ABSTRACT

Manganese dioxide/multi-walled carbon nanotubes MnO$_2$/ MWCNTs nanocomposite are synthesized by hydrothermal method. The crystallographic information of the acid-treated MWCNTs and the MnO$_2$/ modified MWCNTs nanocomposite were characterized by X-ray diffraction (XRD), Transmission electron microscope (TEM) and FT-IR spectra. Optical and electrical properties of MnO$_2$/ MWCNTs / PVA nanocomposite thin film with different concentration were studied. UV-VIS absorption spectra shift at different exposing time, indicated the sensitivity to UV radiation. Optical band gap decreases with increasing time of radiation. Electrical properties of MnO$_2$/ MWCNTs / PVA nanocomposite thin films with different concentration according to different frequency and exposing time of UV radiation showed semiconducting properties and sensitivity to UV radiation.

Keywords: MnO2 / MWCNTs/ PVA nanocomposite, UV radiation, optical and electrical properties.

1. Introduction

Carbon nanotubes (CNTs) can be classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), both of which have been widely explored as an option for high power electrode materials because of their good electrical conductivity and easily accessible surface areas. Furthermore, high mechanical flexibility and open tubular network make them an ideal support for active materials. But the energy density is, however, a concern because its surface area is relatively small [1].

The shape of CNTs are a hexagonal set of carbon atoms rolled in a long, thin, hollow cylinder [2]. CNTs are hopeful materials for the electrodes of supercapacitors, due to their electrical conductivity, low mass density, high surface area and unique internal structure.

MnO$_2$ (Manganese dioxide) attracted large research care due to their characteristic physical and chemical properties and wide applications in energy storage, biosensor, ion exchange and catalysis [3-5]. MnO$_2$ has been considered as a hopeful electrode material for supercapacitors because of its low cost, environmental benignity, and excellent capacitive performance in aqueous electrolytes [6-8]. Recently, MnO$_2$/CNTs nanocomposite has been prepared by different ways to improve the electrochemical use of MnO$_2$ and electronic conductivity of the electrode [9-12]. In recent years, supercapacitors based on MnO$_2$ as electroactive materials are attracting great attention due to the low cost of the raw material, excellent electrochemical performance and environmental compatibility [13].

The aim of the paper is to study the optical and electrical properties of MWCNTs and MnO$_2$/ MWCNTs/ PVA nanocomposite thin film with different concentration and sensitivity to UV-radiation. MnO$_2$/ MWCNTs / PVA nanocomposite are synthesized by hydrothermal method. MnO$_2$/ modified MWCNTs nanocomposite characterize by XRD, TEM, FT-IR and UV-VIS. Optical and electrical properties were studied after exposing UV radiation showing the sensitivity to UV-radiation.
2. Experimental

2.1: Modification of MWCNTs

MWCNTs of 1 gm supplied from (Germany) with the outer diameter of 50 nm over 1.0 m in length was dissolved in 10 wt. % nitric acid (10 ml of nitric acid completed by 90 ml of deionized water). The solution is refluxed under stirring at 600 rpm and temperature at 80 °C for 12 h.

2.2: Preparation of MnO₂ / modified MWCNTs nanocomposite

Weight 0.1 g from modified MWCNTs was added in 25 ml from deionized water by ultrasonic vibration for 2 h. and was added 0.3 g KMnO₄ into the above suspension, and the mixed solution was stirred by a magnetic rod for 2 h. Next that the mixed solution was transferred to a 30 mL ,Teflon-lined, stainless steel autoclave. The autoclave was closed and put in an electric oven at 150°C for 6 h and then naturally cooled to room temperature. Next the hydrothermal treatment, the resultant samples (MnO₂/MWCNTs) were collected by filtration and washed with deionized water. MnO₂/MWCNTs nanocomposite were finally dried in an oven at 100°C for 12 h.

2.3: Preparation of MnO₂ / MWCNTs /PVA nanocomposite thin film

The dried MnO₂/ MWCNTs was added into three different amounts of PVA solutions (0.5, 1, 1.5 wt. %) and stirred at 80°C until a homogenous solution was obtained. The solution was ultrasonicated for 5 h. Then, the solution was poured into Petri dishes, followed by solvent evaporation at room temperature to form MnO₂/modified MWCNTs/PVA thin films.

2.4: Characterization

The crystallographic information of the acid-treated MWCNTs and the MnO₂/ MWCNTs nanocomposite were characterized by X-ray diffraction (XRD), using (Philips PW 1370), with Cu, Kα (λ = 0.154 nm). Transmission electron microscope (TEM, JEOL JEM-3010, 300 kv) was used to characterize the morphology of the modified MWCNTs and MnO₂/MWCNTs nanocomposite. The chemical structures of the MWCNTs and the MnO₂/ MWCNTs nanocomposite were characterized by Fourier transform infrared (FT-IR) spectroscopy using the device (Thermo Nicolet, FT-IR and NEXUS) in the range of 4000 – 400 cm⁻¹. UV-Vis absorption spectra of PVA pure and MnO₂ / MWCNTs / PVA nanocomposite thin films, were measured using UV-Vis spectrometer(6100 Jusco, Japan). At room temperature the electrical properties was measured by using the device (Hioki ,LCR Hitester 3532-50). The frequency dependence of electrical properties for as-prepared samples were measured on the frequency range (100Hz-6MHz).

3. Results and discussion

3.1: XRD

XRD patterns of the MWCNTs, modified MWCNTs and MnO₂/ MWCNTs nanocomposite are shown in Fig.1. XRD pattern of the MWCNTs shows three diffraction peaks at 2θ values of 25.59°, 43.13° and 77.74° which can be indexed as the (002), (101), and (110) planes of graphite carbon[14]. The very sharp peak corresponding to the structure of MWCNTs, modified MWCNTs at 25.59° of 2θ becomes very weak at 26.42° of 2θ in the MnO₂/ MWCNTs nanocomposite, also the peak at 43.13° of 2θ in the MWCNTs shifted to 44.62° and becomes thinner in the MnO₂/ MWCNTs nanocomposite. The new sharp diffraction peak at 9.29° of 2θ in the MnO₂/ MWCNTs nanocomposite can be perfectly indexed as (001) planes of MnO₂ [15-16], after the deposition of MnO₂, indicating that the surfaces of MWCNTs are uniformly covered by MnO₂. The crystalline structure of MnO₂ are composed of one Mn atom surrounded by six O atoms to form an octahedron. The MnO₆
octahedral subunits share vertices and edges to form crystalline tunnel structures by continuously linking to the neighboring subunits [17]. The crystallite size of the modified MWCNTs and MnO$_2$/MWCNTs nanocomposite was calculated using Scherrer's from this Eq. [18]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where: the crystal grain size is $D$ (nm), the Scherrer constant is $K$ (0.89), the X-ray wavelength is $\lambda$ (0.154056 nm) for Cu K$_\alpha$, the full width at half maximum intensity (FWHM) is $\beta$ in radian and the Bragg angle in degree is $\theta^\circ$. The calculations reveal that the crystal grain size of the modified MWCNTs and MnO$_2$/MWCNTs nanocomposite are 7.22nm and 9.96 nm respectively.

![XRD patterns of the modified MWCNTs and MnO$_2$/MWCNTs nanocomposite.](image)

**Fig. 1:** XRD patterns of the (a) MWCNTs and (b) modified MWCNTs and (c) MnO$_2$/MWCNTs nanocomposite.

### 3.2: TEM

The TEM images of modified MWCNTs and MnO$_2$/MWCNTs nanocomposite are shown in Fig.2 (a) and (b) respectively. The average diameter of nanotubes modified MWCNTs is about 10.11 nm. Which is in agreement with results obtained for crystallite sizes in the XRD study. Also, Fig.2 (b) indicates that MnO$_2$ inside the modified MWCNTs in nanocomposite with an average diameter of about 4 nm. These images conform the interaction between modified MWCNTs and MnO$_2$ nanocomposite. Therefore the nanotubes from TEM images for modified MWCNTs and MnO$_2$/MWCNTs nanocomposite are of high purity, with uniform diameter distribution, and contain no deformity in the structure.
3.3: FT-IR Spectroscopy

Fig. 3 shows FT-IR spectra of MWCNTs, modified MWCNTs and MnO$_2$/MWCNTs nanocomposite. It can be noticed that, a broad absorption band at 3430 cm$^{-1}$ attributed to O-H stretching which may be due to ambient atmospheric moisture\cite{19}. Also it can be noticed that this band increase in the broadening and shifted at 3425 cm$^{-1}$, 3420 cm$^{-1}$ in case of modified MWCNTs and MnO$_2$/MWCNTs nanocomposite as shown in table (1). The week band at 2920 cm$^{-1}$ in MWCNTs shifted to 2915 cm$^{-1}$ and 2910 cm$^{-1}$ for modified MWCNTs and MnO$_2$/ MWCNTs nanocomposite is assigned to C–H bending, stretching \cite{20}. The new week band appeared at 2375 and 2347 cm$^{-1}$ in the spectra of modified MWCNTs and MnO$_2$/ MWCNTs nanocomposite disappeared in the spectrum of the MWCNTs is the asymmetric and symmetric CH$_2$ stretching \cite{21}. 

![Fig. 2: TEM of (a) modified MWCNTs and (b)MnO$_2$/MWCNTs nanocomposite.](image)

![Fig. 3: FT-IR spectra of the MWCNTs, modified MWCNTs and MnO$_2$/MWCNTs nanocomposite.](image)
Also, the medium band at 1630 cm\(^{-1}\) in the spectrum of the MWCNTs shifted at 1625 cm\(^{-1}\) in the spectra of modified MWCNTs and MnO\(_2\)/MWCNTs nanocomposite is assigned to conjugated C=C stretching. This finding confirms the hexagonal structure of the MWCNTs [22]. The medium band at 1440 cm\(^{-1}\) in the spectrum of the MWCNTs shifted at 1430 cm\(^{-1}\) in the spectrum of the MnO\(_2\)/MWCNTs nanocomposite is assigned to O-H stretching [23]. The medium band at 1050 cm\(^{-1}\) in the spectrum of the MWCNTs shifted at 1097 cm\(^{-1}\) in the spectrum of the MnO\(_2\)/MWCNTs nanocomposite corresponding to C-O stretching [23]. The presence of these functional groups implies that the as-received MWCNTs already have several functional groups that were introduced during the proprietary synthesis and/or purification processes. The new peak at 500 cm\(^{-1}\) in the spectrum of MnO\(_2\)/MWCNTs nanocomposite can be assigned to the Mn-O and Mn-O-Mn vibrations [24], which is related to the vibration of MnO\(_6\) octahedron. The functionalization of MWCNTs can increase the active sites, which contribute to the combination between MnO\(_2\) and MWCNTs in the preparation process of MnO\(_2\)/MWCNTs material.

**Table 1. Peak positions (cm\(^{-1}\)) and assignment of infrared spectra of investigated various MWCNTs, modified MWCNTs and MnO\(_2\)/MWCNTs nanocomposite.**

<table>
<thead>
<tr>
<th>Wavenumber [cm(^{-1})] MWCNTs</th>
<th>Wavenumber [cm(^{-1})] modified MWCNTs</th>
<th>Wavenumber [cm(^{-1})] MnO(_2)/MWCNTs</th>
<th>relative intensity</th>
<th>Band assignments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3430</td>
<td>3425</td>
<td>3420</td>
<td>Broad</td>
<td>attributed to O-H stretching</td>
<td>[19]</td>
</tr>
<tr>
<td>2920</td>
<td>2915</td>
<td>2910</td>
<td>weak</td>
<td>C–H bending, stretching</td>
<td>[20]</td>
</tr>
<tr>
<td>---</td>
<td>2375</td>
<td>2347</td>
<td>weak</td>
<td>for the asymmetric and symmetric CH2 stretching</td>
<td>[21]</td>
</tr>
<tr>
<td>1630</td>
<td>1625</td>
<td>1625</td>
<td>medium</td>
<td>assigned to conjugated C=C stretching</td>
<td>[22]</td>
</tr>
<tr>
<td>1440</td>
<td>1444</td>
<td>1430</td>
<td>medium</td>
<td>O-H stretching</td>
<td>[23]</td>
</tr>
<tr>
<td>1050</td>
<td>1027</td>
<td>1097</td>
<td>medium</td>
<td>corresponding to C–O stretching</td>
<td>[23]</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>500</td>
<td>medium</td>
<td>Mn O and Mn O Mn vibrations</td>
<td>[24]</td>
</tr>
</tbody>
</table>

**3.4: Optical Measurements**

Fig.4. shows UV-Vis absorption spectra of PVA pure and (0.5,1 and1.5%) of MnO\(_2\)/MWCNTs/PVA nanocomposites. The measurements of absorption spectra were carried out at room temperature for visible wavelength ranging from 200 nm to 800 nm. The absorption spectrum of pure PVA has two absorbance bands at 276 and 340 nm. The first band is assigned to the electronic transitions \(\pi\to\pi^*\) [25] and shifted at 268 nm for the spectrum of 1.5% MnO\(_2\)/MWCNTs/PVA nanocomposite. The second band assigned as n\(\to\pi^*\), the absorption intensity of these bands of the MnO\(_2\)/MWCNTs/PVA nanocomposite films increases with
increasing MnO₂ wt% in the samples and shifted to higher wavelength. As can be seen, the absorbance is unaffected in the UV range (400- 800 nm wavelength) with exposed time and remains unchanged.

![Absorption spectra](image)

**Fig. 4: UV-Vis absorption spectra of PVA pure, 0.5, 1 and 1.5 % MnO₂ / MWCNTs / nanocomposite thin films**

The optical band gap of the samples before and after exposing UV-VIS radiation were calculated and listed in Table (2). It can be noticed that, the value of Eg in case of PVA pure thin film equal to 3.257 ev at room temperature and in agreement with [26] also it decreases with increasing exposing UV-irradiation. The absorption spectra shifted at different exposing time, indicated the sensitivity to UV radiation.

**Table 2: the optical band gap of the samples before and after exposing UV-irradiation**

<table>
<thead>
<tr>
<th>Material</th>
<th>0 hour (Eg/ev)</th>
<th>1 hour (Eg/ev)</th>
<th>2 hour (Eg/ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA pure thin film</td>
<td>3.257</td>
<td>2.750</td>
<td>2.633</td>
</tr>
<tr>
<td>(0.5%)MnO₂/MWCNTs/PVA nanocomposite thin film</td>
<td>2.750</td>
<td>2.660</td>
<td>2.578</td>
</tr>
<tr>
<td>(1%)MnO₂/MWCNTs/PVA nanocomposite thin film</td>
<td>2.475</td>
<td>2.013</td>
<td>1.980</td>
</tr>
<tr>
<td>(1.5%)MnO₂/MWCNTs/PVA nanocomposite thin film</td>
<td>2.013</td>
<td>1.743</td>
<td>1.706</td>
</tr>
</tbody>
</table>
3.5: Electrical Properties:

The most important basic dielectric parameters, which play a major role in the determination of material properties, are the dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), log conductivity (Log $\sigma$) and log resistivity (Log $\rho$). This in turn is related to the dipole moment, polarizability, molecular radius (size) and band gap etc. The variation of $\varepsilon'$, $\varepsilon''$, Log $\sigma$ and Log $\rho$ of PVA pure and MnO$_2$ /MWCNTs/ PVA nanocomposite thin film with different concentration according to different frequency and exposing time of UV radiation were shown in (Fig.5-8). The results showed that the conductivity increases with increasing frequency and UV exposing time of the MnO$_2$ / MWCNTs / PVA nanocomposite thin films as shown in table (3).

Table 3: Data of $\varepsilon'$, $\varepsilon''$, $\sigma$ (Ω.m$^{-1}$) and $\rho$ (Ω.m) for the prepared compounds at different time of exposure to UV, 100 Hz and room temperature.

<table>
<thead>
<tr>
<th>film type</th>
<th>Time of UV-radiation</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon''$</th>
<th>$\sigma$ (Ω.m$^{-1}$)</th>
<th>$\rho$ (Ω.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA pure</td>
<td>0h</td>
<td>2.25</td>
<td>16.92</td>
<td>--18.83</td>
<td>7.23</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>181.13</td>
<td>19.59</td>
<td>--15.96</td>
<td>8.09</td>
</tr>
<tr>
<td></td>
<td>2 h</td>
<td>70.9</td>
<td>159.03</td>
<td>--17.35</td>
<td>8.51</td>
</tr>
<tr>
<td>0.5%MnO$_2$/MWCNTs/PVA nanocomposite</td>
<td>0h</td>
<td>50.3</td>
<td>16.91</td>
<td>--16.67</td>
<td>9.22</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>35.29</td>
<td>223.22</td>
<td>--16.50</td>
<td>8.24</td>
</tr>
<tr>
<td></td>
<td>2 h</td>
<td>2.96</td>
<td>19.54</td>
<td>--15.96</td>
<td>8.76</td>
</tr>
<tr>
<td>1%MnO$_2$/MWCNTs/PVA nanocomposite</td>
<td>0h</td>
<td>9.22</td>
<td>27.6</td>
<td>--16.9</td>
<td>10.07</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>42.03</td>
<td>168</td>
<td>--17.5</td>
<td>9.39</td>
</tr>
<tr>
<td></td>
<td>2 h</td>
<td>9.87</td>
<td>18.79</td>
<td>--17.3</td>
<td>9.84</td>
</tr>
<tr>
<td>1.5%MnO$_2$/MWCNTs/PVA nanocomposite</td>
<td>0h</td>
<td>5.11</td>
<td>50.34</td>
<td>--17.27</td>
<td>9.58</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>5.13</td>
<td>70.12</td>
<td>--16.96</td>
<td>9.84</td>
</tr>
<tr>
<td></td>
<td>2 h</td>
<td>160</td>
<td>85.36</td>
<td>--16.66</td>
<td>10.42</td>
</tr>
</tbody>
</table>

This means that, the resistivity of the nanocomposite thin films decreases by introducing a conductive network into the polymer matrix which improves the conductivity. This may be due to the larger surface area of MWCNTs that serve as a conducting bridge, connecting conducting domains and increasing the effective percolation. Also, interaction of UV radiation with nanocomposite particles which affect the interaction between them. This advantages obtained, is the possibility of improve the charge transport properties of the MnO$_2$ / MWCNTs / PVA nanocomposite thin films.
Fig. 5: Variation of $\varepsilon'$, $\varepsilon''$, $\log \sigma$ and $\log \rho$ of PVA pure thin film.

Fig. 6: Variation of $\varepsilon'$, $\varepsilon''$, $\log \sigma$ and $\log \rho$ of MnO$_2$/MWCNTs nanocomposite/PVA thin film with concentration 0.5%.
Figure 7: Variation of $\varepsilon'$, $\varepsilon''$, Log $\sigma$ and Log $\rho$ of 1% MnO$_2$/MWCNTs/PVA nanocomposite thin film.

Figure 8: Variation of $\varepsilon'$, $\varepsilon''$, Log $\sigma$ and Log $\rho$ of 1.5% MnO$_2$/MWCNTs nanocomposite/PVA nanocomposite thin film.

4. Conclusions

MnO$_2$/MWCNTs nanocomposite were successfully by hydrothermal method with different concentration of MnO$_2$ using a surface oxidation reaction between KMnO$_4$ and MWCNTs. Nanocomposite
were characterized by X-ray diffraction (XRD) and TEM analysis and images confirmed homogeneous dispersion of MnO2/ MWCNTs nanocomposite. The infrared absorption spectrum indicates the presence of conjugated C=C stretching (carbon double bonds), which confirms the safety of the hexagonal structure of the MWCNTs. Sensitivity to UV–irradiation were studied on the optical and electrical properties of the MnO2/ MWCNTs nanocomposite thin films prepared samples have been evaluated. The band gap value were varied due to change in its grain size and time of UV–irradiation. Also, Dielectric properties were affected by radiation. Electrical behavior showed semiconducting properties and sensitivity to UV–radiation. The results indicate the possibility of using MnO2/ MWCNTs nanocomposite as UV detector.

References


