RESEARCH ARTICLE

DOI: 10.54392/irjmt2251

Asian Research Association

INTERNATIONAL RESEARCH JOURNAL OF
MULTIDISCIPLINARY TECHNOVATION

Investigation of Electrochemical Performance of PmAP/WO_3 Composite

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DOI: https://doi.org/10.54392/irjmt2251
Received: 03-04-2022; Revised: 01-07-2022; Accepted: 10-07-2022; Published: 01-08-2022

Abstract: PmAP and PmAP/WO_3 composite are synthesized by chemical oxidation polymerization process. Synthesized materials are investigated by UV Visible, SEM and cyclic-voltagram (CV) techniques. SEM study of as prepared materials is indicated formation of different sized crystals (small and aggregated). In UV Visible spectra analyses, both transitioned (i.e., π-π* transition and charge transfer of polaron band) are observed. Tauc expression is used to estimate optical band gap. Estimated optical band gap is to be 3.09 eV. Oxidation-reduction potential profile is detected in cyclic voltammetry (CV) analyses of PmAP and PmAP/WO_3 composite.

Keywords: Substituted Monomer**,** PmAP, WO_3, Morphology Cyclic Voltammetry (CV)

1. Introduction

In conducting polymer group, polyaniline (PANI) is one of the members. It has distinctive characters such as easy synthesis, low cost, stability in environment, and variety of potential technological applications, particularly electronic and optoelectronic industries. Nonetheless, it has poor processing ability [1-4]. To overcome the lacking, effort has been till going on. Variety of possibility is there to overcome the problem. One possibility is to modify the aniline monomer and improve the processability either chemical or electrochemical polymerization processes. Modified aniline monomer is called substituted aniline monomer [1-4]. Different aniline substitutions are $–OCH_3$ [1], $-CH_3$ [2], $-SO_3H$ [3], -Cl, -F, -I [4], etc and are substituted at ortho and meta positions [1-4]. Normally, ortho-isomer is more favored to the production of substituted conducting polymer. This is because the polymer yields [1-4] if compared to meta-substituted polymer. With substituted aniline based conducting polymer has lower conductivity than without substituted aniline based conducting polymer. This is due to the steric hindrance between amino group and another substituted group of anilinic monomer [1-4]. Thus, ladder structure of polymer is formed. It shows poor processability and low electrical conductivity.

Last decade, conducting polymers/metal oxides composite have become a popular. It has potential application(s) as active electrode material, particularly, lithium batteries [5]. It has own cutting-edge properties because of modification [6, 7]. Presently, core-shell based polymer composite has concerned much more. Core-shell composites demonstrated dual physical properties i.e., core materials and shell materials [8-10]. Core-shell based polymer composite (c/s-MO/polymer) has combined properties of the metal oxide core and conducting polymer shell. This could be greatly widening their applications. Such fields are catalysis, electronics and optics [8-10]. Reports are available on core-shell preparation of composites by chemical preparation and electrochemical method [11-14].

Still, poly (m-aminophenol) polymer is not suitable for engineering applications. In application point of view, different approach has taken to make it suitable for engineering applications. PmAP/WO_3 composite may open new approach to make novel organic-inorganic system, which is helped to improve the desired properties. Tungsten metal trioxide (WO_3) is a hexavalent cation [W^+(VI)]. It is injected through chemically or electrochemically. It is due to its monoclinic structure. In the WO_3 compound, W^+(VI) cation is occupied by octahedrally, whereas Oxygen anion (O^{2-}) is Trigonal planar. This structure is supported to prepare intercalation or delaminated [15-17]. WO_3 is found to be very sensitive to their potentiality in terms of applications (i.e., x-ray screen phosphors, fireproofing, and gas sensors, pigment in ceramics and paints) [18–22].

Author reported synthesis of PmAP and PmAP/WO_3 composite. Synthesized materials are characterized by SEM, XRD, UV-Visible, FTIR and Cyclic voltammeter. Obtained results are discussed.

2. Experimental Details

2.1. Chemicals and Materials

Monomer i.e., meta-aminophenol (mAP) is procured from Loba chemicals Pvt. Ltd., India. Tungsten oxide (WO_3) is purchased (Fluke, Switzerland). From Merck India, Laboratory grade chemicals such as ammonium perdisulphate (APS), hydrochloric acid (HCl), Dimethyl sulphoxide (DMSO) are procured. During synthesis process, deionized water is taken of.

2.2. PmAP Polymer Synthesis

Chemical-oxidation polymerization method is employed to synthesize PmAP polymer. In the synthesis, both meta-aminophenols (mAP) as monomer and ammonium persulfate (APS) as oxidant are used. In the synthesis, monomer (mAP) and oxidant (APS) mole ratio is to be 1:1.5. In polymerization reaction, 3-necked round bottom borosil flask is taken [23]. In three neck system, first neck is thermometer which is measured reaction temperature, second neck (i.e., middle neck) is condenser (to cool down the reaction temperature), and third neck is funnel (to drop chemicals i.e., APS solution). In this synthesis, two type of solution (solution-1 and solution-2) is required. 3.27 g of mAP (0.03 moles) of monomer is put on 50 mL of 1.8 M HCl solution and the solution is called monomer solution. It is designated as Solution-1. 10.26 g APS (0.045 moles) is added on 25 mL distilled water and the solution is called APS solution. It is designated as Solution- 2. During polymerization reaction, temperature is maintained constant i.e., 80 °C. Solution-2 is added slowly drop wise on solution-1 and stirred continuously (14-15 h). Brown colored precipitate is formed. It is kept overnight. Purpose is to convert unreacted monomer to polymer. Brown colored precipitates are filtered, washed (with 4 M HCl) for 2-3 times. It is further washed with deionized water for several times till the filtrate becomes colorless. Deep brown colored precipitates are dried in an oven (at 70 °C) for 10 h. Then, it is collected and kept the dried samples.

2.3. Synthesis of PmAP/WO_3 Composite

PmAP/WO_3 composite is also prepared by chemical oxidation method through acid medium [11]. In the polymerization process, mAP (meta-aminophenol) and APS (ammonium persulphate) ratio is 1:1.5. In the synthesis process, two different type of solutions (Solution A and Solution B) are compulsory. 3.27 g (0.03 moles) of mAP are put on 50 mL of aqueous HCl (1.8 M) to prepare monomer solution. This solution is termed as Solution A. 10.26 g (0.045 moles) of APS is put on 25 mL of water to make oxidant solution. It is named as Solution B. Before doing the polymerization reaction, three necked round bottom flask (RB) is cleaned. Middle neck is fitted with Condenser. It supports to cool the reaction system. Out of other two side neck, Centigrade scale thermometer is inserted in one side neck (for measuring the temperature of reaction). In other side neck, Solution B is added slowly to solution A.

10 wt% WO_3 particles are added to the monomer solution i.e., solution A. It is stirred continuously upto 1 h.

After 1 h, solution B is added drop wise to the solution A through funnel**.** During polymerization reaction, Temperature is maintained (at 80 °C). The polymerization reaction is continuously stirred upto 14 h. Brown colored precipitate is made. It is stayed 12 h to complete polymerization reaction. Corresponding polymer separated by filtering followed by washing. So, brown colored precipitate is filtered and washed with 4 M HCl for 2-3 times (for removing unreacted monomers and oligomers). It is further washed with deionized water for several times till the filtrate becomes colorless. Finally, precipitate is dried at 70 °C in an oven for 10 h. It is collected the dried product.

2.4. Pellet(s) Preparation (PmAP polymer and PmAP/WO_3 composite)

Dried product is grinded to form powders. Powders are used to prepare pellets. Requisite amounts of dried powders (i.e., PmAP or PmAP/WO_3 composite) are taken compression molding (with pelletizer) systems. Pressure (10 MPa) is applied to the moulding system. It is left for five min. Before removing Pelletizer, compression molding system pressure is released. From pelletizer, pellet is removed. Thicknesses and diameter of prepared pellets are measured using slide calipers. It is found to be 1.10 mm and 15.76 mm, 1.09 mm and 15.76 mm, respectively.

2.5. Instrumentations

In UV-Visible spectral analyses, solution technique mode is preferred. Requisite amounts of as-prepared samples are dissolved in dimethyl sulphoxide (DMSO) solvent to prepare transparent solution. UV-Visible analyses are done by Micropack UV-VIS-NIR, DH 2000. UV Visible spectrum is recoded between the wave length region 200 to 1000 nm. Before recording the spectra, base line correction is done. Surface topography of WO_3, poly (m-amino phenol), and poly (m-amino phenol)/WO_3 composites are studied using Carl Zeiss Supra 40 scanning electron microscope (SEM). Before doing the experiment, gold coated powder samples are prepared. SEM instrument is operated at a voltage 4 kV. An electrochemical analysis of poly (m-amino phenol) and poly (m-amino phenol)/WO_3 composites is done. Instrument name is An Auto lab PGSTAT302 potentiostat/galvanostat. In an Electrochemical measurement(s), 0.5 M $HClO_4$ is used.

3. Results and Discussion

Superimposed UV Visible spectra are displaced for both PmAP and PmAP/WO_3 composite in Figure 1. Figure1 A shows peaks at 322 nm (corresponds to π-π* transition) of the benzenoid ring. Also, peak at 530 nm corresponds to electronic excitation (i.e., from Benzenoid ring to Quinoid ring) of PmAP [24, 25].

Figure1B. indicates UV Visible spectrum of PmAP/WO_3 composite. There is shifting of bands from 322 nm to 318 nm and 530 to 514 nm i.e., higher wavelength to lower wave length. Peak area of composite is higher if compared with PmAP. Shifting behavior is due to increase of conjugation length. This shows that more conjugation occurs in PmAP/WO_3 composite material.

Figure 2. indicates optical band gap of PmAP polymer and PmAP/WO_3composites. Energy band gap is estimated with the help of absorption spectra and Tauc expression [26]. Tauc expression is as follows;

$$\alpha h\nu = A\,[h\nu - E_g]^n \text{ ---------------(1)}$$

Various terms are designated as follows;

Here, hν is photon energy

h is Planck's constant

α is absorption coefficient

E_g is optical energy gap

A is the constant (for direct transitions n=1/2).

Graph is plotted between $(\alpha h\nu)^2$ vs. hν. Extrapolated is drawn and is corresponded to $[(\alpha h\nu)^2 = 0$ axis] energy gap (i.e., E_g). Estimated optical band gap **(**E_g) values are found to be 4.45 eV (for PmAP polymer) and 3.85 eV (for PmAP/WO^3 composite). This may happened due to increase in conjugation length.

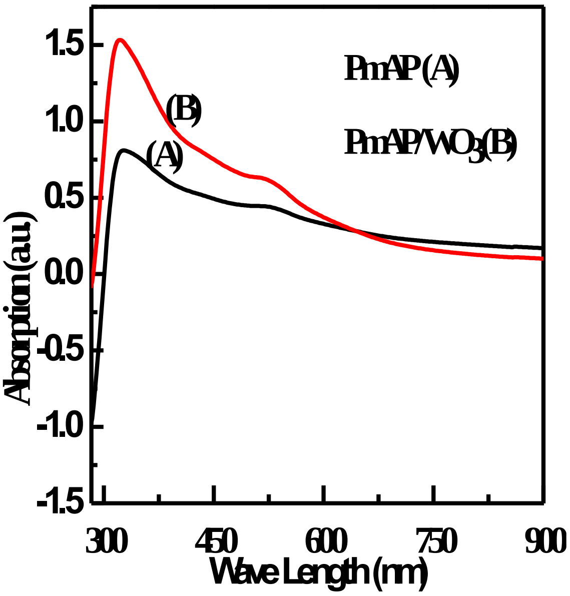

Figure 1. Superimposed UV Visible spectra of PmAP (A) and PmAP/WO_3 composite(B)

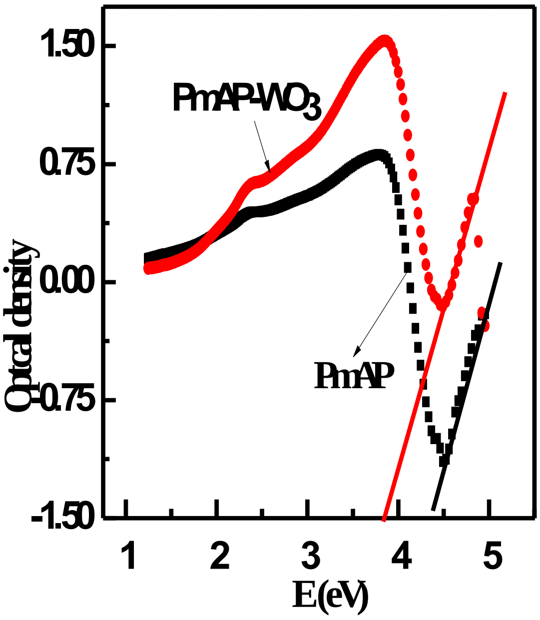

Figure 2. Band gap (right side Figure.1) of PmAP polymer and PmAP/WO_3 composites

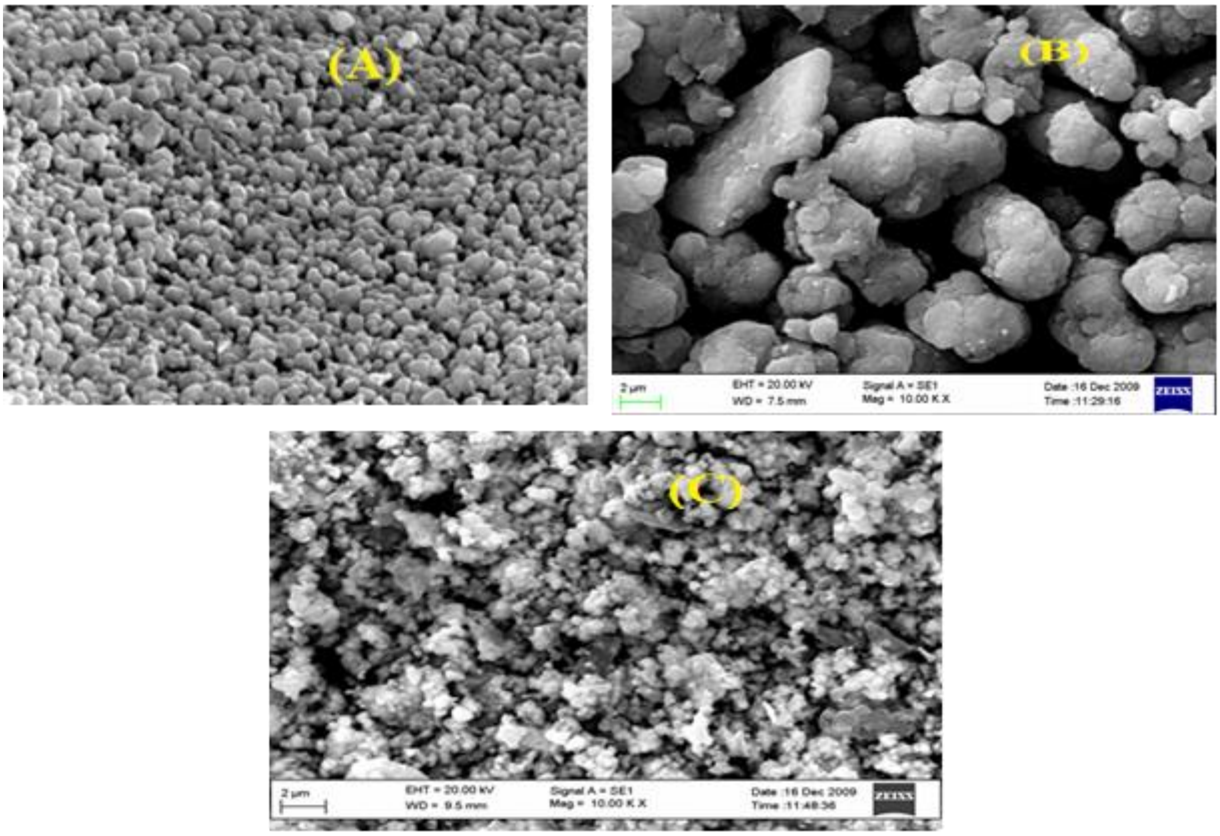

Figure 3. SEM images of WO_3 (A), PmAP (B), PmAP/WO_3 composite (C)

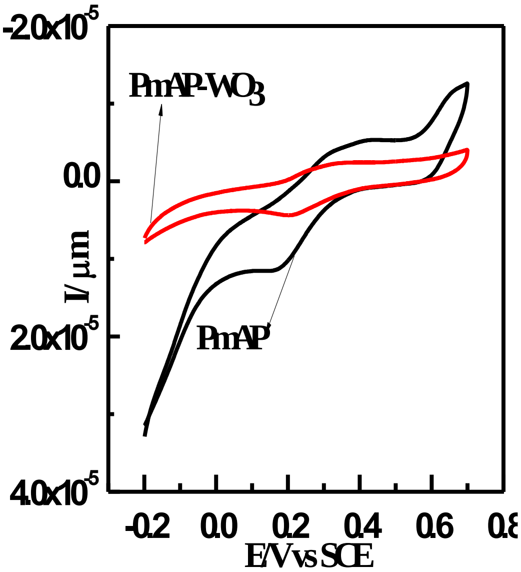

Figure 4. Voltammograms (CV) of PmAP and PmAP/WO_3 composite

Figure 3 (A, B, and C). show SEM images of WO_3, PmAP, and PmAP/WO_3 (10 wt%) composites, respectively. Figure 3A. shows image of Tungsten Oxide (WO_3). It appears as small particle. Figure 3B. indicates surface morphology of PmAP. It exhibits small crystal-like structure. Crystal size is found to be less than 1 µm. Figure 3C. displays surface image of PmAP/WO_3 (10 wt %). It appears to be aggregation of small crystals. Its size is found to be more than 1 µm. This is formed due to interaction between WO_3 particles and PmAP polymer.

For measuring electrochemical performance, a three-electrode arrangement system is employed. In the three-electrode system, silver electrode (for reference electrode), platinum electrode (for counter electrode), and glassy carbon electrodes (for working electrode) are taken. Before doing CV measurement, nitrogen gas (for 10 min) is purged to remove oxygen from solution and maintained inert environment (i.e., N_2 atmosphere is maintained).

Working electrode i.e., glassy carbon electrode (GCE) has electrocapacitive power towards the redox substances [27-30]. Therefore, GCE is regularly pre-treated with $HClO_4$ acid. Potential drop (Ohmic) is operated by Auto lab software between 0.2 and +0.7 V. Used scan rate is 50 Vs.

Oxidation and reduction potentials of PmAP and PmAP/WO_3 composites is measured by, CV measurement. Capacitance is calculated from CV profile [30]. Figure 4. shows CV profile of PmAP polymer. Loop shows an oxidation peak (at + 0.3 V) and a reduction peak (at +0.25 V). In CV profile of PmAP/WO_3 composite is also indicated in Figure 4. Also, it shows an oxidation peak (at + 0.3 V) and a reduction peak (at +0.20 V). Loop area is different (observed from Figure 4). Loop area signifies response of current density.

Both, current density response and loop area (from CV) of PmAP/WO_3 composites is much higher than pristine PmAP polymer. This is clearly showing to high electrochemical performance of PmAP/WO_3 composites. This is remarkably improved owing to the presence of the WO_3 particles, which is present inside the PmAP polymer chains. A Redox peak of the composite is attributed to one redox transition. Hence, it shows pseudocapacitive behavior [31]. Redox transitions occur between a semiconducting state (leucoemeraldine form) and a conducting state (polaronic emeraldine). Faradaic transformation of emeraldine to pernigraniline initiates the redox peaks [32].

Scan rates of measured CVs is 50V/s. It is observed cathodic peaks shift positively and anodic peaks shift negatively. Synergetic effect is resulted due to interaction between PmAP and WO_3. Figure 4. looks like rectangular shaped. It possesses better electrical double-layer capacitance if compared with PmAP polymer.

4. Conclusions

Chemical-Oxidation method is employed to synthesize poly (m-aminophenol) and poly (m-aminophenol)/WO_3 composite using water soluble oxidant i.e, APS. 10 weight percentage WO_3 particles significantly change PmAP polymer structure and, hence, change the PmAP polymer properties. Amounts of π-π* transition and charge transfer spectra of PmAP and PmAP/WO_3 composites are different and is shown in UV Visible spectra. Lower optical band gap is assessed for PmAP/WO_3 composites if compared with PmAP polymer and is estimated by Tauc expression. PmAP/WO_3 is observed crystal-like topography, whereas particle-like morphology is shown in case of PmAP polymer. PmAP/ WO_3 composite are displayed better cyclic voltammetry performance if compared with PmAP polymer.

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Acknowledgements

A financial support and research facility of the work at Metallurgical Engineering Department of Gandhi Institute of Engineering and Technology (GIET) is provided and is gratefully acknowledged. Characterization works is done at Central Research Facility (CRF) of Indian Institute of Technology (IIT), Kharagpur and is gratefully acknowledged

Conflict of interest

The Author has no conflicts of interest to declare that they are relevant to the content of this article.

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