



SYNTHESIS, CHARACTERIZATION AND ENHANCED ELECTRICAL PROPERTIES OF POLYANILINE-TUNGSTEN OXIDE COMPOSITES BY IN-SITU POLYMERIZATION TECHNIQUE

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Abstract:

The conducting polyaniline (PANI) and PANI doped with tungsten oxide (WO₃) with varying wt% of WO₃ are prepared by using in-situ chemical oxidative polymerization method. The X-ray diffraction it clearly reveals that pure PANI is amorphous whereas PANI/WO₃ composites are in crystalline in nature. The electrical conductivity studied by four probe technique at 30 - 200°C. All the composites showed increase in conductivity values with the increase in WO₃ content where the composite with 45% WO₃ content showed highest value of 0.12 S/cm while the lowest conductivity of 0.06 S/cm was found in 5% WO₃ content composite. The dielectric constant shows unusual response with respect to frequency with very high dielectric constant of 4.191X10³ at 3X10⁶ Hz for 45 wt% of WO₃ in PANI, which attributes to the stronger localization of charge carriers and electrical relaxation processes.

Keywords: Polyaniline, Polyaniline-WO₃, XRD, electrical conductivity, dielectric constant.

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DOI: 10.53555/ecb/2022.11.10.49

Introduction

Conducting polymers have been extensively studied for various applications [1, 2]. Among them, polyaniline is one of the most promising due to its unique properties: easy synthesis in aqueous media, excellent ambient stability and simplicity in doping [3, 4]. The doping level can be controlled through a non-redox acid doping/base dedoping process [5]. Polyaniline is generally found in three oxidation states which are namely emeraldine, leucoemeraldine and pernigraniline. Out of these three the emeraldine is most attractive owing to its tunable states. The polyaniline can be synthesized by various routes such as in-situ polymerization, dispersion technique, enzymatic polymerization or by solution blending [6]. The organic electronics whose attributes like light weight, flexible and thin are based on polyaniline. These are applied in display, solar and sensor applications which is mainly because of polyaniline which helps composite or other material help in achieving semiconducting or conductive properties [7, 8]. The demands of high-quality material for electromagnetically compatibilities is alarmingly increasingly [9]. It is well known that the polyaniline based composites with their unique electrical properties are prime candidate material for electronic applications; many studies have been carried out to study the conductivity by both analytical and experimental methods. *Amaechi et al* [10] studied the temperature dependence resistivity of polyaniline/*n*-WO₃ composites by oxidative polymerization technique. The electrical resistivity of the composites assessed in the temperature range of 300 K - 700 K by 2 probe method displayed the semiconductor behavior. *Kumar et al* [11] reported the sensing studies of polyaniline/WO₃ composites prepared by chemical polymerization method. The WO₃ were spread irregularly all over the polyaniline matrix was observed from electron microscopy images. The composites at all WO₃ concentrations showed good sensing ability where the percentage of relative humidity varied from 10% to 85%. Tungsten oxide (WO₃) composites have been developed by *Nirsimha Parvatikar et al* [12] using an 'in situ' deposition process that involves putting fine graded WO₃ in a polymerization mixture of aniline. Thermally activated behaviour is observed in high temperature conductivity measurements. It is possible to see a change in resistance as a function of percent relative humidity (RH). Within a certain range of humidity, the composites in pellet form display nearly linear behavior. At ambient temperature, among numerous visibly active

photocatalysts, tungsten oxide (WO₃) is a transition metal oxide semiconductor with broadly modifiable band gap of $E_g = 2.5-2.8\text{eV}$. WO₃ has lately sparked interest in microelectronics and optoelectronics, colloidal quantum dot LEDs, dye-sensitized solar cells, photocatalysis and photoelectrocatalysis, methanol oxidation catalyst and water splitting photocatalyst as primary catalyst. In wastewater treatment, WO₃ is used as a visible light photocatalyst to generate OH radicals, bacteria killing, and photocatalytic CO₂ reduction into hydrocarbon fuels might all assist the environment. High hydrophobic characteristics and enhanced performance of WO₃ as anode constituents in lithium ion batteries have been described by Yin et al. WO₃ has also been utilised in energy-efficient building windows, flatpanel displays, and optical memory systems. Here in present work we report the synthesis of PANI-WO₃ composites by in-situ polymerization technique. The Structural property of PANI and its composites were characterized using X-ray diffraction. The electrical properties such as AC and DC conductivity of PANI and its composites with varying WO₃ content was studied to understand the conductivity of the composites. Along with this dielectric constant of different composites were also studied.

Experimental Materials-

Polyaniline was prepared by using extra pure and AR grade reagents aniline (99.9%), ammonium persulphate (99.9%), and hydrochloric acid (99.9%) using in situ polymerization method.

Synthesis

Synthesis of PANI and PANI- Tungsten Oxide (WO₃) composites was carried out by polymerization in-situ.

Preparation of PANI

Polyaniline was synthesized by using extra pure and AR grade reagents aniline (99.9%), ammonium persulphate (99.9%), and hydrochloric acid (99.9%) using oxidative polymerization method. Ammonium persulphate (0.2 M) was added drop wise to a stirred solution to prevent warming of the aniline (0.1 M) solution dissolved in 1 M of an aqueous solution of hydrochloric acid (1 N, aniline hydrochloride) at a temperature of 5°C. Following this addition, stirring was continued for 2 hrs using a magnetic stirrer to confirm completion of the reaction. The time of the initial coloration of mixing the reactants depends upon the temperature and concentration of the portico acid. During the polymerization reaction,

HCl was used as a protic acid and the temperature was maintained at lower temperature by using a freezing mixture. The end product was a green-colored precipitate (emeraldine salt). This precipitate was filtered by using Buckner funnel and vacuum pump, washed with deionized water, with acetone in order to remove the oligomers and excess ammonium persulphate, and with 1 N HCl solution to remove the Cl^- ions and unreacted aniline until clear filtrate. Finally, the precipitate was dried in hot air oven for 24 hrs at a temperature of room temperature to achieve a constant mass.

Preparation of PANI-Tungsten Oxide (WO_3) composites

Aniline (0.2 M) was dissolved in 1 M HCl and stirred for 2 hrs to form aniline hydrochloride.

WO_3 was added in the mass fraction to the above solution with vigorous stirring in order to keep the WO_3 homogeneously suspended in the solution. To this mixture, 1M of ammonium persulphate, which acts as an oxidant was slowly added drop-wise with continuous stirring at room temperature for 8 hrs to completely polymerize the monomer aniline. The precipitate was filtered, washed with deionized water and finally dried in a hot air oven for 24 hrs to achieve a constant mass. In this way, PANI- WO_3 composites containing various mass fractions of WO_3 (5% and 45%) in PANI were synthesized.

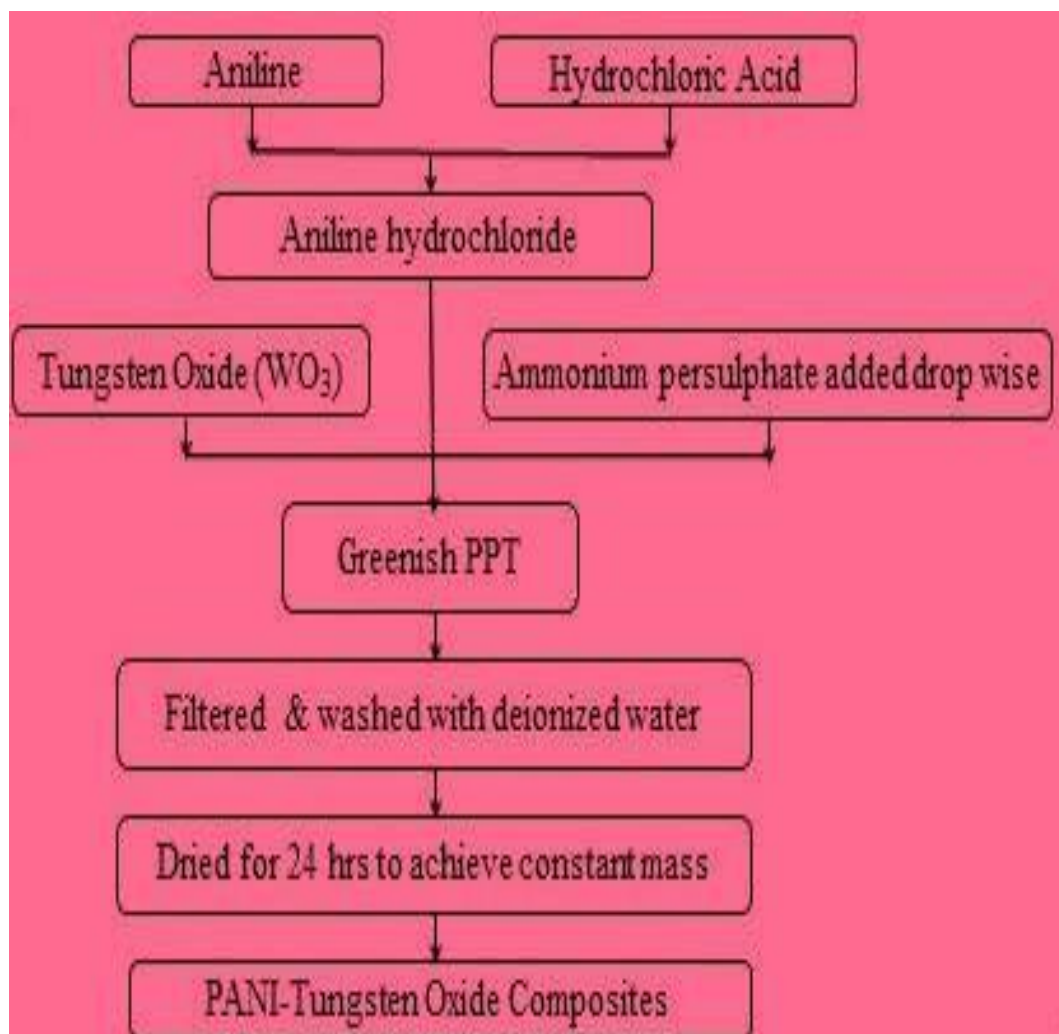


Fig 1: Flow Chart Designed For The Synthesis Of Composite Polyaniline

Characterization

The morphology and the structures of synthesized PANI and PANI- WO_3 composites were studied using X-ray diffraction (XRD) patterns of the powders were taken using Rigaku- Ultima IV, Japan diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda =$ Eur. Chem. Bull. 2022 11(Regular Issue 10), 439-445

1.54 Å). The DC conductivity, AC conductivity and dielectric properties of PANI and all the composites with varying WO_3 concentration were measured by standard four probe method. Ray Diffraction (XRD) Analysis The X-ray diffraction shape of the pure polyaniline is depicted in the

figure 2(a). The broad peak is observed at $2\theta = 25.63^\circ$, which clearly indicates complete amorphous nature which stimulates high mobility of the ions within the substance [13]. Figure 2(b-f) indicates the X-ray diffraction configuration of all composites with the varying WO_3 concentration. Almost all sharp and large peaks show the presence of WO_3 particles in the polyaniline- WO_3 composite. The intense sharp peaks seen at $2\theta = 23^\circ, 24.1^\circ, 33^\circ, 50^\circ$ and 56° to (0 0 2), (2 0 0), (2 0 2), (1 2 0), (2 1 2) planes which shows the existence of WO_3 particles which are having both

monoclinic and orthorhombic phase. All the peaks seen at these 2θ angles were in line with the JCPDS No. 00-024-0747 and also 01-071-0131 which corresponds to monoclinic and orthorhombic phase of WO_3 . However due to overlapping of peaks of polyaniline with that of WO_3 particles is the reason why we are unable to see any peaks corresponding to polyaniline. Here the sharp diffractions peak of all composites indicates strong intensity of crystalline structure of the composites [14].

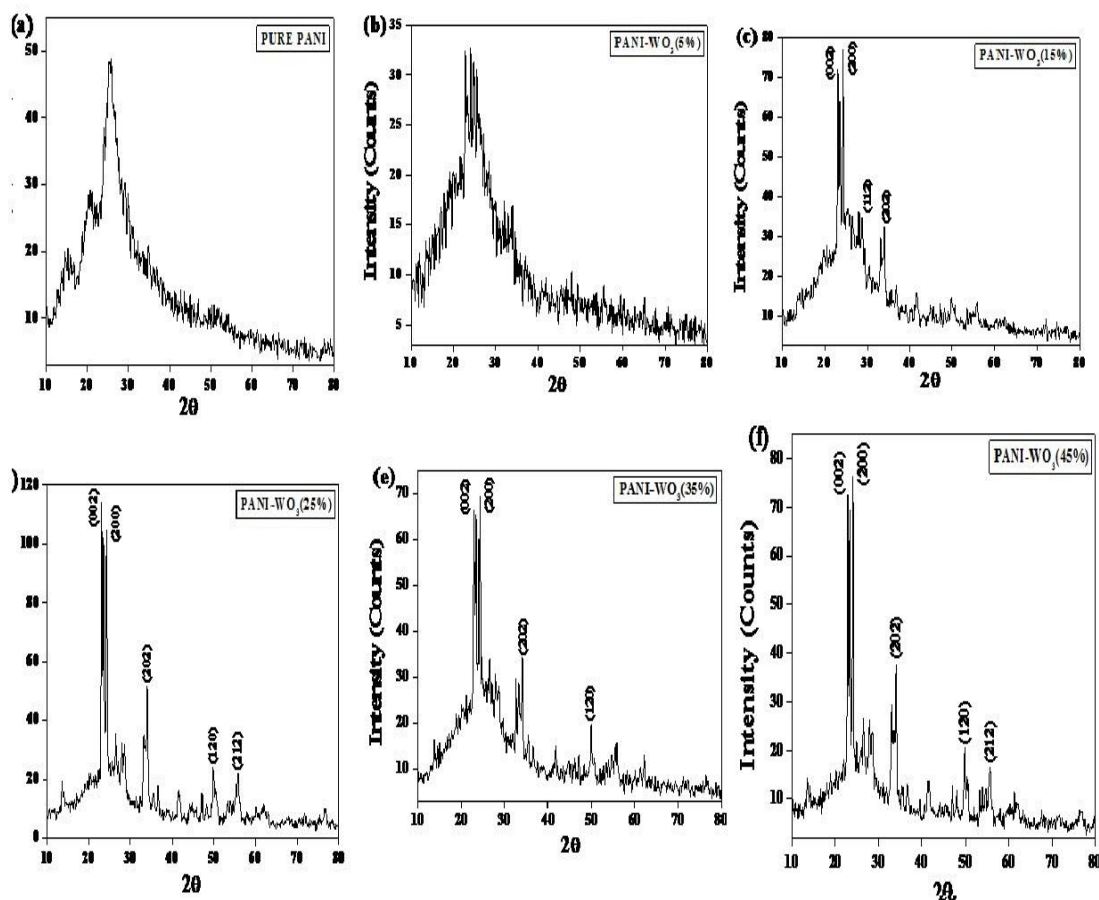


Figure 2: XRD configuration of (a) PANI, (b) PANI/ WO_3 (5%), (c) PANI/ WO_3 (15%), (d) PANI/ WO_3 (25%), (e) PANI/ WO_3 (35%), (f) PANI/ WO_3 (45%).

DC Conductivity Studies

Figure 3 shows the conductivity of PANI and polyaniline- WO_3 composites with varying WO_3 content from 5% to 45%. Here the conductivity was evaluated by applying a four point probe method in the temperature extending from 30 - 200°C. It can be insured that with rise in concentration of WO_3 , the conductivity is found to increase. Among all composites, the one with 45% WO_3 content was found to have highest conductivity of close to 0.12 S/cm while least conductivity value of 0.06 S/cm was noted in *Eur. Chem. Bull.* 2022 11(Regular Issue 10), 439-445

composites with 5% WO_3 content. The rise in conductivity is generally attributed to elongated chain length of polyaniline which help in hopping of charge carriers. But unusual behaviour in conductivity was examined when the temperature was extended from 30 to 200°C. It was viewed that there were two temperature ranges, where the conductivity was noticed to rise with the rise in temperature and these were 70 to 110°C and 160 to 200°C. So the highest conductivity was seen at 200°C for all composites with different WO_3 concentration. As said earlier with the increase in

WO₃ substance and rise in temperature the efficiency of charge communication among the polyaniline and WO₃ increases [15-16]

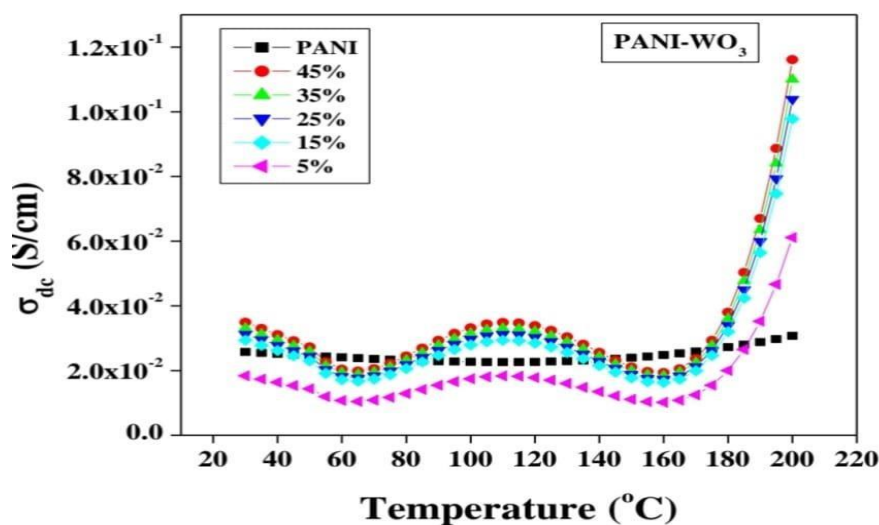


Figure 3: DC conductivity of PANI and PANI/WO₃ composites as a function of temperatures.

AC Conductivity Studies

Figure 4 analyzes the frequency related AC conductivity of the pure PANI and PANI/ WO₃ combination at normal temperature. It is detected that the conductivity of the PANI and compounds are growing as frequency is enlarged in single phase and obtaining nearly constant in higher frequency area i.e, from above 10⁵Hz, the conductivity of PANI and compounds increases by maintaining almost constant value. Doped PANI experiences two types of charged system, one polaron / bipolaron system, which is free to transfer along the chain; the others are attached charges which have restricted mobility. It is noticed from the figure that, as frequency

increases, the conductivity increases because of the movement of polarons along shorter displacements in the polymer chain. It is also noticed that there is an increase in the A.C conductivity for PANI/ WO₃ (15wt%) when compared with PANI/ WO₃ (25 and 35wt%). This is usually due to the increase of isolated polarons and bipolarons and may be due to interfacial polarization. Decrease in conductivity for PANI/ WO₃ (25 and 35wt%) when compared to PANI/WO₃ (15wt%) might be due to serious pinning of polarons thus restricting their hopping hence reducing their conductivity. Similar observation was observed by L.N.Shubha for PANI/TiO₂ [17]

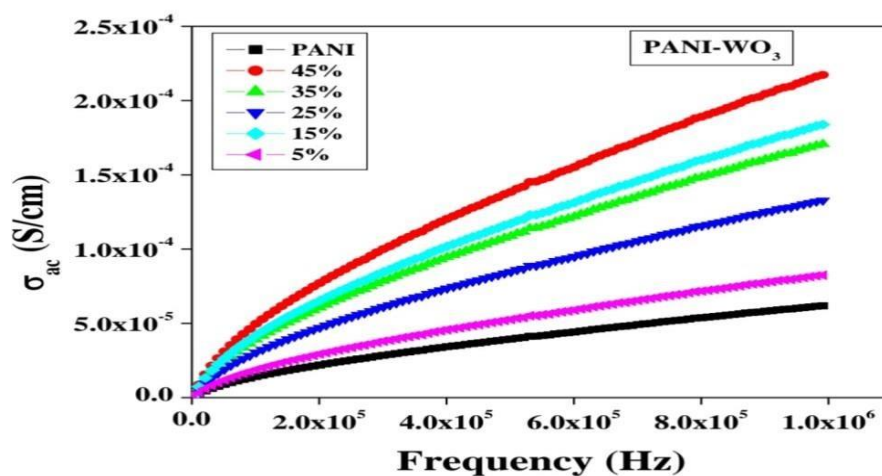


Figure 4: AC conductivity of PANI and PANI/WO₃ composites at different frequency

Dielectric Constant

Figure 5 shows the variation of real part of dielectric constant (ϵ') with frequency (f) for pure PANI and PANI/ WO_3 composites. For pure PANI the real dielectric constant has a value of about 4.942×10^2 at 3.2 MHz, which decreases with frequency, reaching a value of 0.409×10^2 at 5.6 MHz. Such values of real permittivity are related to effects of space charge polarization and electrode polarization. PANI is a semiconducting system with mobile polaron/bipolaron, upon increase in the frequency of the supplied field; the dipoles present in the organization couldn't reorient themselves quickly in response to the supplied field reducing the dielectric constant [18]. Dielectric constants of PANI/ WO_3 composites are

dependent on composition, protonation, temperature and delocalization length. Dependence of ϵ' with frequency of the compounds can be classified into three stages. In the first stage, increases with the increase of frequency within the range of 10^4 to 2.43×10^6 Hz. In the second stage, from 2.43×10^6 to 3.57×10^6 Hz, is greatly lesser value for the pure PANI (4.942×10^2) and much high measure for 45 wt% WO_3 in PANI composite (4.191×10^3), which attributes to the stronger localization of charge carriers. In the third stage, the decrease of ϵ' above 3.57×10^6 Hz frequency might be assigned to the electrical relaxation processes, i.e., the momentary delay in the dielectric constant of a substance with change in the electric field [19-21].

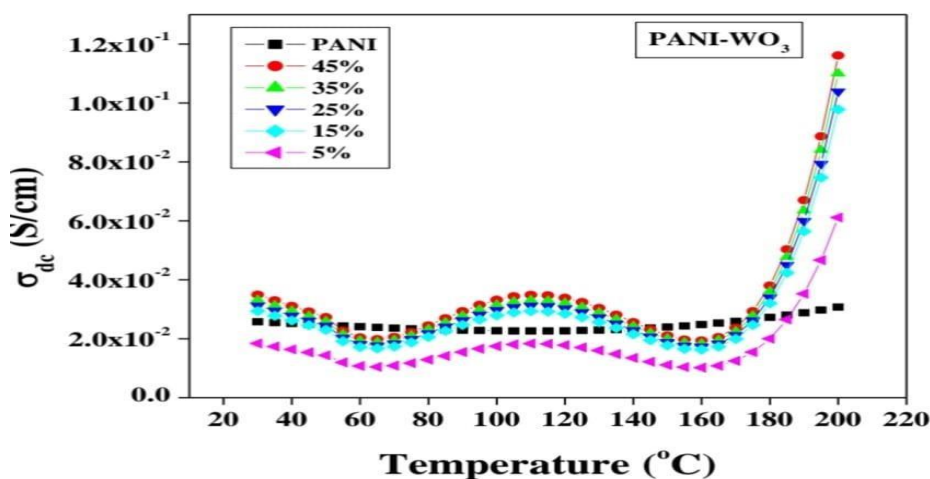


Figure 5: Dielectric Constant of PANI and PANI/ WO_3 composites as a function of frequency

Conclusion

Pure PANI and PANI/ WO_3 composites with varying WO_3 content from 5% to 45wt% have been successfully synthesized by in-situ polymerization technique. The structure of the pure PANI and its composites has been confirmed by X-ray diffraction study. The broad peak of PANI clearly indicates complete amorphous nature. All sharp and large peaks in PANI/ WO_3 composites show the presence of WO_3 particles along with the indication of strong intensity of crystalline structure of the composites. Out of all, the composite with highest WO_3 content of 45% was found to possess highest DC conductivity of 0.12 S/cm at higher temperature of 200°C. The

increased AC conductivity was attributed to the formation of a better charge transport network in the relatively insulating PANI matrix. The improvement in the electrical conductivities of these composites is expected to enhance the potential application of the polymer. The composites showed some interesting dielectric response with very high dielectric constant at low frequency region and strong dependence on content of WO_3 in PANI matrix. It is observed that at low frequencies dielectric constant was found to increase with increasing frequency and then above 3×10^6 Hz dielectric constant is found to decrease with increase in frequency, which is the characteristic feature of disordered materials.

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