Carbon Nanotubes Generated from Polyphenyl Acetylene

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Abstract

The carbonization of polyphenyl acetylene in alumina matrix yields uniform, cylindrical, monodisperse carbon nanotubes with outer diameter almost equal to pore diameter of the alumina membrane used. The electrochemical characteristics reveal that the charge transfer at the composite electrode based on carbon nanotube might be higher compared to that of planar graphite, glassy carbon and composite electrode based on commercially available Vulcan XC72R carbon. Pt-Ru nanoparticles are highly dispersed inside the tube with an average particle size of 1.7 nm as revealed by HR-TEM images.

Introduction

The tubular structure of carbon nanotubes makes them unique among different forms of carbon and thus can be exploited as an alternative material for catalyst support in heterogeneous catalysis [1] and in fuel cell electrodes [2]. It can also find application as tips in atomic force microscope [3] and as gas storage materials [4]. The discovery of carbon nanotube(CNT) was first based on the carbon-arc method [5], the carbon nanotube prepared by this method is more graphitic with low yields thus making the production cost high. The template synthesis [6] and catalytic production methods [7] do not have some of these limitations. The yield obtained in catalytic production method is higher compared to that of the carbon-arc method. Unfortunately there are also some drawbacks. The catalytically fabricated tubules are normally thicker than those obtained by the arc-discharge process. These are also covered by a thick layer of amorphous carbon. The template technique was first introduced by Martin [8] to synthesize the desired materials of nanotubules and fibers composed of polymers[9,10], carbon [11], metal(s) [12] semiconductors [13] and metal oxides [14] within the uniform pores of the membrane. The normal source of carbon to produce the carbon nanotubes are hydrocarbons [15-17]. The complexity involved in the synthesis of carbon nanotubes using gaseous hydro-

carbons is high. The criteria of selecting the carbon precursor is that, it should be rich in carbon content and it should be easily decomposed to give rise to a pure carbon deposit. Polymers such as polyacrylonitrile [18] and polyfurfuryl alcohol [19] have been used as the carbon source to prepare the carbon nanotubes and recently the template aided synthesis of bimetallic nanoparticles filled carbon nanotubes based on polypyrrole as carbon source has been reported [20]. It has been reported that the use of carbon sources which contain nitrogen [21,22] leads to carbon nanotubes containing nitrogen, it is difficult to remove the nitrogen completely and the topology of the carbon nanotube formed is altered as a function of the amount of nitrogen in the nanotube [23].

In this paper, the use of polyphenyl acetylene as the carbon source for the synthesis of carbon nanotubes is reported. Since it is rich in carbon content and only carbon-hydrogen bonds have to be broken during the thermal treatment, it can be an ideal starting material for the preparation of the carbon nanotubes.

Experimental

Synthesis of carbon nanotubes

The polyphenyl acetylene was prepared by photoinitiation [24] of phenylacetylene(Fluka) by $W(CO)_6$ (Fluka). The polyphenyl acetylene/alumina composite was prepared by adding 10 ml of 5% w/w

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polyphenyl acetylene(in dichloro methane) to the alumina membrane(Whatman, 200 nm pore diameter, 60mm thick, 17.34 cm^2) and applying vacuum from the bottom. The entire polymer solution penetrates inside the pores of the membrane by the suction applied. The solvent was evaporated slowly and the membrane was dried in vacuum at 333 K. The composite was then polished with fine alumina powder to remove the surface layers and ultrasonicated for 20 min. to remove the residual alumina used for polishing. The infrared spectrum of the composite membrane confirms the presence of polyphenyl acetylene in the membrane. The composite was then carbonized by heating in Ar atmosphere at 1173 K for 3 h at a heating rate of 283 K/min. This resulted in the deposition of carbon on the channel walls of the membrane. The carbon/alumina composite was then placed in 48% HF to free the nanotubules. The tubules left behind in HF were completely washed with deionised water to remove HF.

Characterisation Methods

Scanning electron micrographs (SEM) were obtained using JEOL 1500 microscope. The carbon nanotubes obtained after the disssolution of the template is immersed in ethanol and ultrasonicated for 20 min. A drop of this suspension was placed on SEM sample holder and sputter coated with gold to prevent charging and imaged. The microscopic features of the sample were observed with high-resolution transmission electron microscope(HR-TEM, Philips EM430ST) operated at 300 kV.

Electrochemical Measurements

The electrochemical characteristics of the carbon nanotube prepared were evaluated using cyclic voltammetry (Wenking Potentioscan (POS73)) with digital X-Y recorder and compared with that of planar graphite, glassy carbon(GC) and commercially available Vulcan XC72R carbon. The electrochemical experiments were performed in 1 M H_2SO_4 between –0.2 V and +0.8 V versus Ag/AgCl at a scan rate of 25 mV/s.

Preparation of Composite Electrodes

The electrodes for the electrochemical measurements were fabricated by dispersing the CNT(after the template removal) in 200 μl of deionised water and 5-10 μl of 5 wt% Nafion solution was then added and ultasonicated for 20 min. A

known amount of the suspension was added on to the Glassy Carbon (GC) electrode and the solvent was slowly evaporated which results in GC/CNT-Nafion electrode. The same procedure was followed for the commerically available Vulcan XC 72R carbon.

Loading of Pt-Ru nanoparticles inside CNT

Pt-Ru nanoparticles were loaded inside CNT as follows, the C/alumina composite obtained (before the dissolution of the template membrane) were immersed in 37mM $H_2PtCl_{6(aq)}$(Hindustan Platinum Ltd) and 73mM $RuCl_{3(aq)}$(Arora Matthey Ltd) 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 823 K for 3 h. The membrane was dissolved in 48% HF for 24 h. to obtain Pt-Ru nanoparticles filled carbon nanotube.

Results and discussion

The scanning electron micrograph shown in Fig.1(after the disssolution of alumina membrane) reveals the formation of bunches of aligned carbon nanotubes projecting perpendicularly from the surface of the SEM sample holder.
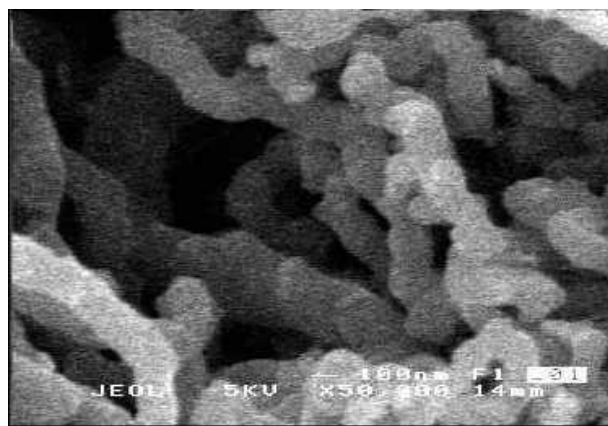

Fig. 1. Scanning electron micrographs of carbon nanotubes projecting perpendicularly from the surface of the SEM sample holder obtained by the carbonisation of polyphenyl acetylene on alumina membrane.

High-resolution TEM pictures shown in Fig 2a show the hollow tubes with slight deformation in the tube probably caused by the vigorous HF treatment. Fig. 2b indicate the formation of cylindrical, monodisperse tube with an outer diameter of almost 200 nm, which corresponds to the channel diameter

of the template used. It is noteworthy from Fig.2c that the tube is transparent under TEM observation conditions, indicating the wall thickness is thin. It is seen from Fig. 2d that the tube end is opened which can be utilised to load the metallic nanoparticles inside. Though the carbon tubes produced by this method are not completely graphitic in nature as those produced by arc-discharge process, their disordered struc-

ture is quite typical of fibers or nanotubes produced by decomposition of hydrocarbons. The carbon nanotubes shown in Fig 2b. are not hollow, but it is clear from other micrographs (Figs. 2a, 2c and 2d) that the nanotubes are hollow in nature. The thick walls of few of the carbon nanotubes (Fig. 2b) might be the reason for not observing the carbon nanotube in hollow morphology.
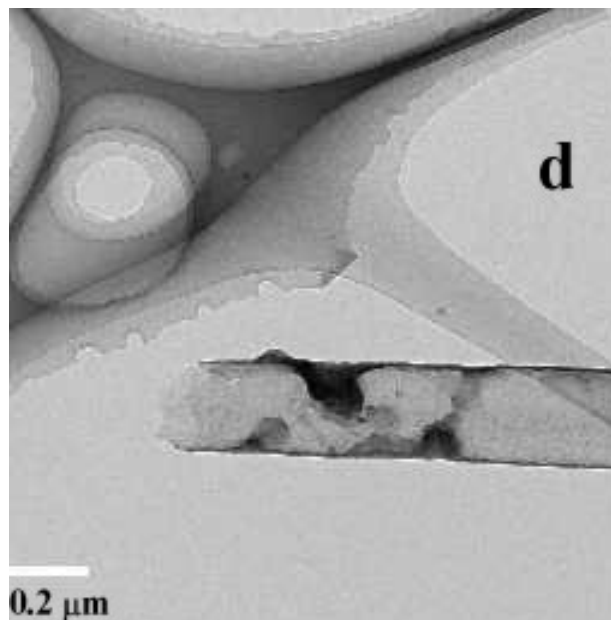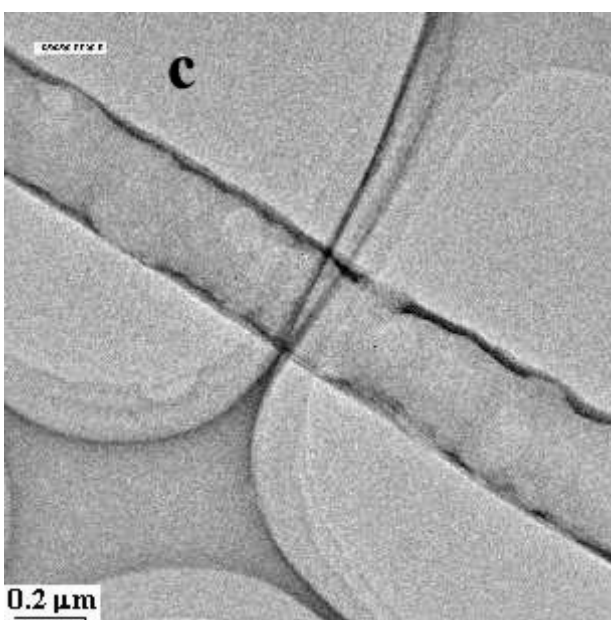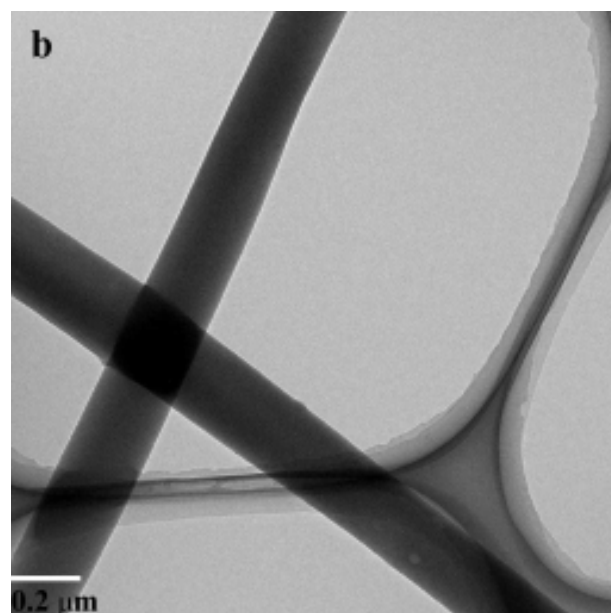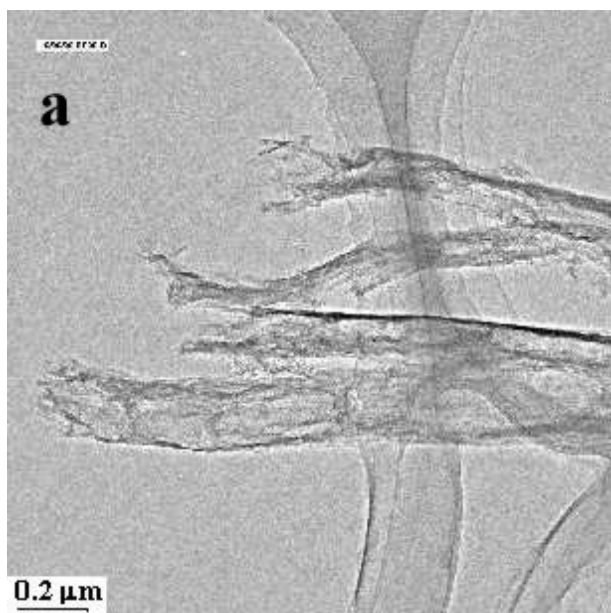

Fig. 2. High- resolution transmission electron micrographs
a)showing the part of carbon nanotubes which are slightly deformed probably due to the vigorous HF treatment.
b)showing the uniform, monodisperse nanotubes
c)showing the cylindrical, hollow and transparent carbon nanotube with the diameter almost equal to that of the pore size of the template used.
d)showing the open end tube which can be utilised to load the nanoparticles

The carbon nanotube-nafion coated glassy carbon(GC/CNT-Nafion) electrode exhibited a well defined peak (Fig.3a) at +0.40 V and +0.38 V with respect to Ag/AgCl in the forward and the backward scans respectively. The cyclic voltammograms obtained with Vulcan XC72R-nafion coated glassy carbon(GC/VulcanXC72R-Nafion) (Fig. 3b), planar graphite(Fig. 3c) and bare glassy carbon electrodes (Fig. 3d) reveal that these electrodes do not exhibit any defined redox peaks. Another interesting feature is that the higher current response of GC/CNT-Nafion electrode as compared to the other electrodes, which suggests the availability of higher electrochemical surface area in the composite electrode based on carbon nanotube. The lower electrochemical response of the GC/Vulcan XC72R-Nafion might be due to the resistance offered by the polymeric binder (Nafion). But in the case of GC/CNT-Nafion electrode the tubular structure (as evidenced from HR-TEM images) of the carbon nanotube still allows effective charge transfer to take place at the nanotube composite electrode. The higher electrochemical surface area available at the composite electrode based on carbon nanotube can possibly be utilised by dispersing the bimetallic nanoparticles inside the nanotube. In order to account for the higher current response, the electroactive surface area of CNT has been evaluated and compared with commercially available Vulcan XC 72R carbon, Graphite and Glassy Carbon electrodes respectively. The electrochemical surface area has been evaluated using cyclic voltammetry. The voltammogram was run in 5 mM $K_4[Fe(CN)_6]$ (which is used as the probe molecule) in 0.1 M KCl at a scan rate of 50mV/sec and at 298 K. The electrochemical surface area has been evaluated from the peak current and by using the diffusion coefficient of $K_4[Fe(CN)_6]$ (0.76×10^{-5} cm^2/sec) in Randel Seveik equation. The electrochemical surface area was found to be 0.2 cm^2, 0.035 cm^2, 0.03 cm^2 and 0.01 cm^2 for GC/CNT-Nafion, GC/Vulcan XC72R Carbon-Nafion, Graphite and Glassy carbon electrodes respectively. From these values, it is clear that the tubular morphology favours the higher electrochemical surface area of the carbon nanotube based electrode.
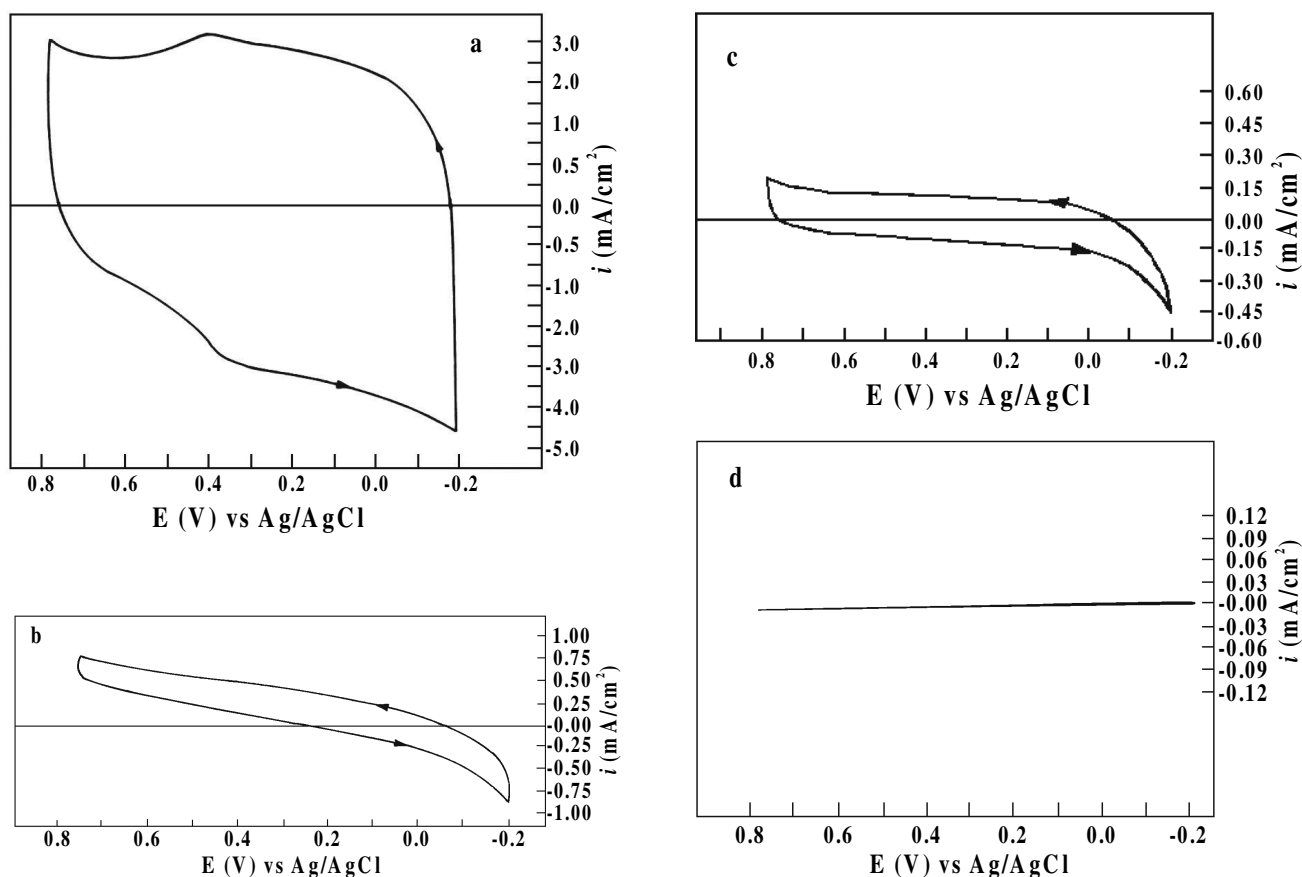
Fig. 3. Cyclic voltammograms of: a)GC/CNT-Nafion; b)GC/Vulcan XC72 R Carbon-Nafion; c)Graphite; d)GC electrodes run in 1 M H_2SO_4 at 25mV/sec and at 298 K.

Fig.4a shows that the platinum and ruthenium nanoparticles are dispersed inside the carbon nanotube with an average particle size of around 1.7 nm, (as determined by statistical average method), it is also seen from the figure that the nanoparticles are present on the inner walls of the carbon nanotube. Fig.4b also reveals the partly graphitic nature of the carbon nanotube with the particles dispersed uniformly in the tube.
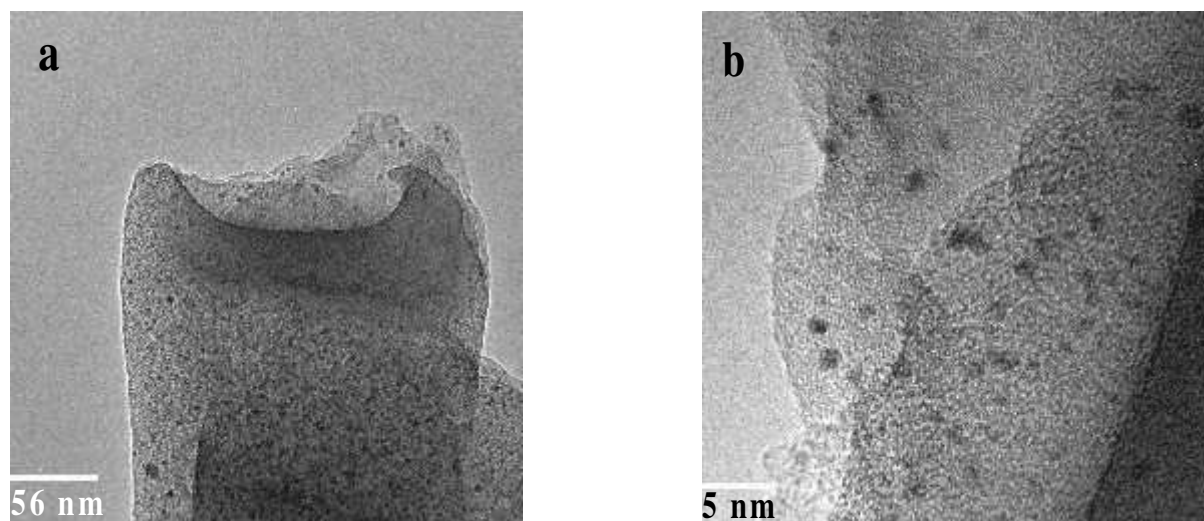

Fig. 4. High-resolution transmission electron micrographs; a)showing the Pt-Ru nanoparticles filled on the inside walls of the carbon nanotube; b)showing the Pt-Ru nanoparticles are highly dispersed with an average particle size of 1.7 nm.

Conclusion

The carbonisation of polyphenyl acetylene in template membrane results in an uniform, hollow, cylindrical, carbon nanotubes. The higher electrochemical response of the composite electrode based on carbon nanotube suggests the availability of higher electrochemical surface area as compared to the planar graphite, glassy carbon and composite based on VulcanXC 72R carbon electrodes. The tubular structure of the carbon has been effectively utilised to disperse the Pt-Ru bimetallic nanoparticles, as it is revealed from the higher electrochemical surface area of carbon nanotube based electrode. The electrochemical surface area of the electrodes follows the order: GC/CNT-Nafion(20)>GC/VulcanXC 72RCarbon-Nafion(3.5)>Graphite(3.0)>Glassy carbon(1.0). Since the binding sites for the bimetallic clusters can be expected to be different in the nanotubes as compared to the bulk carbon support, the bimetallic clusters supported on carbon nanotubes can function effectively for electrode applications in direct methanol fuel cell.

Acknowledgements

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