Microwave Synthesis and Characterization of Multiwalled Carbon Nanotubes (MWCNT) and Metal Oxide Doped MWCNT

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ABSTRACT

Multiwalled carbon nanotubes (MWCNT) and metal oxide doped (MWCNT/MO) was synthesized using domestic microwave oven and characterized by UV-Visible, XRD, impedance, polarization and AFM studies. In UV-Visible spectrum of MWCNT there are two peaks in the region 733 nm, and 340 nm attributed to $S_{2g}$ transition taking place in carbon nanotubes and $\pi \rightarrow \pi^*$. Metal oxide doped MWCNT exhibits their respective M-L transition bands. The band gap energy was calculated using Tauc’s plot and it was found to be best for MWCNT-CuO nanocomposite. XRD studies revealed the formation of MWCNT/MO nanocomposite. The XRD pattern obtained for MWCNT/MO nanocomposite was in good agree with JCPDS file. From the impedance studies it was clear that charge transfer resistance ($R_{CT}$) value increased when a metal oxide was doped into MWCNT. It was also confirmed in Tafel studies that polarization resistance was increased for MWCNT/MO nanocomposite. The surface morphological behaviour was studied by AFM technique. It showed the formation of spherical shaped nanocomposites.

1. Introduction

The field of nanotechnology has experienced a constantly increasing interest over the past decades both from industry and science. Since the accidental discovery of carbon nanotubes (CNTs) during the synthesis of fullerene by Iijima [1], tremendous research has been done on CNTs. CNTs are under intense investigation owing to their spectacular mechanical and electrical properties [2]. Many ways are currently available for the production of CNTs, which are arc-discharge [3], pulsed laser vaporization [4], chemical vapor deposition [5]. However, commercial applications of CNTs have been inhibited by the lack of large-scale production of purified CNTs. Moreover, the intrinsic Vander Waals attraction of CNT towards each other leads easily to entangle agglomerates, which results in their insolubility in most of organic and aqueous solvents. Recently, a microwave-assisted synthesis is enabling technology that has been extensively used in organic synthesis [6-8]. Microwave-assisted modification of CNTs is non-invasive, simple, fast, environmentally friendly, and clean method as compared to traditional methods. Usually, the use of the microwave facilitates and accelerates reactions, often improving relative yields. In case of microwave-assisted functionalization of CNTs, microwave irradiation of CNT reduces the reaction time and gives rise to products with higher degrees of functionalization than those obtained by the conventional thermal methods [9]. A wide range of metals, such as are gold [10], platinum, ruthenium [11], rhodium [12] and copper [13] have been incorporated. It is of current general interest the development of new techniques for the efficient and selective synthesis of CNT's and other carbon nanostructures at the cheapest possible cost. One such possibility is the use of microwave radiation, which over the past few years has played an important role as a thermal tool in organic synthesis due to considerable advantages over conventional methods. Kharrissova has reported the synthesis of vertically aligned carbon nanotubes using a domestic microwave oven [14]. The use of microwave radiation in the synthesis and functionalization of carbon nanotubes or other nanostructures is advantageous because it provides a fast and uniform heating rate that can be selectively directed towards a targeted area. In the present study we have doped some metal oxides in to MWCNT using surfactant by sonication method.

2. Experimental Methods

2.1 Materials

All reagents were of analytical grade and used as received without further purification. Ultra-pure deionized water was used throughout the experiments. Graphite (Micro Fine Chemicals), Cetyltrimethyl ammonium bromide (CTAB), cobalt chloride (Merck), copper sulfate (Merck), nickel sulfate (Merck), ethanol, iron (II) acetate (Merck) were purchased and used in the synthesis.

2.2 Synthesis of MWCNT

Starting material was prepared by mixing 3 g of iron (II) acetate with 7 g graphite powders. The powders were then mixed and placed inside domestic microwave oven and irradiated inside at 700 W until microwave oven reaches about 1000 °C for 12 seconds.

2.3 Functionalization of MWCNT

The MWCNTs are dispersed in 10 mL ethanol then 30 mL of 0.1 M CTAB was added for dispersing the MWCNT. The dispersion was achieved by sonicating the mixture for 30 minutes.

2.4 Synthesis of MWCNT/Metal Oxide Nano Composite

The precursor of the metal oxide is separately dissolved in deionized water. Then, metal oxide solution drop-wise added into the dispersed MWCNT’s and the mixture is sonicated and magnetically stirred for 1 h. After that, the suspensions mixture is transferred into round-bottomed flask and refluxed at high temperature 120 °C. After that, the system is allowed to cool at room temperature. Then, the mixture is filtered and washed with suitable solvent like distilled water and ethanol several times. The resulted composite is dried at 100 °C. The end product embedded with nano-sized metal oxide was collected and characterized.

3. Results and Discussion

3.1 UV-Visible Spectral Studies

The UV-Visible spectrum of carbon MWCNT and MWCNT/MO nanocomposites (figures not given) shows two peaks for MWCNT in the region 733 nm, and 340 nm. It is due to $S_{2g}$ transition taking place in carbon nanotubes and $\pi \rightarrow \pi^*$ transition of $\pi$ electrons present in MWCNT. In the
spectrum of MWCNT/CoO₄, the spectrum has three distinct peaks at 730 nm, 400 nm and 290 nm. The peak at 730 nm is due to $S_z$ transition taking place in CNT. The peak at 290 nm is assigned to the O$^2-$ → Co$^{3+}$ charge transfer [15]. The peak at 730 nm in the UV spectrum of MWCNT/ NiO is assigned to the $S_{z2}$ transition of CNT. The peak at 290 nm is due to $π → π^*$ and 300 nm is due to the NiO transition. In the spectrum of MWCNT-CuO, the peak at 730 nm similar to other peaks due to $S_{z2}$ transition of CNT. The peak at 310 nm is due to $π → π^*$ transition. The peak at 400 nm is due CuO.

3.2 Band Gap Energy

The measurement of the band gap of materials is important in the semiconductor, nanomaterial and solar industries. The term "band gap" refers to the energy difference between the top of the valence band to the bottom of the conduction band electrons are able to jump from one band to another. In order for an electron to jump from a conduction band, it requires a specific minimum amount of energy for the transition, the band gap energy. The band gap energy of insulators is large (>4 eV) but lower for semiconductors (<3 eV). Diffuse Reflectance UV-Vis spectroscopy involves numerous light-sample interactions, spectra may exhibit features associated with the transmission and/or reflection (external and/or internal) of UV-Vis radiation. From the reflectance spectrum band gap energy was calculated using Tauc plot and given in Table 1.

Table 1 Band gap energies of MWCNT and its metal oxide composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>1.82</td>
</tr>
<tr>
<td>MWCNT-CoO₄</td>
<td>1.71</td>
</tr>
<tr>
<td>MWCNT-NiO</td>
<td>1.70</td>
</tr>
<tr>
<td>MWCNT-CuO</td>
<td>1.69</td>
</tr>
</tbody>
</table>

3.3 X-Ray Diffraction Studies

XRD is used to ascertain the quality and crystalline nature of nanotubes. Fig. 1 shows the X-rays diffraction pattern of MWCNT-CoO₄. The pattern shows the intense peak at 2θ=25.9° is due to (002) reflection. The other peaks at the angles 2θ=44.6°, 49.4°, 54.5° and 62.4° are due to the (100), (110), (004) and (110) reflection. The peaks at 23.8°, 33.12°, 35.6°, 40.83°, 44.52°, 59.84°, 63.9° obtained for CoO₄ is similar to cubic structure of CoO₄ [16] with lattice constant a=3.52 Å. The average grain size of MWCNT – CoO₄ is 57.7 nm. Fig. 2 shows the XRD pattern of MWCNT-NiO. In this in addition to diffraction pattern of MWCNT the additional peak at 33.1°, 35.58°, 54.6°, 87.01°, 87.27° corresponds to (111), (200), (220), (311) and (222) planes of face-centered cubic (FCC) crystalline phase of NiO [17]. (JCPDS file No. 04-0835) with lattice constant a=3.648 Å. The average grain size of MWCNT – NiO is 86.88 nm. XRD pattern of MWCNT– CuO nano composite is shown in Fig. 3. It gives a single phase with monoclinic structure. The peak at 33.2°, 49.4°, 54.5°, 62.4° which corresponds the (002), (202), (020) and (113) planes. This is in good agreement with reported refracted values of CuO [18]. (JCPDS No.05-661) with lattice constant a=3.582 Å. The average grain size of MWCNT-CuO is 92.03 nm.

3.4 Cyclic Voltammetric Studies

The LUMO of MWCNT can accept six electrons to form hexaanion. But here we were reporting three electron oxidation-reduction mechanism. The reason for that is functionalization reduces the redox behavior of MWCNT (Fig. 4). The cyclic voltammetric behavior of MWCNT-CoO₄ was given in Fig. 5. The cathodic peak at -0.28 was due to the reduction of Co$^{2+}$, this was the standard reduction potential of Co$^{2+}$. In the case of CuO nanocomposite (Fig. 7) additional to the redox nature of MWCNT, the anodic peak at 0.4 V was due to the oxidation of Cu$^{2+}$.

![Fig. 1 XRD behavior of MWCNT-CoO₄](image1)

![Fig. 2 XRD behavior of MWCNT-NiO](image2)

![Fig. 3 XRD behavior of MWCNT-CuO](image3)

![Fig. 4 Cyclic voltammetric behavior of MWCNT in pH 1.0 at a scan rate of 50 mV/s](image4)

![Fig. 5 Cyclic voltammetric behavior of MWCNT-CoO₄ in pH 1.0 at a scan rate of 50 mV/s](image5)

![Fig. 6 Cyclic voltammetric behavior of MWCNT-NiO in pH 1.0 at a scan rate of 50 mV/s](image6)

![Fig. 7 Cyclic voltammetric behavior of MWCNT-CuO in pH 1.0 at a scan rate of 50 mV/s](image7)
3.5 EIS and Polarization Studies

Electrochemical impedance spectrum (Fig. 8) was studied using GCE modified with MWCNT, MWCNT-CoO₄, MWCNT-NiO, MWCNT-CuO (0.0314 cm²) as working electrode. The cell contains a 1 cm² Pt counter electrode, Ag/AgCl reference electrode. The measurements were carried out in pH 1.0. The impedance parameter such as Rₑ and Cₑ values of MWCNT, MWCNT-CoO₄, MWCNT-NiO, MWCNT-CuO in pH 1.0 media were given in Table 2. The Rₑ values reveal that after modifying with MWCNT/MO composite the resistance was increases because of the passive layer formed by metal oxide. From the Tafel plot (Fig. 9), polarization resistance for the MWCNT and MWCNT/MO coated CGE in pH 1.0 has been estimated by the expression

\[ R_p = \frac{B}{I_{corr}} \]

Where \( B = \frac{b_a b_c}{2.303 (b_a + b_c)} \), \( b_a \) and \( b_c \) are slopes of the anodic and cathodic plot the polarization curves. \( I_{corr} \) is the corrosion current. Parameter governing corrosion such as \( R_p \) and \( I_{corr} \) values were calculated and illustrated. From the values it is clear that metal oxide composites are passive to corrosion compared to MWCNT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( R_p (\times 10^5) ) (Ω cm²)</th>
<th>( C_p (\mu F cm^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>2.1954</td>
<td>5.973</td>
</tr>
<tr>
<td>MWCNT-CoO₄</td>
<td>4.165</td>
<td>3.03</td>
</tr>
<tr>
<td>MWCNT-NiO</td>
<td>6.309</td>
<td>3.743</td>
</tr>
<tr>
<td>MWCNT-CuO</td>
<td>2.462</td>
<td>19.51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>( I_{corr} (\times 10^{-7}) A )</th>
<th>( R_p (\times 10^{6}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>1.912</td>
<td>0.456</td>
</tr>
<tr>
<td>MWCNT-CoO₄</td>
<td>0.4555</td>
<td>0.2032</td>
</tr>
<tr>
<td>MWCNT-NiO</td>
<td>1.697</td>
<td>7.81</td>
</tr>
<tr>
<td>MWCNT-CuO</td>
<td>1.154</td>
<td>13.06</td>
</tr>
</tbody>
</table>

Where \( I_{corr} \) and \( R_p \) gives the corrosion current and polarization resistance respectively.

4. Conclusion

MWCNT have been successfully synthesized by microwave method and MO was incorporated by functionalizing their sidewalls. Then it was characterized by UV-Visible spectroscopy. The band due to \( \pi \rightarrow \pi^* \) was seen at 730 nm. The data obtained from XRD studies coincides well with the PEDPS values of corresponding metal oxides. Cyclic voltammetric studies revealed clearly the redox reaction of MWCNT/MO. From the Tafel plot, polarization resistance of MWCNT/MO in pH 1.0 has been estimated and the values were clear that these composites will be more resistant to corrosion. The AFM photograph shows a spherical growth of metal oxides on the surface of MWCNT.

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References

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