AN EASY TWO-STEP MICROWAVE ASSISTED SYNTHESIS OF SNO_2/CNT HYBRIDS

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ABSTRACT

Tin oxide (SnO_2) - decorated carbon nanotube (CNT) heterostructures were synthesized by microwave assisted wet impregnation method. CNTs of three different aspect ratios were compared. The hybrid samples were characterized by powder X-ray diffraction, Raman spectroscopy, high resolution transmission electron microscopy, BET surface area analysis and DC conductivity measurement. The results showed that the microwave assisted synthesis is a very efficient method in producing CNTs that are heavily decorated by SnO_2 nanoparticles in a very short time (total reaction time of 10 min.), irrespective of their length and diameter. The hybrids showed 100 times increase in electrical conductivity when compared to the unmodified CNTs.

INTRODUCTION

Hybrid structures of nanoparticles (NPs) distributed on CNT surface could potentially display not only the unique properties of nanocrystals and those of CNTs, but also additional novel properties. Attaching NPs on CNTs surfaces could promote direct and effective charge transfer and hence increase device/process efficiency.[1] SnO_2 NPs decorated CNTs are reported to be useful functional composites in many applications including gas sensors[2], fuel cells[3], batteries[4], and supercapacitors.[5] This is based on the fact that the work function of CNTs is approximately equal to that of SnO_2 allowing electrons to travel through the SnO_2 grains to CNTs and then be conducted in the CNTs with low resistance.[6] Over the last few years various techniques have been used to prepare SnO_2/CNT hybrid structures such as wet-chemical[7-10], sol-gel[11], gas-phase[12, 13], supercritical fluid[14] methods, etc. Bai *et al.*[6] reported a microwave–polyol irradiation method for fuctionalizing CNTs with SnO_2 where diethylene glycol was used as the solvent. Prior to the microwave irradiation, the CNTs were oxidized in concentrated HNO_3 at 140°C for 6 h. Microwave assisted synthesis has recently shown remarkable advantages over the conventional synthesis routes such as rapid volumetric heating, high reaction rate, reduced particle size, homogenous and narrow size distribution of particles.[6, 15] In this study, we report a fast and efficient microwave-assisted two-step synthesis for coating CNTs with SnO_2 NPs.

EXPERIMENTAL

Three batches of Multi-Walled Carbon Nanotubes (MWCNTs) produced by chemical vapor deposition (CVD) method were provided by Sigma-Aldrich and correspondingly abbreviated as CNT10 (OD =10–30 nm, ID=3–10 nm, L = 10 μm, 90% purity), CNT200 (OD = 20–30 nm, ID = 5–10 nm, L = 200 μm, 95% purity), and CNT500 (OD = 40–60 nm, ID = 5–10 nm, L = 500 μm, 95% purity). A portion of CNTs (500 mg) were heated under reflux with 5M HNO_3 (10 ml/ 10 mg) at 120°C for 5 min in a microwave reactor (Anton Paar microwave reaction system-Multiwave 3000) at a power setting of 500 W. The solution was filtered and washed with distilled water until the pH of the solution was neutral. The CNTs were then dried in air at 110°C for 12 h. In the second step, 10 g of $SnCl_2$ was dissolved in 400 ml of distilled water and 5 ml of concentrated HCl (37 wt%) was added. The acid treated CNTs were then added to the above solution. The solution was then heated under reflux in the

microwave for 5 min at 500 W and 60°C. The precipitate was then separated from the mother liquor by centrifugation, washed with distilled H_2O several times and dried in air at 110°C for 12 h. The final product was calcined in air at 500°C for 2 h. The SnO_2/CNT composites obtained after microwave treatment with three different types of CNTs were correspondingly abbreviated as CNT10NC, CNT200NC and CNT500NC.

RESULTS AND DISCUSSION

Figure 1 presents a series of TEM images of composite samples at two different magnifications. All the three different batches of CNTs were observed to be heavily coated with SnO_2 NPs. These NPs were uniformly deposited even in the interior surface of the tubes and were spherical with 3-5 nm diameters.

The *G*/*D* ('*G*' for graphitic band and '*D*' for defect band) ratios calculated from the Raman spectra for the CNTs and corresponding SnO_2-containing samples are presented in Table 1. The G/D ratio is greater for composites CNT200NC and CNT500NC compared to pure CNT200 and CNT 500, respectively. This could be due to an enhancement of atomic ordering of crystallinity of the CNTs after they were decorated with SnO_2 NPs [13]. The opposite was observed for CNT10 and its corresponding SnO_2-containing sample CNT10NC and could be due to the interaction between the SnO_2 and the surface group of CNTs rather than the increase in amorphous carbon.[16]

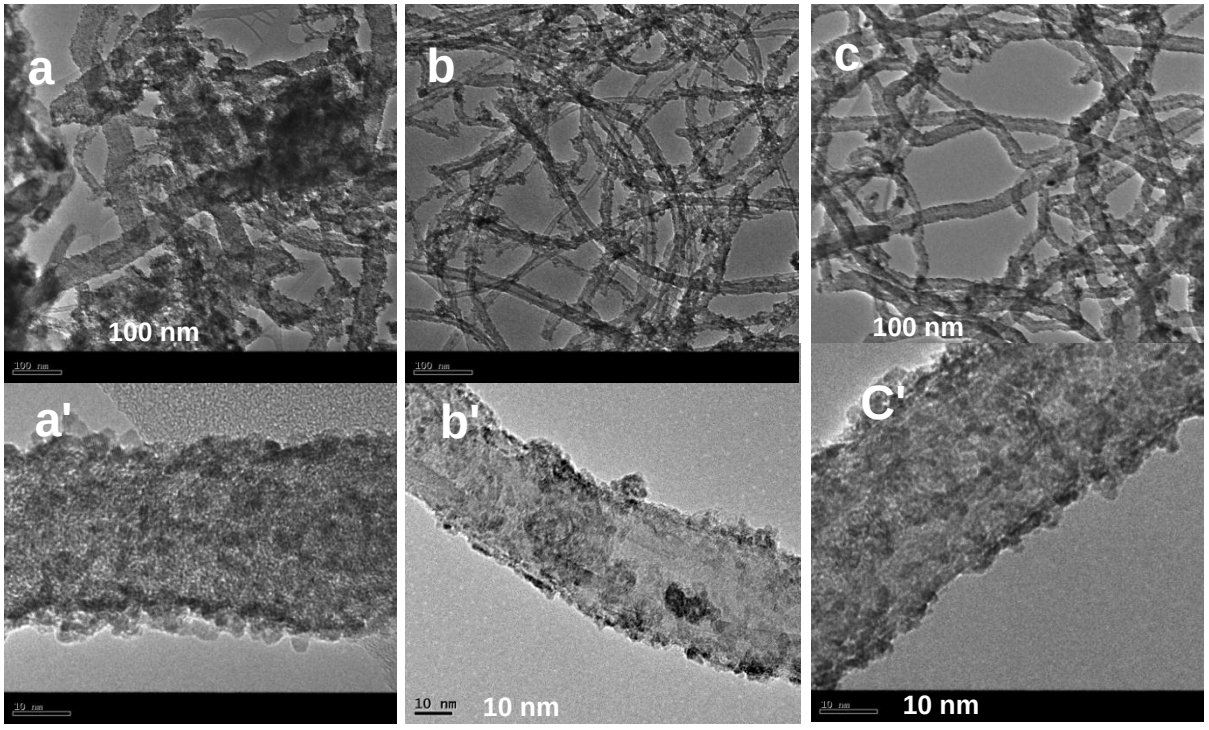

Figure 1. TEM images of various SnO_2/CNT composite samples at two different magnifications: (a & a') CNT10NC; (b & b') CNT200NC; (c & c') CNT500NC.

Table 1. Characteristic peak intensities and *G*/*D* ratios from the Raman spectra of CNTs and corresponding SnO_2-containing composite samples.

Sample	Raman Intensities /a.u.[a]		*G*/*D* ratio
	G-band	*D*-band	
CNT10	16.51	16.68	0.99
CNT10NC	13.86	17.26	0.80
CNT200	14.77	16.52	0.89
CNT200NC	12.61	13.40	0.94
CNT500	15.02	16.67	0.90
CNT500NC	16.35	12.28	1.33

[a] '*G*' for graphitic band and '*D*' for defect band

To further confirm the presence of SnO_2 particles in the composite samples and check the crystalline phases, the prepared samples were analyzed by XRD and the diffractograms are presented in figure 2. All the samples show peaks of C (002) and C (100) phases with d_{002} values of 0.34 nm characteristic of CNTs. The SnO_2/CNT samples show intense peaks corresponding to tetragonal phase of SnO_2. The C (002) peaks appear to be shifted in the composite sample indicating the interaction of SnO_2 nanoparticles with CNTs. XRD results are in line with microscopy observations.

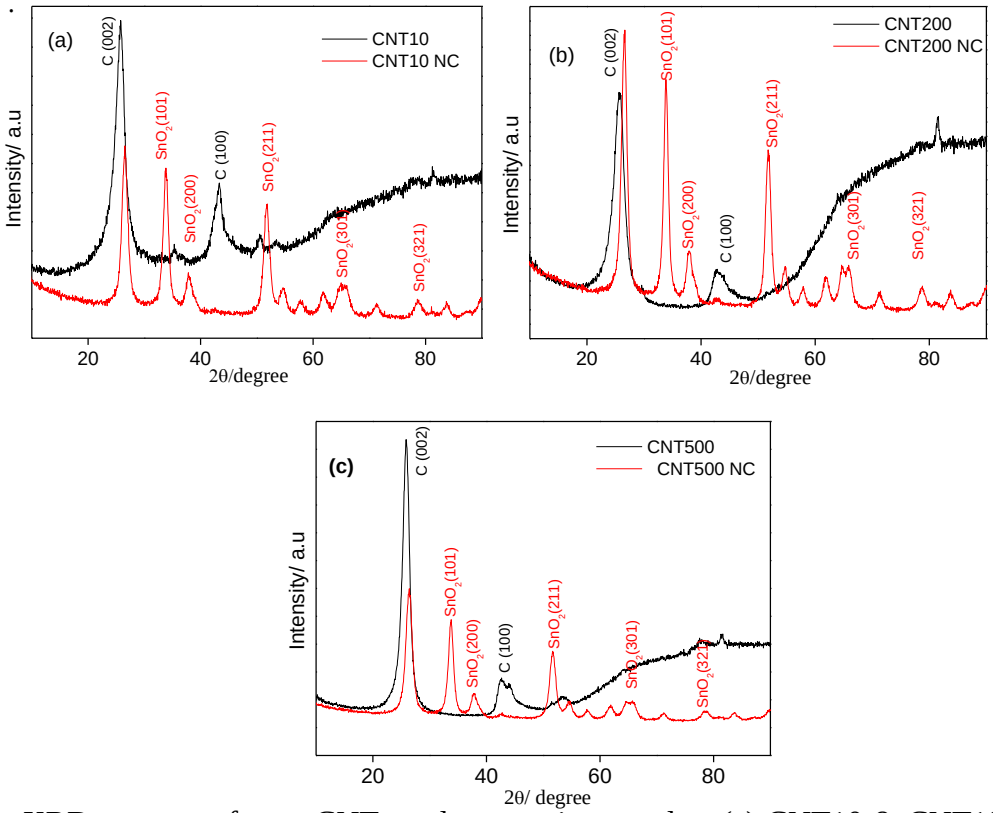

Figure 2. XRD patterns of pure CNTs and composite samples: (a) CNT10 & CNT10NC, (b) CNT200 & CNT200NC, and (c) CNT500 & CNT500NC.

The measured BET surface areas of different CNT samples are given in table 2. Surface areas of the SnO_2/CNT samples are observed to be lower than the corresponding pure CNTs in all the three batches. This indicates the coating of CNT surface with SnO_2 NPs which also contributes to the

increase in pore size. The DC conductivity values of various samples obtained from four point probe measurements are also presented in table 2. The conductivity values increase appreciably for the composite samples. For example, the DC conductivity increases from 3.53×10^{-2} S/cm for the pure CNT200 to 3.23 S/ cm (average of five independent measurements with a maximum error of 7%) for the composite and this represents a 100 times increase in the electrical conductivity. These results indicate that there is effective contact between CNTs and the SnO_2 NPs forming a conducting network which helped in lowering the resistance to the conduction of electrons. Although high concentration of SnO_2 nanoparticles can not contribute to the electrical conduction[17-19], these results indicate that in the present case, the SnO_2 nanoparticle concentration is enough to form a percolating net work, which attributes to presence of high concentration of charge carriers[20] leading to increase in overall conductivity of the system.

On the other hand, the similar composites prepared by conventional wet impregnation method (results not shown here) showed only 10 fold increase in DC conductivity when compared to pure CNTs. This indicates the effectiveness of microwave assisted route for the preparation of such nanocomposites.

Table 2. Data obtained from BET and electrical conductivity measurements of various CNTs and SnO_2/CNT composite samples

Samples	Surface area /$m^2.g^{-1}$	Micropore volume /$cm^3.g^{-1}$	Pore size /nm	Electrical Conductivity/ S/cm
CNT10	129.0	0.4	11.7	2.16×10^{-2}
CNT10NC	103.2	0.4	15.4	8.28
CNT200	129.9	0.4	15.5	3.53×10^{-2}
CNT200NC	119.0	0.4	12.6	3.23
CNT500	129.7	0.4	11.5	2.02×10^{-2}
CNT500NC	107.6	0.5	13.5	4.01

CONCLUSIONS

We have described a simple, fast and efficient method to synthesize SnO_2 NPs decorated CNTs. The method serves equally good for the surface functionalization for CNTs with different aspect ratios. Nanoparticles of 3-5 nm were uniformly deposited on the CNT surface in a total reaction time of 10 min. The composites thus prepared exhibited 100 times increased electrical conductivity when compared to the pure CNTs. Our ongoing work will focus on the gas-sensing ability and catalytic efficiency of composite materials.

ACKNOWLEDGEMENTS

SCM, SKP and SSR thank the DST and the CSIR, South Africa for financial support.

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