

Synthesis and Characterization of Multi-Walled Carbonnanotube/Poly (Para Aminophenol) Composites

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Abstract

In the present research program we wish to present the preparation and characterization of poly(*p*-amino phenol) (PPAP)/carboxylic acid-functionalized multiwalled carbon nanotube (*c*-MWCNTs) nanocomposites by in situ polymerization method using ammonium persulfate as an oxidant. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that a tubular layer of composite was coated on the surface of carbon nanotubes with a thickness of 25–42 nm. The UV-vis and FTIR analysis provided an evidence for the formation of nanocomposites. XRD spectra showed that the crystalline nature of composite was not affected much by the addition of *c*-MWCNTs. As the content of *c*-MWCNTs was increased, the electrical conductivity of the nanocomposite increased due to the interaction between polymer and nanotubes that enhances electron delocalization.

Keywords: Poly para(aminophenol), multi-walled carbon nanotube; nanocomposite, oxidative polymerization.

Introduction:

Aminophenols are interesting members of the class of substituted anilines. The hydroxyl group in the phenyl ring can be oxidized to quinone and quinone can be reduced again. Thus unlike aniline and other substituted anilines, they have two oxidizable groups (-NH₂ and -OH). Therefore, they could show electrochemical behavior resembling anilines and/or phenols. An important factor would be the relative position of the amino and hydroxyl group in the aromatic ring. Although literature is also available on electrochemical and spectroelectrochemical studies of the *m*- and *p*-isomers [1,2] *p*-aminophenol (PAP) has attracted most attention due to the formation of an electroactive polymer during its chemical and electrochemical oxidation [3-6]. Poly (*para*-aminophenol) (PPAP) has been investigated with electrochemical, spectroelectrochemical, ellipsometry and impedance measurements [7-11] and applied in sensors, biosensors and corrosion protection [12-15].

Carbon nanotubes (CNTs) have a novel structure, a narrow distribution size, highly accessible

surface area, low resistivity, and high stability [16-18]. It has been shown experimentally that the introduction of CNTs into a polymer matrix improves the electric conductivity as well as the mechanical properties of the original polymer matrix [19-21]. Composites of carbon nanotube and polypyrrole were also prepared to enhance its electrochemical capacitance performance [22]. The high surface area and conductivity of CNTs may improve the redox properties of conducting polymers. Recently, it has been found that single-walled carbon nanotube and polyaniline (SWCNT/PANI) composites with good uniformity can be formed by the polymerization of aniline containing well dissolved SWCNT [23]. The CNT in the composites adhere strongly to the PANI matrix by the formation of a charge-transfer complex rather than the weak van der Waals interactions between them, which improves dispersion of SWCNTs into the PANI matrix, and results in enhanced electric conductivity. CNTs have been aligned through different techniques such as template-directed fabrication, template-free chemical vapor deposition, self-assembly, mechanical

stretching, electrophoresis, etc. [24–28]. However, when CNTs introduced into a polymeric matrix, disperse randomly, they lose their orientations. Because of the unique one-dimensional structure of nanotubes, a high anisotropy is expected for nanotube–polymer composites. Hence, fabrication of high-performance nanotube-based composites should take into consideration the alignment of CNTs in a certain direction. Melt [29] or electrical spinning [30] of a composite through a narrow hole leads to nanotube alignment, but the method provides only fibers. The use of perpendicularly aligned CNTs for making composite materials with polymers should offer additional advantages to many applications with great ease [31]. Magnetic field assisted alignment of carbon nanotubes in a polymeric matrix is another very powerful strategy [32,33].

Aminophenols are interesting members of the class of substituted anilines. The hydroxyl group in the phenyl ring can be oxidized to quinone and quinone can be reduced again. PPAP gives a surface film of interesting electrochemical and electrochromic properties when it is electropolymerized in acidic solution. Hence the composites from para-amino phenol and multiwalled carbon nanotube may improve the electrical properties of the material.

The extensive literature survey reveals that some work has been carried out in aminophenol and their application in different field. But no attempt has been made to synthesize conducting poly (*p*-amino phenol) and its nano composites. So we have under taken to synthesis poly (*p*- amino phenol) by chemical oxidation method and its nano compound using *c*-MWCNTs. The synthesis of P(PPD)/MWCNTs nanocomposites via in situ polymerization method has not been studied yet. In the present study, we wish to report the preparation of P(PPD)/*c*-MWCNTs nanocomposites by in situ polymerization method. A number of techniques have been used to analyse the nanocomposites such as UV-visible FTIR, SEM, TEM, and XRD. The electrical conductivity of the composites has also been reported.

Materials and Methods

Materials

Para aminophenol was purchased from Aldrich. Multi-walled CNT (90% purification) used in this study was purchased from Cheap Tubes (USA, 10–20 nm diameter). Other reagents like ammonium persulfate (APS) hydrochloric, sulfuric, and nitric acid (Sigma Chemicals) were of analytical grade. The

solvents were purified using vacuum rotary evaporator under reduced pressure and their boiling point was checked for their purity.

Oxidation of MWCNTs

0.5 g of MWCNTs was dispersed in 40 ml of concentrated H₂SO₄ and HNO₃ with a volume ratio of 3:1 using an ultrasonicator for 10 min. The mixture was stirred at 60°C for 24 h and then washed several times with deionized water until the *p*_H reached 7. The resulting acid- functionalized MWCNTs were filtered with 0.2 μm PTFE membrane filter and dried in a vacuum at 70°C for 24 h. This treatment produced carboxylic acid groups (–COOH) on the surfaces of MWCNTs at their defects and shortened the length of the tubes.

Preparation of poly (para amino phenol)

The poly (para aminophenol) (PPAP) was synthesized by chemical oxidative method in acidic medium using standard procedure. The monomer, *p*-aminophenol was initiated by the drop wise addition of ammonium peroxydisulphate (APS) as an oxidizing agent and conc. HCl as a dopant under constant stirring at 30 °C. After complete addition of the oxidant, the reaction mixture was continued to stir for five hours and the reaction vessel was placed in the refrigerator overnight. The product was filtered and washed with distilled water until the filtrate was colourless and the polymer was dried and powdered.

Preparation of PPAP /*c*-MWCNTs nanocomposites

Each of 2 and 5 wt% *c*-MWCNTs (based on the weight of PPAP) was dispersed in the solution of 0.015 mol PPAP in 100 ml of 0.1 M HCl by ultrasonication for 10–15 min. Then, the solution of 0.015 mol APS in 50 ml of 0.1 M HCl was added drop by drop into the previous solution which was stirred constantly in an ice bath in a period of 30 min to initiate the polymerization. The reaction was kept for 24 h. Acetone was then poured into the reaction mixture to stop polymerization and to precipitate the PPAP /*c*- MWCNTs nanocomposite. The purification and drying procedures were the same as those for the synthesis of the bare polymer.

Solubility Test

The solubility of the polymer and its nano compound in different solvents are presented in table-1. From the table it was clear that the PPAP and its nano compound are completely soluble in DMSO and they

are partially soluble in THF, DMF, methanol and acetone but insoluble in nhexane.

Table-1: Solubility test for the synthesized Poly *P*-Amino Phenol and its nano compound

Solvent	PPAP	PPAP/MWCNT
DMSO	++	++
DMF	+	++
Methanol	+	++
Acetone	-	+
Hexane	-	-

++ *Excellent + good - not soluble*

Characterization:

UV-vis absorption spectra measurement

For the absorbance measurements the solids (in the untreated, as obtained, form) were dissolved in N-methylpyrrolidone (NMP) and the UV-vis spectra were recorded in the range 300–1000 nm. Then, hydrochloric acid was added to reduce the (co)polymer and the absorption spectra were recorded again. All the UV-vis measurements were performed using a Shimadzu PC3101 spectrophotometer, under computer control.

IR spectra

The Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet 8700 spectrometer, in the range 400–4000 cm^{-1} .

Mechanism for composites

Mechanism for the composites

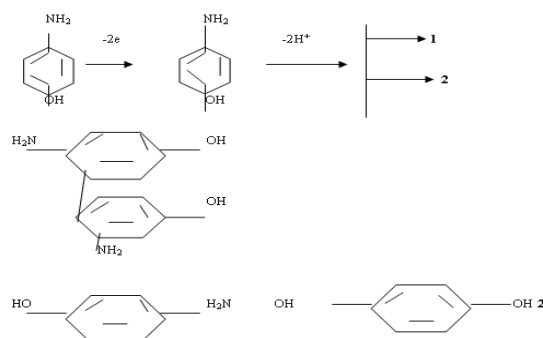


Fig-1 Mechanism for the electropolymerization of *p*-aminophenol

XRD

X-ray diffraction (Rigaku, D/Max, 2500V, Cu-K α radiation: 1.54056 \AA) experiments were carried out on both the plain PmClAn and the composite samples. Wide-angle X-ray diffractograms were recorded at temperature of 300 C after isothermal crystallization at this temperature for 1 h in the range of 0-70(2 θ).

SEM

Morphology of the PmClAn/c-MWCNTS composite was investigated using a Philip XL 30 scanning electron microscope at an accelerating voltage of 25 kV. The sample was fractured at liquid nitrogen temperature and then was coated with a thin layer of gold before observation.

TEM

Transmission electron microscopy (TEM) experiments were performed on a Hitachi H-8100 electron microscope with an acceleration voltage of 200 kV.

Conductivity

The standard Van Der Pauw DC four-probe method was used to measure the electron transport behaviors of PPAP and PPAP /c-MWCNT composites. The samples of PPAP and PPAP /c-MWCNTs were pressed into pellet. The pellet was cut into a square. The square was placed on the four probe apparatus, providing a voltage for the corresponding electrical current could be obtained. The electrical conductivity of samples was calculated by the following formula: σ (S/ cm) = $(2.44 \times 10/S) \times (I/E)$, where r is the conductivity, S the sample side area, I the current passed through outer probes, and E the voltage drop across inner probes.

Results and discussion

Uv-visible Spectrophotometer:

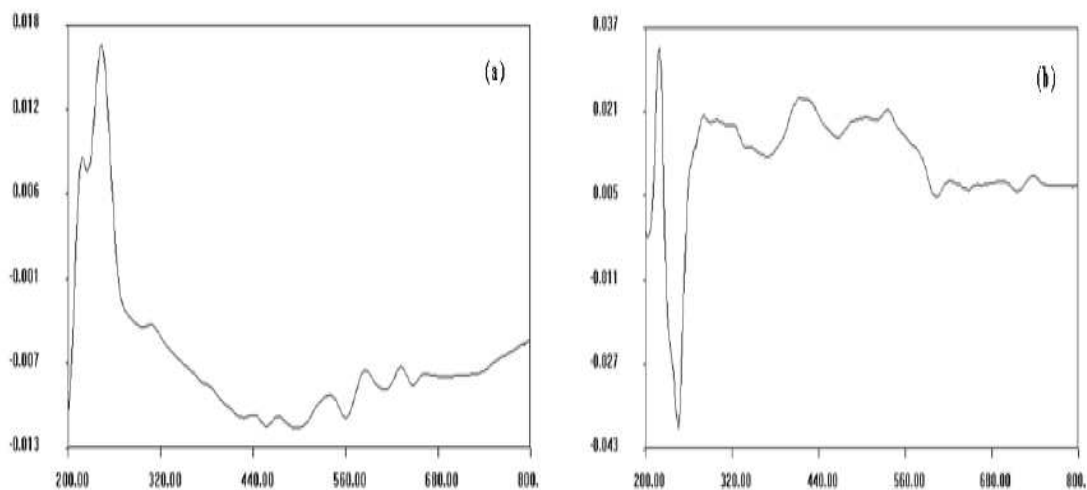


Fig 2.: UV-Vis absorption spectrum of a) PPAP (b) PPAP/MWCNTs

The UV-vis spectra of PPAP and PPAP/MWCNT are shown in Fig 2. The first absorption band appears in the region of 238-389nm is assigned to the $\pi - \pi^*$ transition of the benznoid ring. It is related to the extent of conjugation between the phenyl rings along the polymer chain. The absorption band at 589 and 632nm was believed to be $n - \pi^*$ transition, which correspond to non-bonding lone pair electron transitions of hetero atoms like nitrogen and oxygen respectively. PPAP/ MWCNTs additionally has other two peaks around 468 and 740nm are assigned to the polaron transitions. From the UV-vis spectral characterization, it is clear that some polarons are obtained in the π - conjugated backbone of the polymer by the addition of an emulsifier MWCNTs. The observation of polaron bands is consistent with a high degree of doping and good solubility of the polymer nano compound

FTIR :

Fig. 3 displays the FT-IR spectra of ortho-aminophenol (a), PPAP (b), and PPAP/MWCNTs (c). FTIR spectrum for para-aminophenol shows a typical profile with two peaks at 3378 cm^{-1} and 3311 cm^{-1} due to the asymmetrical and symmetrical N-H

stretching vibrations, two peaks at 1510 cm^{-1} and 1473 cm^{-1} are the characteristic bands of the C- C stretching vibration mode for benzenoid rings, and the bands at 1401 cm^{-1} and 1220 cm^{-1} can be attributed to the C-O-H deformation vibration and the C-O stretching vibration respectively. Spectrums b and c present PPAP and PPAP/MWCNT patterns which synthesized at different conditions. The spectrum of PPAP shows two peaks at 3380 cm^{-1} and 1602 cm^{-1} due to the characteristic bands of the N-H stretching vibrations and the axial stretching of the C O groups in the POAP structure. The peaks in the region of 1400-1600 cm^{-1} are attributed to the stretching of C-H and C C groups. The peak at 1384 cm^{-1} is clearly seen that could be assigned to the C-N stretching vibration of a secondary aromatic amine. The band at 1121 cm^{-1} is ascribed to the stretching of the C-O-C linkages and further support the o-aminophenol changed into PPAP. The spectrum of PPAP/MWCNT (c) is similar in the main peaks to that of the PPAP attern however with different intensity, and it is well known that the peaks of pristine MWCNTs is very weak. These results confirm that the MWCNTs have been dispersed in the polymer matrix.

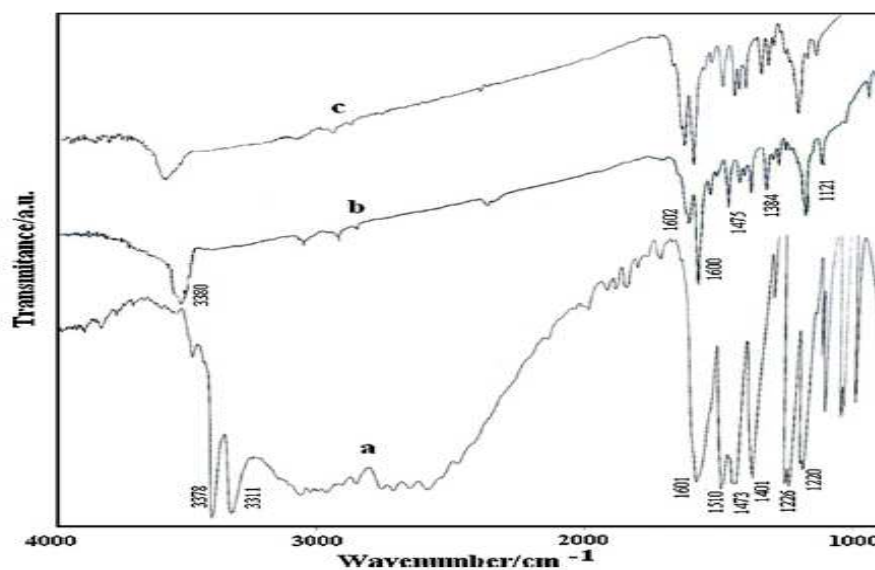


Fig. 3 FT-IR spectrum of (a) ortho-aminophenol, (b) POAP, and (c) POAP/MWCNTs.

XRD :

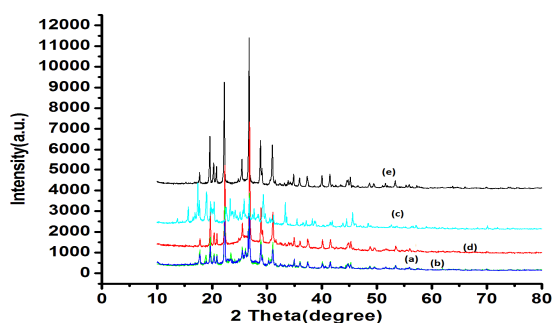


Fig 4 X-ray diffraction data of a PPAP/c-MWNT (0%); b PPAP/ c-MWNT (1%); c PPAP/c-MWNT (2%); d PPAP/c-MWNT (5%) e PPAP/c-MWNT (10%);

The XRD of these nanocomposites shows peaks at $22^{\circ}, 27^{\circ}$ which are similar to pure PANI matrix, revealing that no additional crystalline order have been introduced in to the composites. The increase in the overall intensity of the peak at 25° with increasing functionalized MWCNTs content can be attributed to

the concentration of MWCNTs, which have higher scattering factors. From the figure.5.8 it is observed that the crystalline of the nanocomposite is found to be enhanced/increased by the inclusion of MWCNTs in polymer matrix which is quite obvious.

Scanning Electron Microscopy and Transmission Electron Microscopy

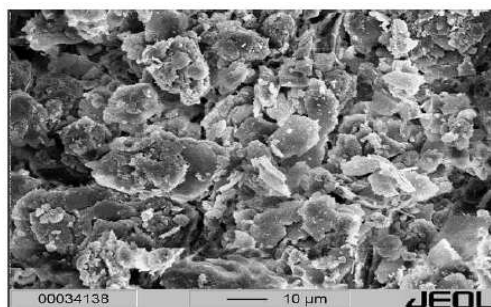


Fig 5 SEM image PPAP/MWCNTs

The morphology of the synthesized poly (*p* - aminophenol) nano compound was measured by SEM and is shown in Fig 5. From the figure it was evident that the morphology of the resultant nano compound is flakes in shape. This confirms that the synthesized PPAP/ MWCNTs falls under the category of nano compound.

TEM:

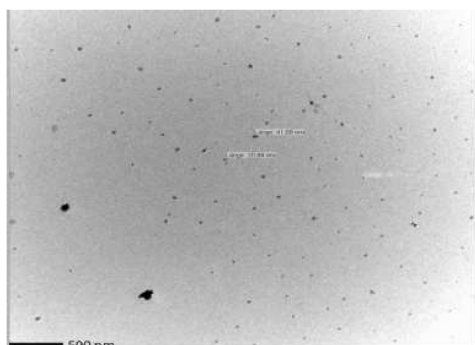


Fig 6 TEM Image of PPAP/MWCNTs

The size of the synthesized poly PPAP nano compound measured by transition electron microscopy is given in fig 6. The result clearly indicates that the size of the nano compound is found to be 25-42nm at 12K with the magnification of 20,000x. This confirms that the synthesized PPAP/MWCNTs falls under the category of nano compound.

Conductivity

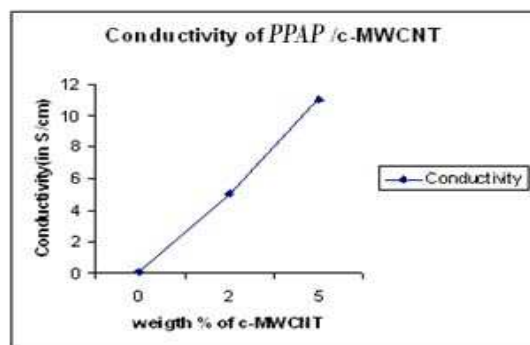


Fig 7 Conductivity of PPAP/c-MWCNT

Conductivity of bare polymer and nanocomposites was measured using a four-point probe method at room temperatures shown in the Figure 7. The conductivity of neat PPAP is nearly negligible i.e 0.06×10^{-6} S/cm this indicates that the bare polymer is almost very very low conductivity. In contrast, the nanocomposites showed better conductivity and the conductivity increased with increasing c-MWCNT content. Interestingly, with increase in c-MWCNTs content from 2% to 5%, the conductivity of the nanocomposite increased by 5×10^{-6} for 2% of c-

MWCNT to 11×10^{-3} for 5% c-MWCNT. This improvement is due to the π - π^* interaction between the surfaces of c-MWCNTs and the quinoid ring of PPAP which effectively improved the degree of electron delocalization between the two components, as confirmed by FT-IR and UV-Vis spectra.

Conclusion

We have successfully synthesized nanocomposites consisting of PPAP and acid-functionalized MWCNTs using insitu polymerization. Morphological studies by SEM and TEM revealed the core-shell structure of nanocomposite with nanotube as the core and a coating layer of PPAP as the shell with a thickness of 25-42 nm. The addition of c-MWCNTs into the polymer improved electrical conductivity, but did not influence the crystalline nature of the bare polymer to any great extent, as confirmed by XRD. The bare polymer was almost very very low conductive; however, the nanocomposites showed better conductivity, ranging from 5×10^{-6} to 11×10^{-3} S/cm. The improved conductivity can apparently be understood from the interaction between c-MWCNTs and the polymer chains.

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