of their new potential application [25, 26].

Among a large number of inorganic nanoparticles, silica particles have been widely chosen for both research and industry because of their excellent optical, electrical and thermal properties [27–29]. They are widely used in many fields, such as thixotropic agents, thermal insulators, composite fillers, drug delivery, and paints [30]. At present, nanosilica materials are synthesised via several methods including the thermal decomposition technique, sol–gel processing technique, vapour-reaction, and water-in-oil mircro-emulsions. In this Letter, the Stöber process (this method is based on the hydroxide-catalysed hydrolysis of an alkoxysilane) was employed to synthesise multi-walled CNTs (MWNTs)/silica (SiO$_2$) core–shell nanocomposite. The core–shell nanostructure is characterised by Fourier-transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive spectrometer (EDS). This Letter has implications for the development of new MWNTs nanocomposites used in electronic and electromagnetic devices such as magnetic carries, inductors, converters, and electromagnetic wave absorbers [31].

2. Experimental: The MWNTs (MWNTs, 95% purity) were purchased from Shenzhen Nanoport Company. Tetraethyl erthosilicate (TEOS, 98%) and (3-aminopropyl) triethoxysilane (APS) as a silica source, ammonium hydroxide (NH$_3 \cdot$ H$_2$O, 27%) as a catalyst, and all other reagents were used as received without further purification. MWNTs with carboxylic functional group (MWNTs-COOH) were obtained via oxidation using the concentrated sulphuric acid and nitric acid mixture treatment. A 2 g of MWNTs with 120 ml concentrated sulphuric acid/nitric acid mixture (3:1 v/v) were sonicated for 8 h in a Bunsen beaker, then were vigorously stirred on an electromagnetic stirrer for 24 h. After standing for 6 days at room temperature, the mixture was filtered under vacuum through 220 nm Millipore polycarbonate membrane and washed several times with distilled water until the pH of the filtrate became 7. The resulting solid was dried under vacuum for 24 h at 60°C to obtain carboxylic-acid-functionalised MWNTs.

The MWNTs/SiO$_2$ core–shell nanocomposite was fabricated by a two-step Stöber process. Step 1: 0.3 ml of the silane coupling agent (3-aminopropyl) triethoxysilane was attached to 0.5 g of MWNTs-COOH in 50 ml of ethanol solutions for reacting the amine groups of (3-aminopropyl) triethoxysilane with the carboxyl

groups of MWNTs-COOH under continuous stirring. Step 2: Two types of solutions which were denoted as solution I and solution II were prepared separately. Solution I consisted of 1.6 ml of TEOS and 9 ml of ethanol, whereas solution II was 250 ml of ammonium hydroxide (0.8 M). Solution I was mixed together with the product of step 1 under continuous stirring. Then, solution II was added as slowly as possible to above solution under rigorous stirring. After 24 h, N,N-dimethylformamide (DMF) was added to the mixture with stirring, and then the water and ethanol were removed under reduced pressure. After the suspension of DMF was filtrated under vacuum through 220 nm Millipore polycarbonate membrane and washed several times with dimethyl benzene, it was dried in a cabinet dryer at 120°C for 24 h. The sample obtained above, which was placed in a ceramic boat, was heated at 500°C under nitrogen atmosphere in a tubular furnace for 30 min. Finally, silica coated MWNTs core–shell composite was obtained.

Fourier-transformed infrared spectroscopy (FTIR, Nicolet750 Magna-IR) was conducted to study the surface functional group change after surface oxidation and core–shell structure formation. Phase analysis of the as-prepared powder was conducted using X-ray powder diffraction employing an X-ray powder diffractometer (RIGAKUD/ Max-A) using Cu Kα radiation ($\lambda = 1.5405$). X-ray diffractometer was operated at 60 kV and 40 mA at a 2θ range of 10°–70° employing a step size of 0.02 and a speed of 5°/min. The microstructure of the synthesised composites was observed by transmission electron microscope (TEM, JEM-2100). Elemental analysis of the as-prepared MWNTs/silica core–shell nanocomposite was performed using EDS system (INCA) attached to a scanning electron microscope (SEM, JSM-6700F).

3. Results and discussion: Fig. 1 shows the schematic representation used to prepare MWNTs/SiO$_2$ core–shell nanocomposite according to a two-step Stöber process including (3-aminopropyl) triethoxysilane-surface seeding and the shell grows. MWNTs-COOH synthesised by oxidation treatment with concentrated sulphuric acid/nitric acid mixture was chemically treated with the silane coupling agent (3-aminopropyl) trimethoxysilane in ethanol solvent. The method of silica particles polymerised onto a planar surface by (3-aminopropyl) trimethoxysilane as coupling agent is also well known and wildely used, although there has been a few reports of silica particles polymerised onto the spherical metal particles by the method. As far as we aware, there is few reports on the synthesis of a complete silica nanolayer coating onto MWNTs surface by this method. In our work, the reaction of the complex ions with MWNTs-COOH surface is assumed to occur via the mechanism as shown in Fig. 1. Then, TEOS and ethanol mixture were added with continuous stirring and the silica polymerised onto the MWNTs surface, yielding a thin silica shell after 0.8 M ammonium hydroxide was dropped off in 12 h.

The FTIR spectra of MWNTs before and after acid treatment are present in Fig. 2. It is obvious that there is no significant functional
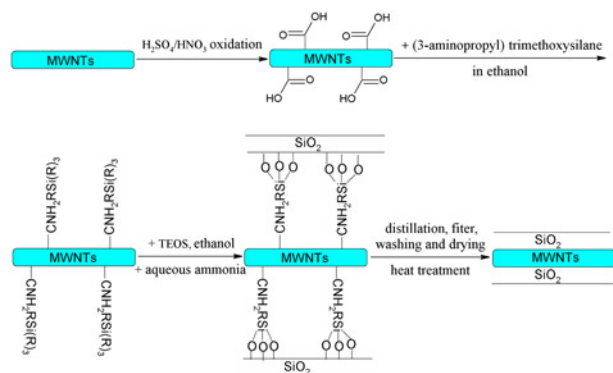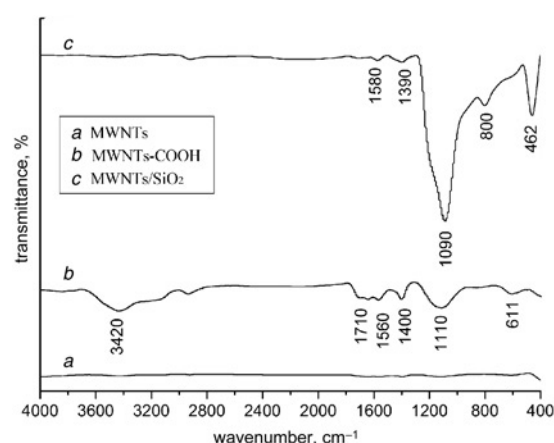
Fig. 2 *FTIR spectra of*
a Oxidized MWNTs for 24 h
b Oxidized MWNTs for 6 days
c MWNTs/SiO$_2$ core–shell nanocomposite

group detected on the untreated MWNTs from the FTIR spectrum (Fig. 2*a*). After acid treatment, it is clearly seen from Fig. 2*b* peaks at 1110, 1400, 1560, 1710, and 3420 cm^{-1} corresponding to C=O, O–H, and C–O bonds in COOH functional groups, respectively. The broad shoulder peak at 3420 cm^{-1} is identified to the O–H stretches of terminal carboxyl groups. The peaks, which locate in 1710 and 1110 cm^{-1} most likely correspond to the carboxylic C=O and C–O stretching vibrations. It was presumed that the absorption peak at around at 1560 cm^{-1} arises from the C=C stretching mode which is activated by sidewall attachment. These polar functional groups which exist at the tip and on the outer shell of the tubes make them easily dispersed in polar solvents and served as reactant for the formation of a monolayer of NHRSi(OR)$_3$ that is thought to be helpful for inducing the formation of SiO$_2$ shell. Fig. 2*c* shows the resulting FTIR spectrum of the MWNTs/SiO$_2$ core–shell nanocomposite. As can be seen in the spectrum, there are strong absorption peaks at 462, 800, and 1090 cm^{-1}, just as those from commercial grade silica, indicating the presence of silica shell.

Fig. 3 gives the X-ray diffraction (XRD) patterns of MWNTs-COOH and MWNTs/silica core–shell nanocomposite, respectively. The pattern (Fig. 3*a*) for MWNTs-COOH shows two peaks at 26.1° and 44.6°, corresponding to the (002) and (101) reflections, respectively. The peaks assigned to MWNTs at $2\theta = 26.1$ in the patterns (Figs. 3*a* and *b*) can be clearly indicated that the MWNTs structure was not destroyed after oxidation
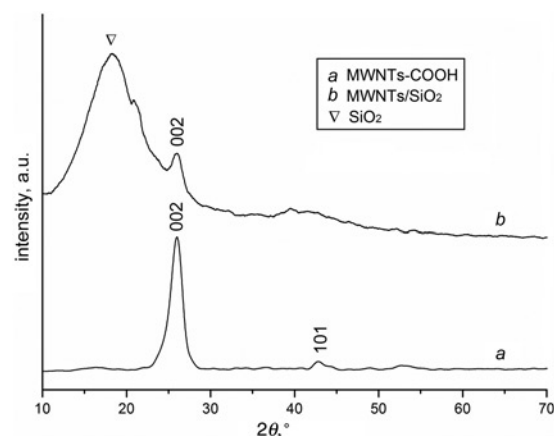
Fig. 1 *Schematic diagram for the MWNTs/SiO$_2$ core–shell nanocomposite*

Fig. 3 *XRD patterns of*
a MWNTs
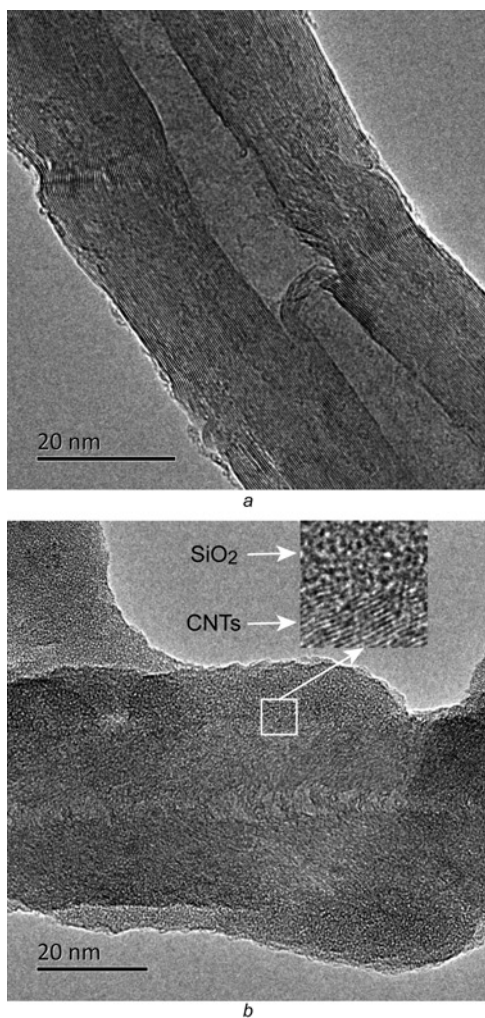*b* tMWNTs/SiO$_2$ core–shell nanocomposite

Fig. 4 *TEM images of*
a MWNTs
b MWNTs/SiO₂ core–shell nanocomposite

treatment and subsequent heat treatment. Furthermore, the silica shell is amorphous, as evident from the presence of a broader bump centred at $2\theta = 18.4$ shown in Fig. 3*b*. The amorphous silica can be readily coated on the MWNTs and the amorphous silica is preferable for applications in thixotropic agents, thermal insulators, composite fillers, drug delivery, paints and so on. Thus, silica coated MWNTs composite may be used in these areas.

TEM images (Fig. 4) were taken by dipping a copper, respectively, grid in a dispersion of MWNTs and MWNTs/silica core–shell nanocomposites in ethanol. By comparing Figs. 4*b* with 4*a*, it is found that the nanocomposites showed the core–shell structure and the outer surfaces of MWNTs were wrapped with a
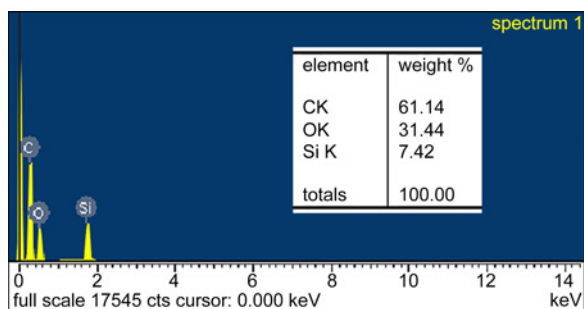

Fig. 5 *EDS spectrum of the MWNTs/SiO₂ core–shell nanocomposite*

SiO₂-coating of 5–10 nm thickness. The TEM studies show SiO₂ coated on MWNTs is amorphous in structure, which is consistent with the result of XRD. Chemical composition of the MWNTs/ silica core–shell nanocomposite was studied by EDS analyser. Fig. 5 indicates the presence of only C, Si, and O. These data clearly confirmed that the resulting nanocomposite consists of MWNTs and SiO₂ without any chemical contamination.

4. Conclusion: SiO₂ coated MWNTs with core–shell nanostructures are synthesised by a two-step Stöber process. The core–shell nanostructure is characterised by FTIR, XRD, TEM, and EDS. TEM observation revealed that a SiO₂ shell was uniformly coated on the surface of MWNTs with a thickness of about 5–10 nm. The results can have important implications for the preparation of CNT core–shell nanocomposites. Based on the silica which can be doped with functional species, for example biological macromolecules, fluorescent, and magnetic, catalyst, it is expected that the MWNTs/SiO₂ core–shell nanocomposite will provide an excellent platform for the development of the potential applications, such as biosensors, optics, catalytics, and magnetics.

6 References

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