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Fabrication of nanowires with polymer shells using treated carbon nanotube bundles as macro-initiators†

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Nanowires with polymer shells were produced *via* radical grafting polymerization of methyl methacrylate using treated carbon nanotube bundles as macro-initiators, thereby providing an efficient way to produce high grafting ratio nanocomposites.

Functionalization or modification of carbon nanotubes (CNTs) has attracted increasing attention over the past years[1–4] due to the growing interests in exploitation of their unique chemical and physical properties. Attachment of surface polymer chains is expected to endow CNTs with much more effective dispersibility in a wide range of solvents and has become one of the dominating methods to modify CNTs. Up to now, biomacromolecules and synthetic polymers have been grafted or assembled onto the convex surface of CNTs *via* covalent bonds[5,6] or "chemisorption".[7,8] There have been a number of reports describing the attachment of polymers to carbon nanotubes *via* free radical grafting polymerization.[9,10] However, in most of the reported methods, the grafting efficiency (fraction of total polymer grafted) and grafting ratio (ratio of grafted polymer to nanotube product) were low and the structures of the final carbon nanocomposites were uncontrollable, or in bulk forms. In this communication, we report fabrication of CNTs or CNTs bundle–poly(methylmethacrylate) core–shell nanowires *via* a controlled surface grafting radical polymerization of methyl methacrylate using treated carbon nanotube bundles as macro-initiators. It should be noted that CNTs, as reported by Jia *et al.*,[11] can be initiated by free radical initiators to open their π-bonds, which implies that CNTs participate in PMMA polymerization and form a strong chemical bonding interfacial adhesion between the CNTs and the PMMA matrix. For example, Park and co-workers[10] have produced multi-walled nanotube composites with PMMA prepared by *in-situ* bulk polymerization. They believed that C–C bonds were formed between MWNTs and PMMA during the polymerization initiated by the radicals on multi-walled carbon nanotubes (MWNTs).

During our investigation, a similar approach to grafting polystyrene onto single-walled carbon nanotubes (SWNT) was reported.[9] We were prompted to disclose our method because it is distinctly different in the controlling mechanism, in the process, and in the structures of the final nanocomposites. In the previously reported methods, the radical initiator (benzoyl peroxide or potassium persulfate) was used directly to initiate the grafting polymerization of styrene and thus substantive non-grafted polymers were formed during the polymerization. As a result, the grafting efficiency and grafting ratio was low. We believe that the grafting efficiency and the grafting ratio can be optimized using carbon nanotubes as macro-initiators. This process resembles the process of using nanotubes as seeds to perform grafting polymerization. The basics of the method are illustrated in Fig. 1. The adsorption of initiator species is a key step to control the polymerization initiating from the CNTs surface. Owing to their porous nature, MWNTs allow selective adsorption and this has been widely studied by many researchers.[12] Free radical initiator species can be selectively absorbed by MWNTs and this makes it possible for MWNTs acting as a supporter or macro-initiator to fulfill free radical polymerization. This can be accomplished using the following procedure: (1) a quantitative amount of potassium persulfate was dissolved in hydrogen peroxide solution (a small quantity of sodium dodecyl sulfate (SDS) was introduced to improve the wettability of MWNTs), and dried MWNTs synthesized by the catalytic chemical vapor deposition (CCVD) method were dispersed into the initiator solutions and kept gently stirring in ice-water bath for 2–5 h for the adsorption of initiator species. (2) MMA monomers containing divinyl benzene as crosslinking agent were emulsified with a sodium dodecyl sulfate aqueous solution in a glass flask under N_2. (3) The nanotubes/initiator blends were centrifuged and the resulting carbon nanotubes were dispersed into the glass flask immediately and then the flask was put into a water bath of an ultrasonic cleaner. (4) the reductive initiator ferrous sulfate was dissolved in water and dropped into the flask. The polymerization was first performed under ultrasound at 60 °C for 30 min and then the flask was put into an 80 °C water-bath reacting for 3 h under magnetic stirring. The morphology and structure of the resulting CNTs–PMMA nanocomposites were confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) (for details see ESI†).

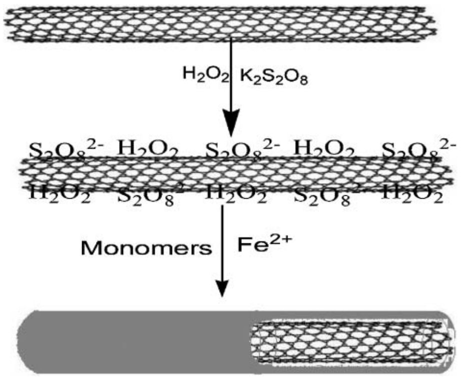

Fig. 1 Schematic of the method for preparation of the CNTs bundle wires with PMMA shells.

This process involves two important conditions, adsorption of initiators on the CNTs surface and initiation and growth of the polymerization from the CNTs surface. We found that only the $K_2S_2O_8/H_2O_2$–$FeSO_4$ initiating system can effectively initiate the grafting polymerization of MMA onto the CNTs surface and solely using $K_2S_2O_8$ or H_2O_2 as initiators led to a low grafting efficiency and there is almost no grafted polymer formed on the CNTs surface. This may due to the limited adsorption capacity of CNTs to absorb a sort of initiator species and at the same time part of the free radicals are captured by the CNTs. When $K_2S_2O_8$–H_2O_2 mixtures were used as initiators, the electronegative $S_2O_8^{2-}$ and

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† Electronic supplementary information (ESI) available: Details of experimental procedures, SEM, TEM and TGA analysis. See http://www.rsc.org/suppdata/cc/b4/b412282h/

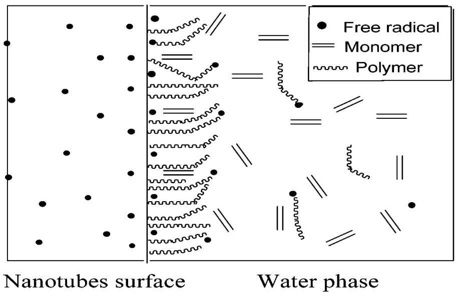

Fig. 2 Schematic illumination of the surface-initiating free radical grafting polymerization.

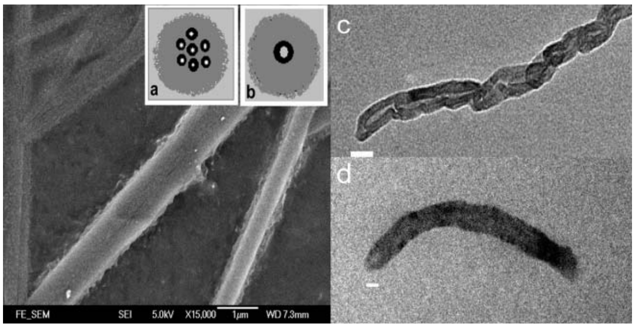

Fig. 3 SEM (left) of MWNTs bundle wires with PMMA shells and the cross-section model of the bundle wires (a) and single wire (b). TEM image (right) of pristine MWNTs (c, bar = 50 nm) and PMMA-grafted nanotubes (d, bar = 100 nm).

neutral H_2O_2 initiator species can be best absorbed by the CNTs and thus lead to adequate initiator concentrations on the CNTs surface to initiate the grafting polymerization. We also believe that there is a cooperating initiating process in using $K_2S_2O_8/H_2O_2$–$FeSO_4$ as the initiating system. The polymerization process is schematically described in Fig. 2. When the carbon nanotubes with absorbed initiators were dispersed into the emulsion containing monomers and reductive initiators, the monomer and reductive initiator diffused from the aqueous phase to the carbon nanotube surface initiating the polymerisation; with the growth of the polymer's molecular weight the polymer deposited onto the nanotubes surface and some of the polymer chains graft onto or permeate into the walls and tangle with the nanotubes and as a result the nanotubes will be plated with a layer of polymers stabilized by the SDS micelles; because of the strong sorption, the oxidative initiators are firmly immobilized by the porous nanotubes and only a few oxidative initiators diffuse into the aqueous phase and initiate the free radical emulsion polymerization to form PMMA homopolymers.

From the SEM image shown in Fig. 3 we see that the carbon nanotube bundle wires have different diameters. This may due to the CNTs showing a trend to form multi-tube bundles micelles in SDS aqueous solution[13] and then the bundles are grafted by PMMA. Owing to the high grafting ratio of PMMA, the diameters of the carbon nanotube bundle nanowires are in the range of 0.1–1 μm which is much larger than that of the pristine MWNTs (the diameters of the pristine MWNTs are about 10–30 nm as reported by the supplier and by TEM, see ESI†). Fig. 3 shows TEM images of the pristine MWNTs (c) and typical PMMA-grafted nanotubes (d). Although the TEM images are not very clear to show the PMMA coating shells, diameter and structural changes of MWNTs are observed, indicative of PMMA coatings on MWNTs. These changes in diameters and structure suggest that PMMA was grafted onto the CNTs' surface because otherwise the adsorbed PMMA homopolymers should have been removed after repeated washing with THF after the grafting reactions. The grafting ratio can be further confirmed by TGA (see ESI†). The difference in the weight loss between the PMMA-grafted nanotubes and the pristine nanotubes shows that PMMA were grafted onto the carbon nanotubes' surface forming the PMMA coating shells.

In conclusion, we have developed a straightforward and efficient process for grafting PMMA onto multi-walled carbon nanotubes with high grafting ratios that promises to produce useful nanocomposites, and which may readily be extended to a range of other vinyl polymers. The reaction parameters may be adjusted to control the grafting ratio and efficiency.

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