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Preparation of a Pt–Ru bimetallic system supported on carbon nanotubes

B. Rajesh,[a] K. Ravindranathan Thampi,[b] J.-M. Bonard[c] and B. Viswanathan*[a]

[a]Department of Chemistry, Indian Institute of Technology, Madras, Chennai, 600 036, India. E-mail: bviswanathan@hotmail.com
[b]Laboratoire de Photonique et Interfaces, Ecole Polytechnique Federale de Lausanne, CH-1015, Switzerland
[c]Institut de Physique Experimentale, Ecole Polytechnique Federale de Lausanne, CH-1015, Switzerland

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Pt–Ru nanoparticles (1.6 nm) were supported on carbon nanotubes (200 nm diameter, 8–10 μm length) obtained by the carbonisation of polypyrrole on an alumina membrane.

There is considerable current interest in developing nanostructured materials, as they find potential application in various fields of materials research.[1] Among these, carbon nanotubes and filled carbon nanotubes find application in nano-electronic devices,[2] as tips in atomic force microscopes,[3] as possible catalyst support materials in heterogeneous catalysis,[4] in fuel cells[5] and as gas storage materials.[6–8] Carbon nanotubes were first prepared by Iijima[9] using a carbon-arc method. The carbon nanotubes prepared by this method are graphitic in nature. The low yields obtained make the production cost high. The template synthesis[10] and catalytic production methods[11] avoid some of these difficulties. The yield obtained in the catalytic production method is higher than that of the carbon-arc method. Unfortunately there are also some drawbacks. The catalytically fabricated tubules are thicker than those obtained by the arc-discharge process and are covered by a thick layer of amorphous carbon. Among the different strategies employed to synthesize the nanostructured materials, template synthesis is an elegant approach. The template aided synthesis of nanostructured materials allows the size, shape and purity of the resulting nanostructured material to be controlled as the growth of the nanomaterial is arrested by the restricted dimensions imposed by the template. This technique was first perfected by Martin and Parthasarathy[12] to synthesize the desired materials within the pores of the template membrane with a cylindrical pore of uniform diameter and has been used to make nanotubules and fibers composed of polymers,[13,14] carbon,[15] carbon nitride,[16] metal(s),[17] semiconductors[18] and metal oxides.[19]

The general source of carbon to produce the carbon nanotubes is hydrocarbons,[20–22] but the complexity involved in the synthesis of carbon nanotubes using gaseous hydrocarbons is high, so an alternative and easy way should be employed to synthesise these materials avoiding gaseous and toxic hydrocarbons. Polymers such as polyacrylonitrile[23]and polyfurfuryl alcohol[24] have been used as the carbon source to prepare the carbon nanotubes. However carbon nanotubes containing nitrogen like C_3N_4 and CN nitrogen have been predicted to be materials of super hardness and metallic properties.[25,26] To date only a small quantity of nitrogen ($\leqslant$4–5%) has been incorporated into carbon nanotubes and/or filaments.[27] There are reports on the generation of aligned $C_{13}N_x$ ($x \leqslant 1$) nanofibers by the pyrolysis of melamine over laser patterned Fe or Ni substrates.[28] These materials were supposed to contain a uniform distribution of nitrogen with the morphology depending on the nitrogen concentration. Subsequently an aligned $C_{49}N_x$ ($x \leqslant 1$) nanofiber has also been synthesized by pyrolysing a mixture of ferrocene and melamine at around 950 °C in an argon flow.[29] Hydrogen free C/N nanotubes have also been synthesized using the precursor of 2,4,6-triazido-*s*-triazine (C_3N_{12}) by igniting it in a cylindrical copper container.[30] The striking feature of these studies on the formation of nitrogen containing nanotubes is the necessity for the presence of metals like copper and iron. The tubes so formed are graphitic in nature.

In this communication we report the synthesis of carbon nanotubes using polypyrrole as the carbon source which is formed *in situ* during the polymerisation of pyrrole in the alumina membrane. We also report the synthesis of platinum–ruthenium nanoparticle filled carbon nanotubes which are important catalytic materials for application in fuel cells.

The polypyrrole coatings were applied by a reaction coating approach[31] by suspending alumina membrane (Whatman, Anodisc 47, pore diameter *ca.* 200 nm) in an aqueous pyrrole (0.1 M) solution containing 0.2 M ferric chloride hexahydrate. Slowly, toluene-*p*-sulfonic acid was added and polymerisation was carried out for 3 h. The surface layer of polypyrrole which is formed in the membrane is removed by polishing with fine alumina powder and the sample then undergoes ultrasonication for 20 min to remove the residual alumina used for polishing. The formation of polypyrrole on the alumina membrane was confirmed by using IR spectroscopy. The polypyrrole coated alumina membrane was then dried and placed in a quartz boat and carbonised at 950 °C in an Ar atmosphere for 5 h at a heating rate of 10 °C min^{-1} . The resulting carbon/alumina composite was immersed in 48% HF for 24 h to remove the template. The residue was thoroughly washed with deionised water to remove the HF and dried at 110 °C for 1 h. The elemental analysis of the carbon nanotube synthesised was carried out using a Heraeus CHN analyser which showed a rich percentage of carbon with $<1\%$ H and $<2\%$ N.

The microscopic features of the sample were observed with a JEOL 1500 scanning electron microscope (SEM) and a high-resolution transmission electron microscope (TEM, Philips EM430ST operated at 300 kV). The samples were dispersed in ethanol under sonication and dropped on the SEM sample holder and carbon coated TEM grids and imaged. Fig. 1a shows the formation of monodisperse, hollow, carbon nanotubes. Fig. 1b shows the cylindrical tube with an open end, which can be utilised to fill the nanoparticles. It also reveals that their outer diameter is almost the same as the diameter of the pores of the alumina membrane used. It is noteworthy from Fig. 1c that the tubes are transparent under TEM observation, indicating that the tube walls are very thin. The SEM image (Fig. 2) shows the scanning electron micrograph of the aligned tubular nanofibers projecting perpendi-

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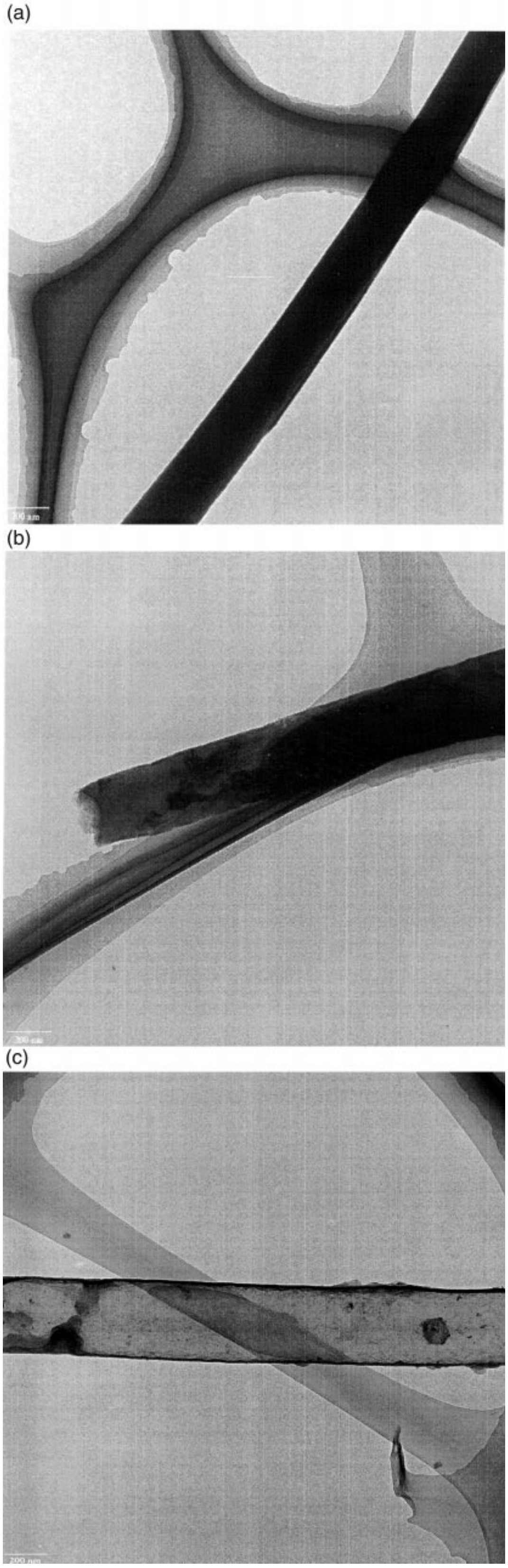

Fig. 1 High resolution transmission electron micrographs: (a) showing the monodisperse, uniform carbon nanotube obtained by carbonisation of polypyrrole on an alumina membrane; (b) showing the cylindrical tube with an open end and with an outer diameter almost equal to that of the channel diameter of the template used; (c) showing the tube to be transparent, which indicates that the walls of the carbon nanotube are very thin.

Fig. 2 Scanning electron micrograph of aligned nanofibers projecting perpendicularly from the surface of the SEM sample holder.

cularly from the surface of the SEM sample holder. Though the carbon tubes produced by this method are not completely graphitic as are those produced by the arc-discharge process, their disordered structure is quite typical of fibers or nanotubes produced by decomposition of hydrocarbons.

It is of interest to compare the quality and texture of the material synthesized with other nitrogen containing nanotubes and fibers reported in the literature. HREM images of the nitrogen containing nanotubes obtained by the detonation of 2,4,6-triazido-*s*-triazine in a copper container showed that the product is mainly graphitic in nature with multiwall and faceted onion structures. The particles were of various diameters reaching up to 100 nm, with hollow tubes and possess a faceted structure. On the other hand, the nanocomposites obtained from the decomposition of melamine on laser etched Fe films exhibited corrugated and/or compartmentalized morphologies with relatively thin walls. These walls consist of several graphitic layers aligned along the fiber axis. In general the degree of tubular perfection decreased with an increase in nitrogen incorporation. The nanotubes obtained in this study also exhibited aligned graphitic layers with thin walls. The iron ions used for the initiation of polymersation, after reduction to their metallic state could have been the catalytic centres to promote the formation of nitrogen containing carbon nanotubes. The similarities between the nitrogen containing carbon nanotubes reported in the literature and the ones reported in this work are: (i) the relatively thin walls, (ii) wide inner cores, (iii) graphitic nature of the nanotubes and (iv) alignment along the fiber axis.

The platinum–ruthenium nanoparticle filled carbon nanotubes were prepared by immersing the carbon/alumina composite (after the carbonization of polypyrrole) in 37 mM $H_2PtCl_6(aq)$ and 73 mM $RuCl_3(aq)$ for 5 h to allow the salts to penetrate inside the nanotube. The composite was then dried at room temperature and reduced in a flow of H_2 at 550 °C for 3 h. The membrane was then dissolved in 48% HF for 24 h to leave Pt–Ru nanoparticle filled carbon nanotubes. TEM pictures (Fig. 3a and b) show that the platinum and ruthenium nanoparticles are highly dispersed inside the carbon nanotube with an average particle size of around 1.6 nm. It is evident from these figures that most of the bimetallic nanoparticles are present inside the tube. This is due to the preparation procedure, *viz.*, the metal precursors were loaded on the carbon/alumina composite before the dissolution of alumina by HF.

The X-ray photoelectron spectroscopy (XPS) measurements of Pt–Ru nanoparticle filled carbon nanotubes were carried out using a Perkin Elmer PHI 5500 ESCA system using Mg-K_α as the excitation source. The peak binding energies of Pt $4f_{7/2}$ at 71.4 eV and $4f_{5/2}$ at 74.4 eV suggest that the Pt particles are present in the zero valent state. The Ru 3d spectrum has been obscured by the C 1s spectrum, but the deconvoluted spectrum shows a doublet with peak binding energies of 280.6 eV($3d_{5/2}$) and 284.8 eV($3d_{3/2}$) which confirms the presence of Ru particles. The absence of a signal due to aluminium suggests that the alumina membrane has been completely dissolved.

In conclusion, the thermal decomposition of a polypyrrole coated alumina membrane yielded hollow, cylindrical, mono-

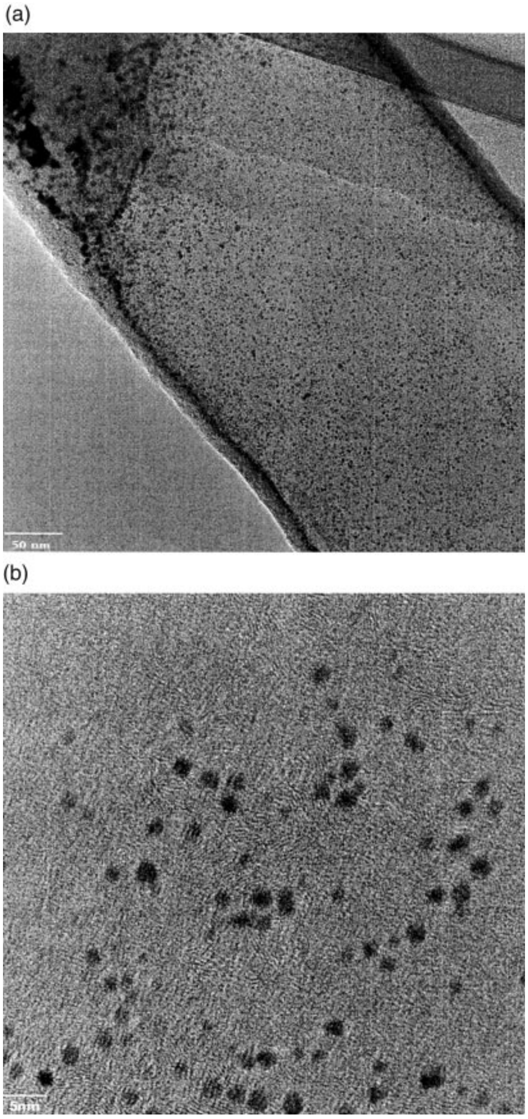

Fig. 3 (a), (b) High resolution transmission electron micrographs of Pt–Ru nanoparticle filled carbon nanotubes.

disperse, aligned carbon nanotubules or fibers with an outer diameter of about 200 nm and a length of about 10 µm. The bimetallic particles are strongly entrapped inside the tube as reflected by the fact that the particles appear to be quite stable even after the vigorous treatment of the composite in concentrated HF. The template technique allows the preparation of platinum–ruthenium nanoparticles which are highly dispersed inside the carbon nanotube with an average particle size of around 1.6 nm and which can be used as the possible catalyst material in Direct Methanol Fuel Cells.

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