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Single-step *in situ* synthesis of double bond-grafted yttrium-hydroxide nanotube core-shell structures†

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Novel MMA–Y(OH)$_3$ nanotube core-shell structures have been successfully prepared with double bonds successfully grafted on the surface through a single-step *in-situ* hydrothermal method.

There has been increasing research interest in the fabrication of organic–inorganic nanocomposite materials because of their potential to provide a myriad of unique, value-added properties including enhanced solubility, conductivity, mechanical properties, optoelectronic, and flammability resistance.[1–8] Materials with distinctive structural features and/or novel properties, *e.g* carbon nanotubes, are usually effective components which may endow the new system with unexpected characteristics. Herein we report a novel nanotube-based organic–inorganic composite: double-bond-grafted yttrium hydroxide nanotube core-shell structures.

Very recently, we developed a simple hydrothermal synthetic way to prepare series of rare earth compounds nanowires, nanotubes and inorganic fullerene-like nanoparticles on a large scale.[9] Stemming from aqueous solutions, these structures usually have affluent surface hydroxyls and can be easily functionalized through a solution-based method, which together with the unique optical and magnetic properties of rare earth ions make them rather appealing to composites applications. Nanotubes are apparently especially superior to other structures due to their having inner and outer surfaces which may produce abundant active sites for further functionalization. In this paper, we report a facile and one-pot hydrothermal approach to covalent functionalization of the inner and outer sidewalls of Y(OH)$_3$ nanotubes (YNTs).

Generally, functional molecules with ester groups can be used in this process. Here methyl methacrylate (MMA) has been chosen as an example. The covalent functionalization involves the irreversible esterolysis of a bifunctional molecule, methyl methacrylate (MMA), and the formation of Y(III)–O bonds on the hydrophilic surface of YNTs in water. This leads to amphipathic composite nanotubes synthesis by attachment of carbon–carbon double-bonds chains to YNTs without disrupting the original structure (Fig. 1). Both the forming of the YNTs and C=C attachment were achieved in a single step.

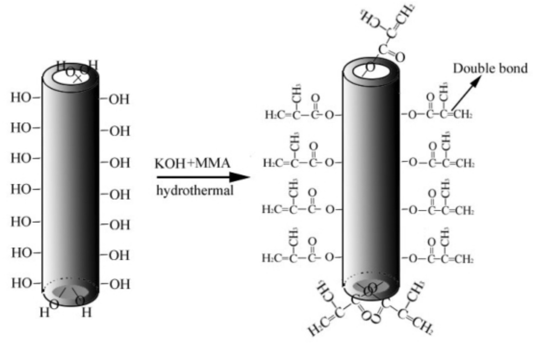

Fig. 1 Schematic of Y(OH)$_3$ nanotubes formation and subsequent grafted of carbon–carbon double-bonds.

In a typical synthesis, 1 g Y$_2$O$_3$ was dissolved in 10% hydrochloric acid to form a clear aqueous solution, then 10% KOH solution was added to adjust the pH of the system to be 12 ~ 14. MMA (20 ~ 60 wt% of Y$_2$O$_3$) was dropped into the as-obtained colloidal precipitate and the mixture was transferred into a 50 ml autoclave (diluted to 80% of the capacity with distilled water) and dispersed ultrasonically for 1 h, then the autoclave was sealed and kept at 180 °C for about 5 h. After that, the autoclave was allowed to cool to room temperature naturally. Then the white precipitate was filtrated, washed sequentially with water, chloroform and ethanol to remove MMA and ions possibly remnant in the final products, and dried at 50 °C in air.

As shown in Figs. 2a and 2b, uniform nanotubes-polymer core-shell structures have been successfully obtained with initial MMA usage of 20 ~ 60 wt% of Y$_2$O$_3$. Most of the YNTs dispersed on the copper TEM grids have open-end nanotubes morphologies with inner diameter of 50 ~ 140 nm, outer diameter of 100 ~ 220 nm and lengths up to several micrometers. Differing from unfunctional YNTs (see supporting information†), the inner and outer surface of functional nanotubes is rough and the wall is thicker. Thorough element composition analysis of these nanotubes has been performed by energy-dispersive X-ray analysis (EDXA), which reveals that yttrium was presence in these nanotubes and potassium was absent (Fig. 2c).

The structural characteristics of the composites have been carried out by means of X-ray powder diffraction (XRD). As shown in Fig. 3, the diffraction patterns of different composites reserve the typical peaks which are consistent with those of pure YNTs (Fig. 4a). Meanwhile, it is interesting to find that they display several peaks obviously not belonging to YNTs or PMMA (supporting informa-

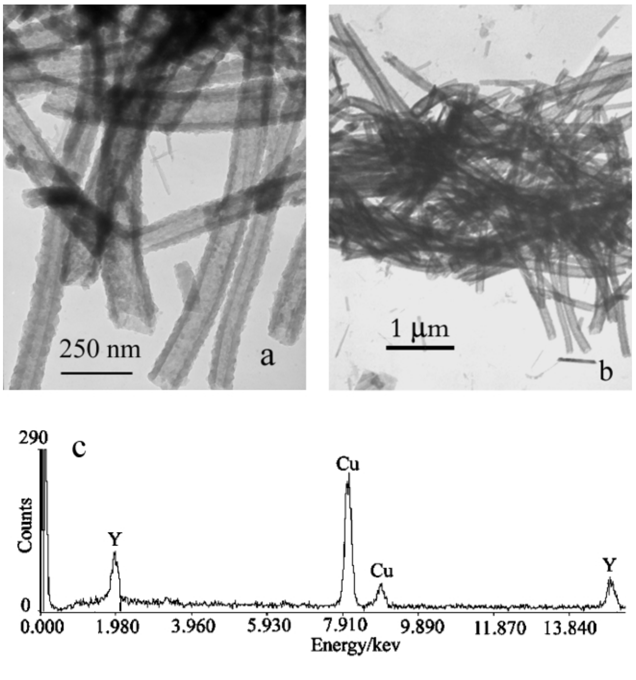

Fig. 2 TEM images of composite nanotubes (a, b). and EDXA spectrum (c) taken from the same samples with Fig. 2b.

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† Electronic supplementary information (ESI) available: Figs. S1–S4. See http://www.rsc.org/suppdata/cc/b3/b311740e/

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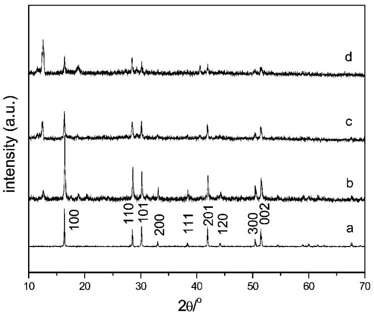

Fig. 3 XRD patterns of YNTs (a), composites containing of 20 wt% (b), 40 wt% (c) and 60 wt% (d) of Y_2O_3.

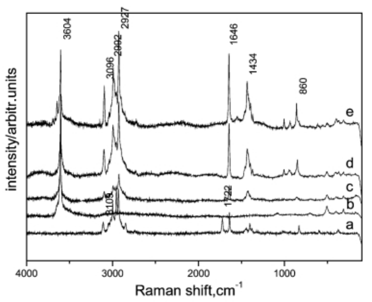

Fig. 4 Raman spectra of pure MMA (a) and $Y(OH)_3$ (b), composites containing 20 (c), 40 (d) and 60 wt% (e) of Y_2O_3.

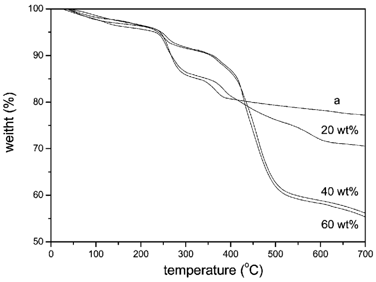

Fig. 5 TGA of $Y(OH)_3$ (a) and composites.

tion†) whose heights increase proportionally to the weight percentage of MMA. Especially for 60 wt% (Fig. 3d) the intensity of the peak at 7.04 Å is stronger than any other peaks, indicating the introduction of some additional nanoscale organic–inorganic orders to these new composites. This observation has also been confirmed by Raman and IR studies.

The Raman spectra of these composites are far different from those of their constituents. As shown in Fig. 4, all characteristic bonds of $Y(OH)_3$ in three composites (20, 40 and 60 wt%) are observed. From 20 wt% on, these spectra represent the characteristic peaks of MMA except for the bond of ν (C=O) (1722 cm^{-1}) which is relevant to the weight percentage of MMA. For example, bonds at 3604 cm^{-1} can be assigned to ν (O–H) of $Y(OH)_3$ (indicating that partial –OH have been reserved on the surface of $Y(OH)_3$ nanotubes), 3096 cm^{-1} to ν(=C–H), 2992 and 2927 cm^{-1} to ν(–C–H), and 1434 cm^{-1} to $\delta(CH_3)$. These changes also can be seen at the IR spectra (see supporting information†).[10] From 40 wt% on, the composite spectra clearly display different characteristics due to ν ($-CH=CH_2$) (3010, 2973, 1645 and 935 cm^{-1}), ν ($-CH_3$) (1461 and 1371 cm^{-1}) and ν (–COO–) (1550 and 1430 cm^{-1}), and these differences increase with the MMA weight percentage. It is worth noting the disappearance of ν (C=O) (1727 cm^{-1}) and the remarkable increase of the intensity of ν (–COO–) (1550 and 1430 cm^{-1}), which provide as evidences of the producing of $-(COO)_3Y$.

Generally, an ester will hydrolyse in an alkaline solution when it is heated, to give the relevant alcohol and salt. The pronounced difference of Raman and IR spectra gives unambiguous evidence for a hydrolyzation of MMA and a subsequent reaction with $Y(OH)_3$ for the synthesis of methyl methacrylate yttrium. And most importantly, the double bonds ($-CH=CH_2$) have been successfully grafted to these nanotubes. TEM, EDAX and XRD also evidence the formation of this new type MMA–$Y(OH)_3$ composite nanotube.

In order to obtain additional confirmation of the organic substance content, thermo-gravimetric analysis (TGA) was performed on composites at all concentrations. The TGA was carried out under a nitrogen atmosphere. The resulting curves are shown in Fig. 5. The masses remaining at 700 °C are almost entirely due to the remaining Y_2O_3. The curve of composites with 20 wt% of Y_2O_3 is similar to the one of pure $Y(OH)_3$. Comparison of the curves reveals that there is a retardation at the onset of the decomposition for the composites with high MMA loading (40 and 60 wt%). These plots also show that the functional parts are 8.67, 27.33 and 28.31 wt% of $Y(OH)_3$ for 20, 40 and 60 wt% (of Y_2O_3) respectively, indicating a tendency towards saturation of the organic content.

Photoluminence of 60 wt% composites (measured in solid state at room temperature) also revealed some interesting features. The exciting wavelength is 250 nm and its emission spectrum is at 538 nm, which can not be observed in pure MMA or $Y(OH)_3$ (see supporting information†). These may be caused by the intramolecular charge-transfer interaction between the excited electron-donating carbon–carbon double bond of the methacrylic group and the electron-accepting yttrium, indicating an effective electron transport path.

It is also interesting to note that the composite nanotubes disperse better than unfunctional YNTs in some organic solutions such as benzene, chloroform and petroleum ether, and these can be attributed to the introduction of carbon chains to these nanotubes. Owing to the high reactivity of C=C, the composite nanotube as effective confined-templates can be easily further functionalized through a simple reaction, which may supply more potent synthetic ways for one-dimensional (1D) nanostructures. On the other hand, the composites will disperse well in the polymer matrix because of their hydrophobicity and the C=C also can bond with polymer which will result in good interfacial adhesion. So there may be new opportunities on offer in regions such as optoelectronic and nanoscale devices, low dimensional physics and material science, *etc*.

In summary, a novel type of MMA–$Y(OH)_3$ nanotube has been successfully fabricated *via* a simple one-step hydrothermal process, which can be further expanded to the preparation of new types of composites of polymer and rare earth nanotubes, nanowires and IF nanoparticles. We believe that these distinctive structures will offer new possibilities in many research areas.

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