Improvement in structural and electrical properties of cuprous oxide-coated multiwalled carbon nanotubes

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Abstract. In the present work, cuprous oxide (Cu_2O) nanoparticles are coated on multi-walled carbon nanotubes (MWCNTs) using Fehling's reaction. The coating of Cu_2O nanoparticles on the nanotubes was confirmed by SEM and X-ray diffraction (XRD) spectra. The calculated I_D/I_G ratio of Cu_2O (using 3% CuSO_4 by wt)-coated MWCNTs by Raman spectra is found to decrease to 0.94 as compared to 1.14 for pristine MWCNTs. It shows that the presence of Cu_2O nanoparticles on nanotubes decreases the inherent defects present in the form of some pentagons/heptagons in the honeycomb hexagonal carbon atoms in the structure of graphene sheets of MWCNTs and increases the crystalline nature of MWCNTs, which is also confirmed by the XRD peaks. Whereas the value of I_D/I_G ratio increases to 1.39 for sample 2 (using 5% CuSO_4 by wt), which represents the structural deformation. Moreover, the electrical conductivity of MWCNTs was increased by 3 times after coating the nanotubes with Cu_2O (using 3% CuSO_4 by wt).

Keywords. Composites; structural studies; electrical properties; lithography.

1. Introduction

Recently, there has been rapid progress in the field of nanotechnology by fabricating devices utilizing carbon nanotubes (CNTs) (Iijima 1991; Peng *et al* 2009; Riehemann *et al* 2009). The properties of CNTs are keenly modified by the attachment of organic and inorganic compounds such as metals, metal oxides and polymers (Ebbesen 1996; Balasubramanian and Burghard 2005). CNTs have high reactivity and can also easily interact with nanomaterials. This is the main reason behind the enhancement in the structural, electrical, mechanical and sensing properties of CNT composites (Khan and Aziz 2012). Uniform coating of CNTs with nanomaterials has already become a challenging area of research owing to their applications in optoelectronic devices, fuel cells and sensors (Olek *et al* 2006; Zebli *et al* 2009; Kim *et al* 2012; Subramaniam *et al* 2013). Attachment of CuO , Cu_2O , TiO_2 , ZnO , Cu-doped ZnO and NiO nanoparticles to CNTs has shown great promise for high efficiency in heat transfer applications, electrochemical supercapacitors and gas sensor devices (Reddy *et al* 2008; Zein and Boccaccini 2008; Liaoa *et al* 2009; Chen *et al* 2012). Jha and Ramaprabhu (2008) have decorated MWCNTs with copper nanoparticles by chemical reduction method. They found that thermal conductivity of the composites increased with the concentration of MWCNTs (Jha and Ramaprabhu 2008). Experimental results reveal that

Cu_2O -decorated MWCNTs have weak ferromagnetic properties. Xu Long-Shan *et al* (2007) have studied thermal expansion coefficient of MWCNTs/copper composites. They have observed that the thermal expansion coefficient decreased with increased concentration of MWCNTs in the composites with copper (Xu Long-Shan *et al* 2007).

In the present work, composites of cuprous oxide nanoparticles with MWCNTs were prepared by chemical route and then enhancement in their structural and electrical properties with respect to pristine MWCNTs investigated using a fabricated device.

2. Experimental

2.1 Synthesis of MWCNTs-based nanocomposites

The pristine MWCNTs were procured from Global Nanotech (Mumbai, India) with a purity level >95%. These have been synthesized by CVD method and purified by acids treatment. The process of samples preparation includes three major steps. First, 3% by wt solution of CuSO_4 precursor, called Fehling's solution, with tartaric acid and sodium hydroxide was prepared. A sufficient amount of purified MWCNTs was sonicated in this prepared solution for 1 h using an ultrasonication bath. Finally, this mixture was stirred at 60 °C for 1.5 h. During stirring 0.25 mL formaldehyde as a reducing agent was added drop-wise and then centrifuged. This mixture was washed many times with ethanol and then with distilled water and dried in vacuum. This prepared powder is named as sample 1.

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The same method was applied for 5% by wt of CuSO_4 solution to obtain sample 2. The chemical reactions involved during the synthesis of cuprous oxide are

When MWCNTs were suspended in Fehling's reagent solution and subjected to sonication, the MWCNTs could absorb the copper ions that were complexed with tartrate. Further, by drop-wise addition of formaldehyde into the prepared solution, copper ions (Cu^{2+}) were reduced into copper oxide particles on the surface of MWCNTs. In this procedure, MWCNTs acted as templates for the growth of Cu_2O nanoparticles. The sonication treatment prevented the aggregation of nanoparticles on the nanotubes.

2.2 Physical characterizations

XRD spectra of three powder samples were recorded on Rigaku Miniflex using $\text{CuK}\alpha$ X-rays with wavelength 1.54 Å. Raman spectra of pristine MWCNTs and prepared samples were recorded on Renishaw using the excitation wavelength 514.5 nm of Ar^+ laser in the region 100–4000 cm^{-1} . SEM images of all the samples were taken via Raith Two. The electrical response of the prepared samples was recorded by a Proxima probe set up. For carrying out these studies, both samples were dispersed in N,N-dimethyl formamide (DMF) by taking 0.2 mg (2% by wt) of each sample in 10 mL solution of DMF.

2.3 Device fabrication

For sensor fabrication, first, a pattern of interdigitated electrodes (IDEs) was made using Klevin software with finger width 10 μm , finger length 100 μm and a gap between the two fingers being 5 μm . A thin layer of SiO_2 of thickness 120 nm was deposited on Si wafer by dry oxidation. The designed mask has been prepared by a laser writer and was transferred on to the prepared wafer using photolithography technique (double side aligner-EVG 620). A chromium–gold layer of thickness 100 nm ($\text{Cr} = 20 \text{ nm}$, $\text{Au} = 80 \text{ nm}$) was deposited on the developed substrate by a thermal evaporator. Finally, Cr–Au was removed by wet etching to get the desired device. The optical image of fabricated IDEs is shown in figure 1. Then thin films of synthesized composites were drop-casted on IDEs using a micropipette. The solvent was removed by heating the device, retaining only a network of composites in between the electrodes.

3. Results and discussion

As shown in figure 2(a), XRD spectra of P-MWCNTs show a broad diffraction peak at $2\theta = 25.5^\circ$ corresponding

to the (002) plane of graphite carbon atoms. The width and position of the diffraction peak (002) are related to the structural ordering of the nanotubes (Gupta and Farmer 2011). The same diffraction peak appears at $2\theta = 26.2^\circ$ for Cu_2O -coated nanotubes (samples 1 and 2) as shown in figure 2(b–c). Due to strong interaction between nanotubes and Cu_2O nanoparticles, a significant shift towards higher angle occurred (figure 2b–c) which resulted in a compressive stress and hence interplanar spacing of the tubes is changed (Hee *et al* 2002; Zhi *et al* 2006). Moreover, the calculated average d -spacing value using Bragg's law for Cu_2O -coated nanotubes is found to increase to 3.39 Å as compared to 3.47 Å for pristine nanotubes. The other diffraction angles at $2\theta = 29.8, 36.7, 38.1, 42.7, 44.3, 61.6$ and 77.6° in figure 2(b–c) are assigned to (111), (400), (200), (420), (220), (311) and (222) planes for the cubic structure of Cu_2O by comparing the results with reported JCPDS data card no. 050667 and 011142. The average calculated crystallite size of Cu_2O particles in samples 1 and 2 were found to be 10 and 15 nm. The lower crystallite size always corresponds to lower loading of nanoparticles and the higher crystallite size to higher metal loading or vice versa (Randeniya *et al* 2010).

Raman spectroscopy is a powerful technique used to characterize carbon-based nanomaterials, like fullerenes and CNTs. Raman spectra (figure 3a) show the presence of three bands, viz. D-band at 1361 cm^{-1} , G-band at 1595 cm^{-1} and G'-band at 2700 cm^{-1} for the pristine MWCNTs.

Figure 1. Optical image of a fabricated device.

Figure 2. XRD spectra of (a) pristine MWCNTs, (b) sample 1 and (c) sample 2.

Figure 3. Raman spectra of (a) pristine MWCNTs, (b) sample 1 and (c) sample 2.

Moreover, D-band indicates the presence of the disordered carbon structure of nanotubes and is related with breathing mode of sp^3 sites present in carbon tubes in the form of rings. G-band, known as graphitic mode, is observed due to stretching vibration of any pair of sp^2 sites (Bokobza 2009; Tessonnier *et al* 2009; Gallegos *et al* 2011). The intensity ratio of D-band to G-band (I_D/I_G) is related to degree of disorder of the nanotubes and inversely proportional to the crystalline nature of CNTs (Shan *et al* 2007; Gallegos *et al* 2011). As shown in figures 3(b–c), these characteristic peaks are still present in the Raman spectra of Cu_2O -coated nanotubes.

Table 1. Raman analysis of all three samples.

Sample name	D band	G band	G' band	I_D/I_G	L_a (nm)
Pristine MWCNTs	1361	1596	2702	1.14	14.6
Sample 1	1350	1588	2695	0.94	17.7
Sample 2	1347	1576	2692	1.39	11.9

Therefore, the inherent structure of the pristine tubes is retained after coating of nanoparticles. The calculated value of I_D/I_G ratio for pristine MWCNTs is 1.14. For sample 1, the value of intensity ratio is decreased to 0.94. It means that attachment of Cu_2O nanoparticles on MWCNTs have decreased the inherent presence of defects in the form of some pentagons or heptagons in the honeycomb structure of graphene sheets in MWCNTs and increased the crystalline order of MWCNTs. The calculated value of I_D/I_G for sample 2 has been increased to 1.39. The increased value of I_D/I_G for sample 2 can be due to the introduction of functional groups (discussed in FT-IR) and also crystallinity of MWCNTs is decreased. The insertion of functional groups on the nanotubes walls is interpreted as defects in the structure (Tessonnier *et al* 2009). The intensity of G'-band is increased (figure 3b) to a high value for sample 1 as compared to sample 2. The intensity of this peak depends strongly on the metallicity of the nanotubes, which means that sample 1 contains high electrical properties as compared to sample 2. In addition, the Raman spectra of Cu_2O nanoparticles attached nanotubes contain new band at 2932 (figure 3b) and 2925 cm^{-1} (figure 3c), which is the combination of D and G band. The appearance of this combination band also confirms the attachment of Cu_2O nanoparticles, giving rise to enhancement of the Raman combination band due to resonance effect. We have also calculated the crystallite size (L_a) from the following formula (Cancado *et al* 2006)

$$L_a \text{ (nm)} = \frac{560}{E_L^4} \left(\frac{I_D}{I_G} \right)^{-1}.$$

The crystallite size of sample 1 has been increased to 17.7 nm as compared to 11.9 nm size of sample 2. The detailed Raman analyses of all samples are shown in table 1.

Figure 4(a–c) shows SEM images of pristine MWCNTs and the prepared samples. SEM images of figures 4(b–c) clearly indicate that there is an interface between MWCNTs and Cu_2O nanoparticles. The good bonding between MWCNTs and Cu_2O and the presence of a network structure of MWCNTs at intergranular positions is also clearly depicted in SEM images.

FT-IR spectra of pristine MWCNTs are shown in inset of figure 5. The spectra of sample 1 contain a broad peak centred at 3412 cm^{-1} corresponding to O–H stretching vibration. This same peak in sample 2 appears at 3435

Figure 4. SEM image of (a) pristine MWCNTs, (b) sample 1 and (c) sample 2.

Figure 5. FT-IR spectra of sample 1 and sample 2.

and 3461 cm^{-1} . Some peaks are absent in sample 1, but present in sample 2, viz. 1025 and 1109 cm^{-1} corresponding to C=O stretching vibration, 1437 and 1484 cm^{-1} related to C-H, 1597 cm^{-1} for C=C stretching vibration and 1720 cm^{-1} related to C=O stretching vibration. It is clear that, when the concentration of CuSO_4 precursor is increased, more and more functional groups are attached on to the MWCNTs walls.

Figure 6. I - V characteristics of all three samples.

The electronic transport properties of pristine and Cu_2O -coated tubes were investigated by depositing thin films of these samples on the top surface of IDEs. The variation in current-voltage characteristics of three samples are shown in figure 6. The contact improvement between the tubes and electrodes was avoided by annealing the device at 100°C before drop casting the films on the top surface. I - V characteristics for sample 1 show higher

Figure 7. (a) Temperature-dependent I - V characteristics of sample 2 and (b) variation in resistances with the temperature.

conductivity as compared to sample 2 and pristine tubes. These results agree with the analysis of Raman spectroscopy as discussed earlier. Also, the linear I - V curve indicates the ohmic contacts between Cu_2O nanoparticles and nanotubes. Figure 7 shows temperature-dependent I - V characteristics of sample 2. The inset of this figure presents the I - V characteristics of pristine tubes. The increase in the current or the decrease in the resistance (figure 7b) observed with increasing temperature indicates the semiconducting behaviour of Cu_2O -coated nanotubes. Similar type of behaviour has been reported by Hoa *et al* (2010) in their work.

4. Conclusions

The effect of precursor concentration on the structural and electrical properties of pristine MWCNTs is studied in the present work. Raman spectroscopy and SEM have been utilized to ascertain the composite formation and also its analysis led to the conclusion that sample 1 contains good crystalline and conductive nature of the nanotubes. Owing to its improved electrical properties, the present route provides a simple approach to synthesize nanotubes-based nanocomposites, which finds application in gas sensor and semiconducting technology.

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