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PREPARATION, STRUCTURAL AND MORPHOLOGICAL STUDIES OF MANGANESE DOPED MWCNT NANOCOMPOSITES

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ABSTRACT - Manganese doped Multiwalled carbon nanotubes were synthesized through a solvo thermal method. The surface morphology and structural analyses of the MnO_2 doped MCNT have performed by Transmission electron microscope (TEM), Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and Energy dispersive spectroscopy (EDS). Morphological characterization reveals that three-dimensional hierarchy architecture built with a highly porous layer consisting of interconnected MnO_2 uniformly coated on the CNT surface. The XRD and EDS results confirmed that the prepared samples containing MnO_2/CNT in pure form without impurities. It also reveals that birnessite-type MnO_2 is formed through the solvo thermal synthesis. The phase transition was take place at the annealing temperature of 400 °C – 500 °C. The Optical properties of the prepared samples were examined by Uv-visible spectrometer.

Keywords- [MnO_2 doped CNT, Solvo thermal method, CNT, MnO_2, Supercapacitors]

1. INTRODUCTION

In recent years, manganese oxides (MnO_2) have attracted more research interest due to their unique physical and chemical properties. It has wide applications in the field of catalysis, ion exchange, molecular adsorption, biosensor, and energy storage (1-7). Specifically, manganese dioxide has been considered as a one of the promising electrode material for supercapacitors because of its low cost, environmental friendly and excellent capacitive performance in aqueous electrolytes (8-10). The charge storage in aqueous electrolytes is based either on the adsorption of cations at the surface of the electrode material or on the intercalation of cations in the bulk of the electrode material. In order to attain high capacitive performance, a large surface area and a fast ion/electron transport of the electrode material are essential. Hence, extensive research has been concentrate on the synthesis of nanostructured MnO_2 as the nanoscale powder, which provides not only a high specific surface area, but also a fast ion and electron transport. Various forms of MnO_2 including nanorods (11), nanotubes, nanosheets, nanoflakes (12), nanospheres (13) and nanoflowers (14) have been synthesized. However, the reported specific

capacitance values for the various nanostructured MnO_2 electrodes are still low to the theoretical value, which may be due to its poor electronic conductivity of MnO_2. So in order to increase the capacitive performance of MnO_2, conductive additives can be to improve the electron transport. Due to their excellent electrical conductivity and high surface area Carbon nanotubes (CNT) have been considered as effective material for super capacitors electrode, the additional phase mainly including electrically conducting polymers (ECPs) and multivalent metal oxide (15). Recently, MnO_2/CNT nanocomposites have been prepared by various methods to improve the electrochemical utilization of MnO_2 and electronic conductivity of the electrode.

In order to increase the MnO_2 loading in the composite while retaining the formation of a nanoscopic MnO_2 phase, depositing a highly porous MnO_2 layer on the CNTs could be a strategy to achieve this goal. However, a facile and fast synthesis of a uniformly distributed

MnO_2 porous layer on the CNTs is still a challenge. In the present work, a facile solvo thermal synthesis has been designed to deposit a uniform and highly porous MnO_2 layer interconnected with the surface of the CNTs.

2. EXPERIMENTAL

Commercial multiwalled CNTs (Outer diameter:10±1 nm, Inner diameter:4.5±0.5 nm&Length:3-6µm, surface area 280-350 m^2/g (BET), south west nano technologies.Inc., USA). This material produced by the Catalytic chemical vapor deposition (CCVD) method and its purity was higher than 98%. A typical synthesis process of the MnO_2/CNT nanocomposite is described as follows. Firstly, 0.1 g CNTs was dispersed in 100 ml deionized [DI] water by ultrasonic vibration for 2 h. Subsequently, 0.665 g MnO_2 added with 15 ml of HCl and 15 ml DI water and it was mixed with above suspension. Then mixed solution was stirred by a magnetic bar for 1 h. 15 ml of Ammonia solution was added drop by drop. Finally, the precipitation composite products were obtained through filtering, water washing and drying processes. The prepared MnO2/CNT was calcinated further at 400 and 500 °C.

3. CHARACTERIZATION

The surface morphology and structural analyses of the MnO_2 doped MCNT have performed by Transmission electron microscope (TEM), Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and Energy dispersive spectroscopy (EDS). The Optical properties of the prepared samples were examined by fluorescence spectrum and Uv-visible spectrometer.

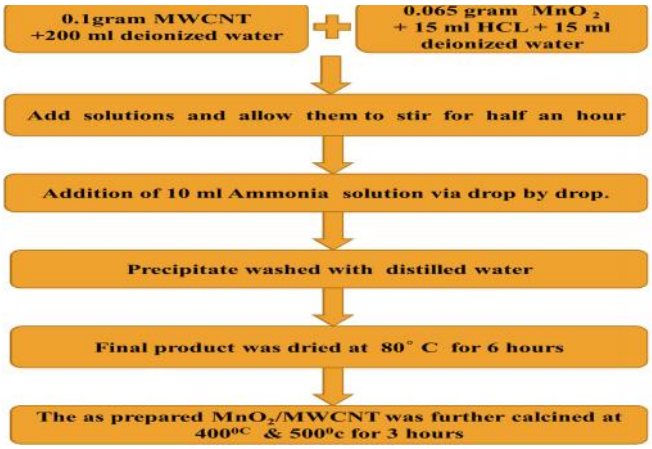

Figure 1- Systematic diagram of preparation of MnO_2 doped MWCNT

4. RESULTS

4.1. XRD STUDIES

XRD patterns of the CNTs, the pure MnO_2 powder, and the MnO_2/CNT nanocomposites are shown in Figure 1. The XRD pattern of the CNTs shows three diffraction peaks at 26.5° and 43.2° which can be indexed as the (002) and (100) reflections of graphite, respectively. The diffraction peaks which appeared at 2θ = 28.8°, 37.5°, 56.2°, and 60.3° matched well with the diffraction peaks of (211), (301), (600) and (521) crystal planes of MnO_2 standard data (JCPDS card PDF file no. 44-0141). The lattice parameters of prepared MnO_2 are a = 9.7875 and c = 2.8600, which are highly identical to the standard values (JCPDS card PDF file no. 44-0141, a = 9.7847, c = 2.863). The cell volume of caddice-clew-like MnO_2 is 273.97 $Å^3$ which is also highly identical to the standard values (274.1 $Å^3$). The average grain size of the prepared MnO_2 crystal is calculated to be 32 nm according to the Scherrer equation $D = K\lambda/\beta\cos\theta$ using the strongest diffraction peak of (211) where D is crystal grain size (nm), K is the Scherrer constant (0.89), λ is the X-ray wavelength (0.154056 nm) for Cu Kα, β is the full width at half maximum (FWHM) of the peak (211), and θ is the angle of diffraction peak. The XRD pattern of the MnO_2/CNT nanocomposite shows that the diffraction peaks from the birnessite-type MnO_2 phase can be observed while the diffraction peaks from the CNTs are not obvious due to the uniform coating of the MnO_2 layer. The XRD pattern of MnO_2/CNT samples annealed at 400 and 500 °C was confirms that the while increasing the annealing temperature the crylstallinity of MnO_2 was increased.

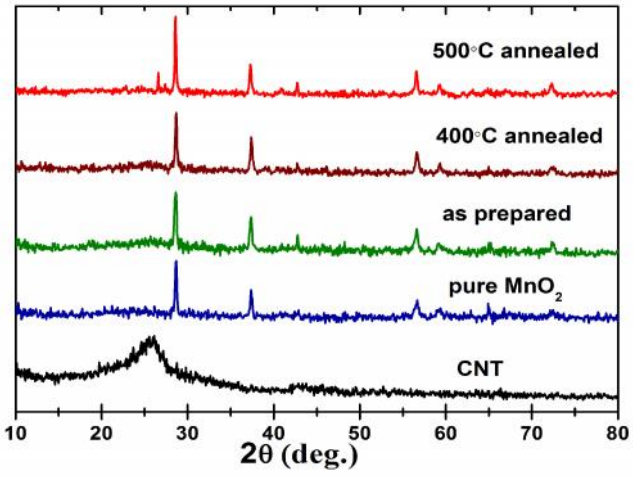

Figure 2- XRD patterns of the (a) pristine CNTs, (b) pure MnO_2, and (c) MnO_2/CNT nanocomposite.

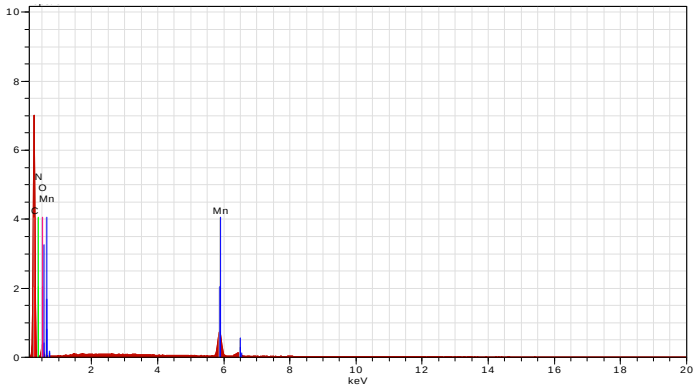

Figure 3- EDS spectrum of the MnO_2/CNT nanocomposite.

Energy dispersive spectrum of MnO_2 doped MWCNT was showed in the figure 2. The results are reveals that the prepared sample has only Mn, O and C content without any impurities. When the annealing temperature was increased to 500 °C the amount of carbon content decreases while amount of MnO_2 content was increased. It shows that at 400 °C MnO_2 and CNT are in amorphous nature. it can be modified to high crystallinty. While increasing the annealing temperature to 500 °C. So we can deduce that the nanoparticles decorated on surfaces of MWNTs are MnO_2 doped CNT nanoparticles.

4.2. OPTICAL STUDIES

In the semi-conducting materials, the optical band gap (E_g) is defined as the energy where the absorption coefficient has a value $>10^4$ cm^{-1}. In order to calculate band gap (E_g) value of prepared samples we make use of the following Tauc relation.

$$\alpha h\gamma = A\,(h\gamma - E_g)^m$$

where A is absorption coefficient given by $\alpha = 2.303 \log (T/d)$ (d is the thickness of the sample and T is the transmission coefficient), $h\gamma$ is the photon energy. Fig. 5 shows the plots of $(\alpha h\gamma)^2$ versus $h\gamma$ for all the samples under investigation. The values of E_g have been estimated by taking the intercept of the extrapolation to zero absorption with photon energy axis i.e. $(\alpha h\gamma)^2 = 0$.

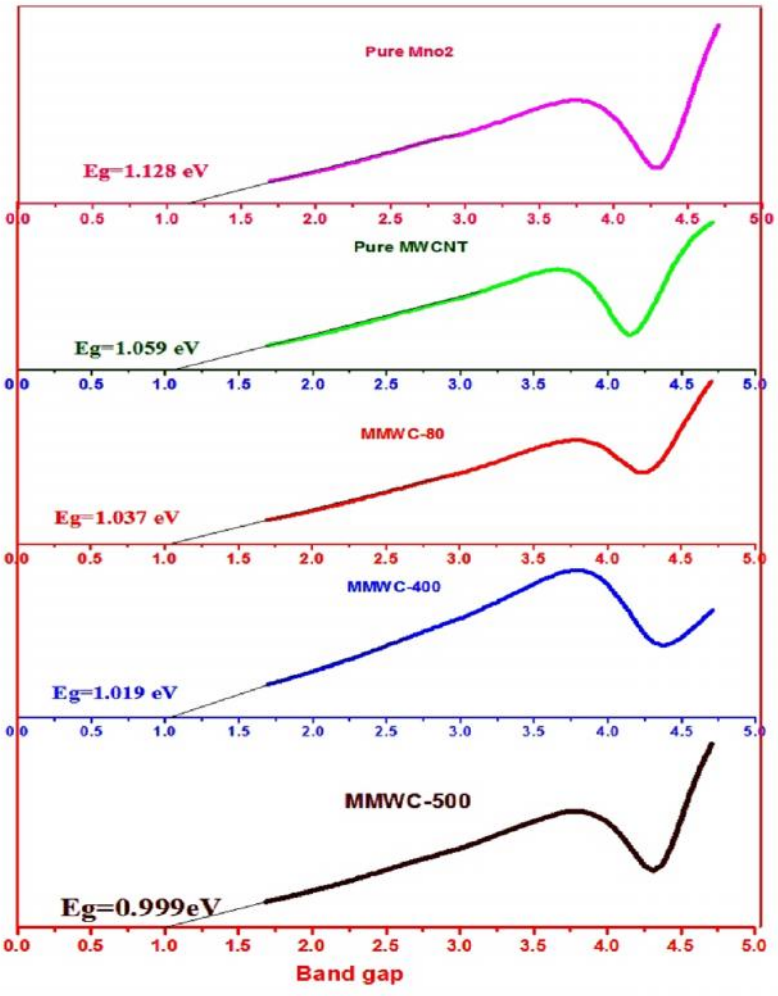

Figure 3- Tauc plot of the MnO_2, MWCNT, MnO_2/CNT nanocomposite at room temperature and annealed at 400 and 500 îC.

Band gap value was found to be 1.128 eV for pure MnO_2. It was decreases to 1.037 eV due to addition of MWCNT. Further the value of bandgap was decreases to 0.999 eV due to its annealing effect. Variation of bandgap with respect to annealing temperature and crystalline size were shown in the figure 4. When the crystalline size increases the band gap value started to decreases. The same results were occur while increasing annealing temperarure. This change in the value of E_g depends on several factors like grain size, carrier concentration, lattice strain etc. But for these prepared samples we assume the crystallinity and grain size of the MnO_2 doping MWCNT were the main reason and hence reflected as the variation of energy gap value.

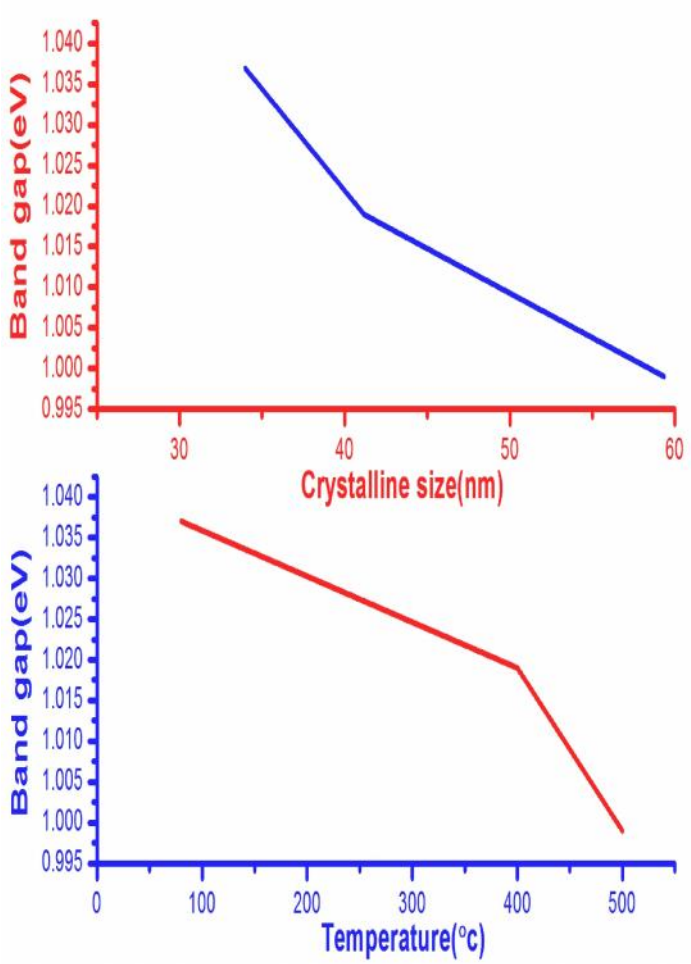

Figure 4 - Bandgap variation with respect to crystalline size and Annealing Temperature of prepared samples.

4.2. MORPHOLOGICAL STUDIES

Morphologies of the CNTs, the birnessite-type MnO_2 powder, and the MnO_2/CNT nanocomposite are characterized by FESEM and TEM as shown in Figure 4. It can be observed in Figure 5A that the diameter of the CNTs is about 20 to 50 nm. When the annealing temperature was 400 °C the prepared MnO_2 doped MWCNT shows low number MnO_2 was attached with the MWCNT. While increasing the annealing temperature to 500 °C the MnO_2 particles decorated on the MWCNT (Fig.5C &D).

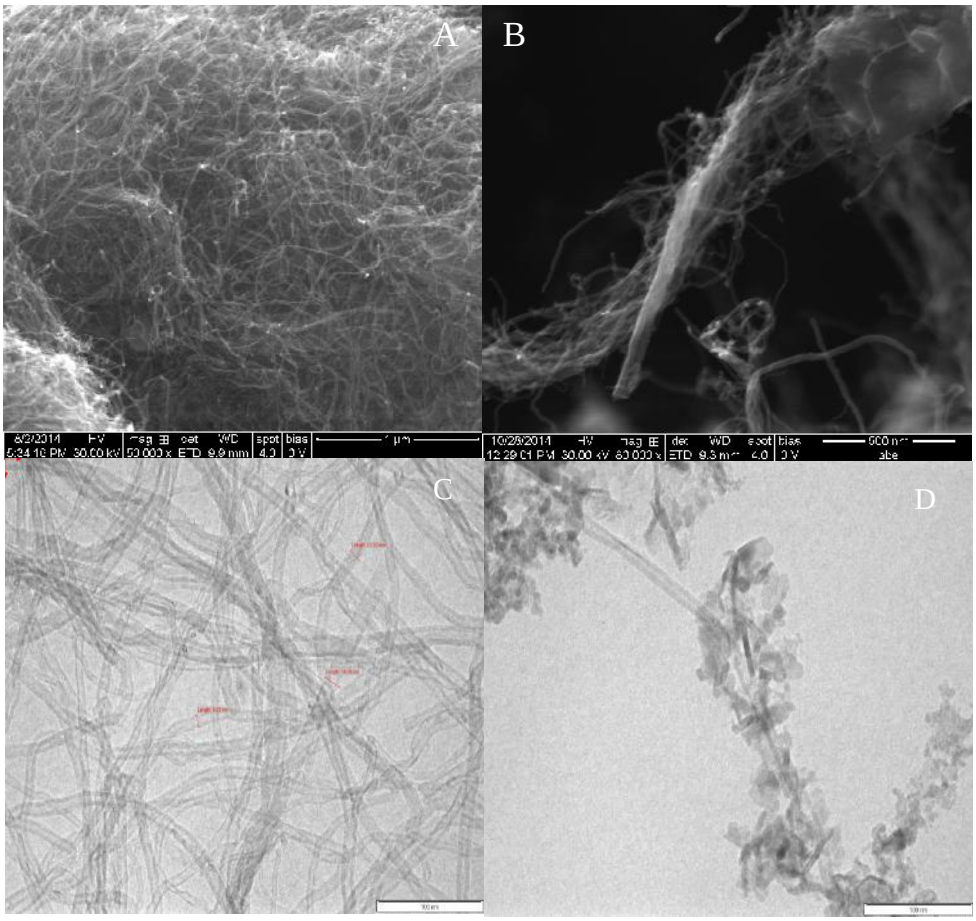

Figure 5- SEM images of Pure MWCNT (A), (B) and TEM images of MnO_2/CNT nanocomposite annealed at 400 îC (C) & 500 îC (D).

CONCLUSION

Manganese doped Multiwalled carbon nanotubes were synthesized through a solvo thermal method. The surface morphology and structural analyses of the MnO_2 doped MCNT were performed by Transmission electron microscope (TEM), Field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and Energy dispersive spectroscopy (EDS). Morphological characterization reveals that three-dimensional hierarchy architecture built with a highly porous layer consisting of interconnected MnO_2 uniformly coated on the CNT surface. The XRD and EDS results confirmed that the prepared samples containing MnO_2/CNT in pure form without impurities. It also reveals that birnessite-type MnO_2 is formed through the solvo thermal synthesis. The phase transition was take place at the annealing temperature of 400 °C – 500 °C. The Optical properties of the prepared samples were examined by Uv-visible spectroscopy. The band gap value of prepared samples were varied due to change in its grain size.

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