



Synthesis and Characterization of Ag₂O Doped Polyaniline

Mahantappa Limbitot^{*}, Sangshetty Kalyane^{**}, Nagbasavanna Sharanappa^{***} and Kamalakanth Lagali^{****}

^{*} Department of Physics, Bheemanna Khandre Institute of Engineering and Technology,
Bhalki, Bidar, Karnataka, India,

^{**} Department of Physics, Bheemanna Khandre Institute of Engineering and Technology,
Bhalki, Bidar, Karnataka, India

^{***} Department of Post-Graduate studies in Physics, Sharnbasveshwar College of Science,
Kalaburagi, Karnataka, India

^{****} Department of Chemistry, Sharnbasveshwar College of Science, Kalaburagi, Karnataka, India

(Corresponding author: Mahantappa Limbitot)

(Received 16 September, 2016 Accepted 19 October, 2016)

(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: Silver oxide/Polyaniline (Ag₂O/PANI) conducting polymer was synthesized by chemical oxidative polymerization method. The synthesized polymers were characterized by XRD, SEM, FTIR and DC conductivity. The XRD patterns shows crystalline phase as increasing doping concentration from 0 to 40%. SEM micrographs exhibit agglomeration of particles having irregular shape. Fourier transform infrared spectroscopy revealed the formation of bond stretching. The electrical conductivity of the Ag₂O/PANI is higher than the pure PANI.

Key Words: Ag₂O/Polyaniline composite, X-ray diffraction, Fourier transform infrared spectroscopy, electrical conductivity.

I. INTRODUCTION

Conducting polymers have the electrical properties like that of metals, and the attraction of them is that they have the characteristics of organic polymers such as light weight, resistance to corrosion, flexibility, lower cost apart and the added advantage that they can be tailor-made to the requirements of the application through modifications in the polymer structure and varying the functional groups in the organic moiety. The current commercial applications of conducting polymers are in thin film transistor, batteries, antistatic coatings, electromagnetic shielding, artificial muscles, light-emitting diodes, gas- and bio-sensors [1], fuel and solar cells, fillers [2], corrosion protective coatings [3], etc. Generally conducting polymer can be used in electrical, electronic, plastics, medical industries, etc. Lattice consisting of mass points connected by rigid bonds are central springs are important model constructs that have application in such different fields as structural engineering, architecture and material science, let us consider a simplex conjugate polymers polyacetylene where unit of CH₃ are linked linearly with alternate double and single bonds with two carbon and two hydrogen's atoms. The two kekule structures derived from this structure is doubly degenerate energetically. Two energetically equal structures at a point couple to give a surface effect known as kink or

solution. The term solution means a solitary wave, implying a non-linear phenomenon involving non-dispersive transport of energy in dispersive medium. In conjugated system, solutions may be neutral, positively or negatively charged according to the number of Electrons in the π orbital. In difference between the number of bonds and the number of degrees of freedom in these lattices determines the numbers of their zero-frequency 'floppy modes'. When these are balanced, the system is on the verge of mechanical instability and is termed isostatic [4]. In conducting polymer systems, two types of hopping processes are involved. The carriers can hop from one chain to an adjacent one, that is, inter-chain hopping. The conjugational defects in the chain lead to intra-chain hopping of carrier that moves along chain [5].

Silver being multivalent forms various phases like Ag₂O, AgO, Ag₃O₄, Ag₄O₃, and Ag₂O₃ by interacting with oxygen [6]. These oxides have different crystalline structures leading to a variety of physiochemical, electrochemical, electronic and optical properties. The most observable and stable phases are Ag₂O and AgO [7]. The recent interest in silver oxide is for its potential use in optical memories. Fortui and Weitzman [8] reported that silver oxide is a p-type semiconductor with a band gap of 1.2 eV while other studies have shown that Ag_xO films have a wide range of energy band gap of between 1.2 and 3.4 eV [9,10].

This wide range of band gap is as a result of different stoichiometries, crystalline phases, and properties arising from different deposition techniques. Our aim is to synthesize silver oxide doped polyaniline to enhance the crystalline and conducting properties.

II. MATERIALS AND METHODS

A. Preparation of polyaniline

Ammonium per sulphate (0.2 M) was added drop wise to a stirred solution to prevent warming of the aniline (0.2 M) solution dissolved in 1 mol of an aqueous solution of hydrochloric acid (1N) at a room temperature. Following this addition, stirring was resumed for 2 h using a mechanical stirrer to ensure completion of the reaction. The time of the initial coloration of mixing the reactants depends upon the temperature and concentration of the protonic acid. During the polymerisation reaction, HCl was used as a protonic acid and the temperature was maintained at room temperature. The end product was a green-coloured precipitate. This precipitate was filtered, washed with deionised water, with acetone in order to remove the oligomers and excess ammonium persulphate, and with 1N HCl solution to remove the Cl⁻ ions and unreacted aniline. Finally, the precipitate was dried in an air oven for 24 h at a temperature of 50°C to achieve a constant mass.

B. Doped with Ag₂O

Synthesis of the PANI–Silver oxide composites was carried out by polymerisation in situ. Aniline (0.2 mole) was dissolved in 1N HCl and stirred for 15 min to form aniline hydrochloride. Silver oxide was added in the mass fraction to the above solution with vigorous stirring in order to keep the Ag₂O homogeneously suspended in the solution. To this mixture, 0.2 M of ammonium persulphate, which acts as an oxidant was slowly added drop-wise with continuous stirring at room temperature for 8 hrs to completely polymerise the monomer aniline. The precipitate was filtered, washed with deionised water, and finally dried in an oven for 24 hrs to achieve a constant mass. In this way, PANI–Ag₂O composites containing various mass fractions of Ag₂O (5wt%, 10wt%, 20wt%, 30wt% and 40wt%) in PANI were synthesized.

III. RESULTS AND DISCUSSIONS:

A. X-ray diffraction analysis

Figure 1 reveals the XRD patterns of pure polyaniline (Pani) and Pani–Ag₂O (5wt%), Pani–Ag₂O (10wt%) and Pani–Ag₂O (20wt%), Pani–Ag₂O (30wt%) and Pani–Ag₂O (40wt%) respectively. Basically pure pani is

having amorphous nature it become crystalline after doping Ag₂O. Prominent broad peak of pani is $2\theta = 25$ degree and Ag₂O has sharp peak of maximum intensity at 32.7 degree other weak peaks are 54.7, 58.9 degree and as doping concentration increases showed the enhanced in the sharpness of the peaks and intensity of (111) reflection indicated the increase in the crystallinity of the pani. The diffractions (111), (220) and (222) reflections related to the cubic structure of Ag₂O (ICCD Card No: 00-41-1104). As doping concentration increased from 5% to 40% along with (111) reflection at 32.7 degree additional two diffraction peaks at 44.1 and 54.8 degree are correspond to the (200) and (220) reflections of metallic silver (ICCD Card No: 00-004-0783).

B. Scanning electron microscope analysis

As evident from figure 2 SEM image of polymer samples of pure polyaniline (Pani), pani–Ag₂O (5wt%), pani–Ag₂O (10wt%), pani–Ag₂O (20wt%), pani–Ag₂O (30wt%), pani–Ag₂O (40wt%) respectively synthesized by oxidation polymerization method, exhibit agglomeration of particles having irregular shape.

C. FTIR Analysis

Figure 1 and 2 showing the Fourier transform infrared spectroscopy of (a) Pure Pani, (b) Pani–Ag₂O–5wt%, (c) Pani–Ag₂O–10wt%, (d) Pani–Ag₂O–20wt%, (e) Pani–Ag₂O–30wt%, (f) Pani–Ag₂O–40wt%. This is useful technique for characterizing materials and providing the information on molecular structure, vibrations and bonding stretches in the compound. When irradiated with infrared light (photons), sample can transmit, scattered or absorb the incident radiation. Absorbed infrared radiation usually excites molecules into higher energy vibrational states this can occurs when the energy of the light matches the energy difference between two energy states. Infrared spectroscopy is particularly useful for determining the functional groups present in a molecule. Many functional groups vibrate at nearly the same frequencies independent of their molecular environment. Further many subtle structural details can be gleaned from frequency shifts and intensity changes arising from the coupling of vibrations of different chemical bond functional groups. The band at 3450 cm⁻¹ is attributable to N–H stretching. The bands at 1668 and 1496 cm⁻¹ corresponded to quinoid and benzenoid structure of PANI, respectively. Also the band at 1293 cm⁻¹ assigned to C–N stretching of a secondary aromatic amine. This interaction may weaken the bond strengths of C=N, C=C and C–N in PANI macromolecule.

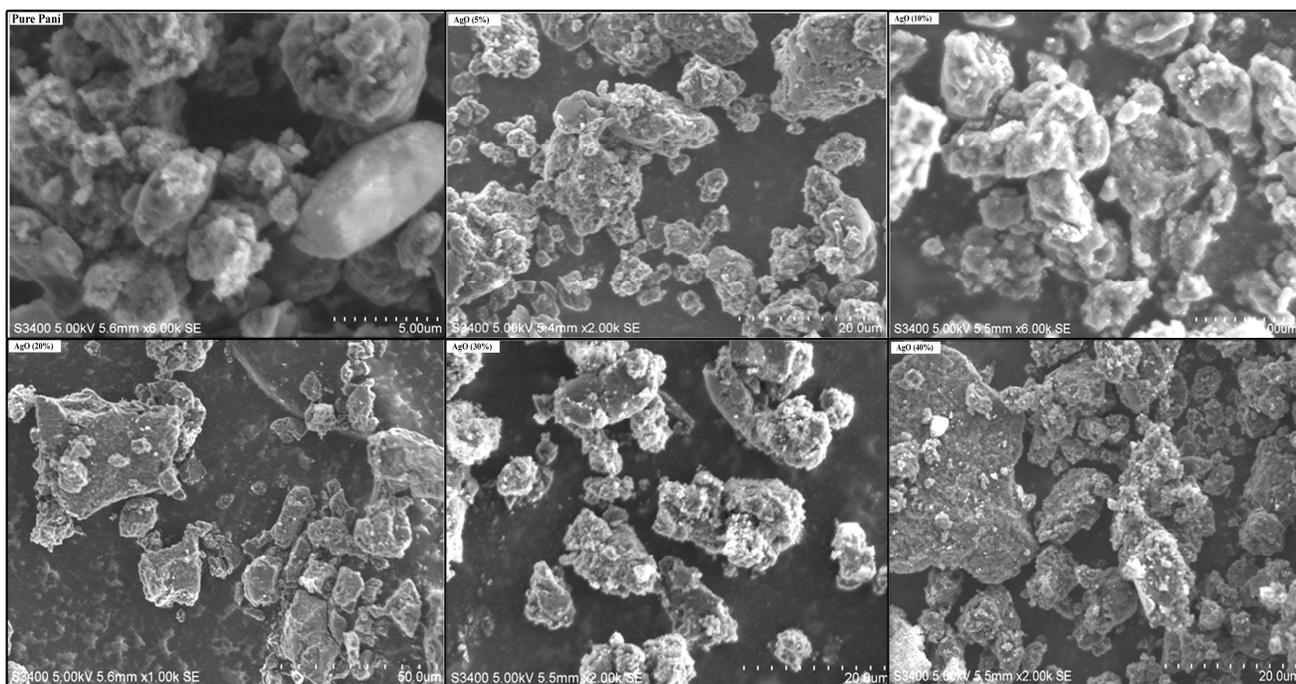


Fig. 1. X-ray diffraction patterns of Pure Polyaniline and doped Ag₂O (5wt%, 10wt%, 20wt%, 30wt%, 40wt%).

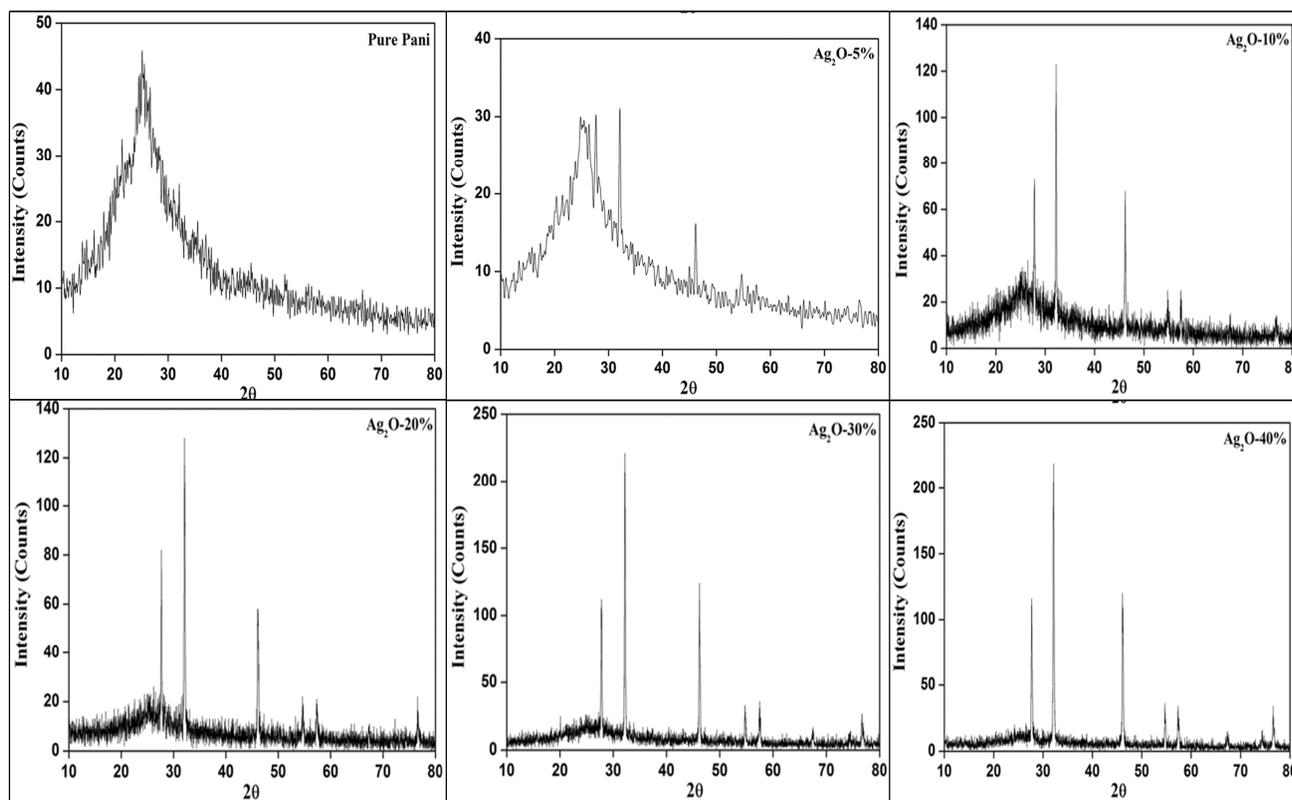


Fig. 2. SEM micrographs of Pure Polyaniline and doped Ag₂O (5wt%, 10wt%, 20wt%, 30wt%, 40wt%).

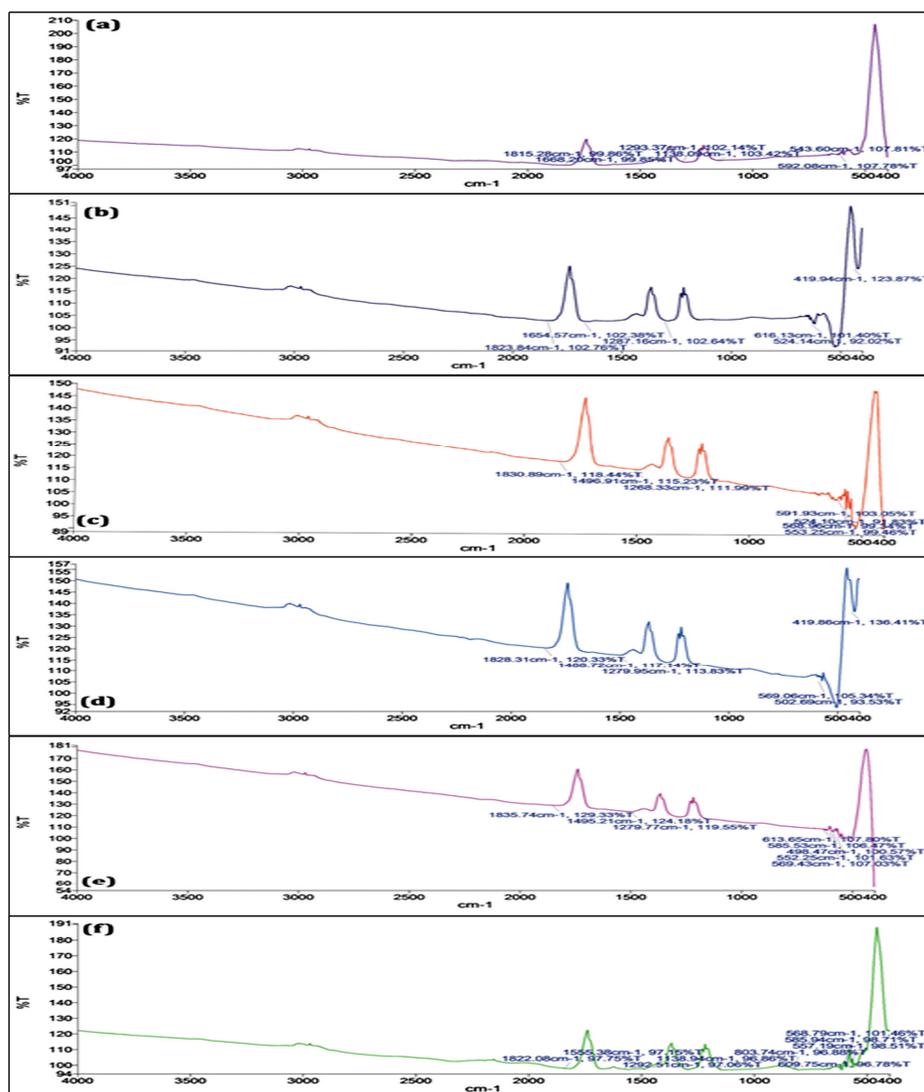


Fig. 3. FTIR spectroscopy of Pure Polyaniline and doped Ag₂O (5wt%, 10wt%, 20wt%, 30wt%, 40wt%).

D. DC Conductivity analysis

Figure 1 shows the DC conductivity studies of pure pani and doped pani with Ag₂O in different concentration of 5%, 10%, 20%, 30% and 40%. The samples were coated with conducting silver paste for providing good electrical contact and were placed between the two electrodes for the measurement. As doping concentration and temperature increases there is an increase in the conductivity of the pani. Electrical conductivity was carried out using two probe method over a temperature range RT-220⁰C. Conductivity remains constant at the range of RT-175⁰C except Pani-Ag₂O (40%) it showed increase in conductivity from starting.

This enhancement of conductivity may be due to hopping (charge particles) and also for extended chain length of pani in which charge carriers possess sufficient energy to hope between various favourable localized sites. Basically Ag₂O is a p-type semiconductor with a band gap ranging from 1.2 to 3.4 eV due to the change in the stoichiometries, structure and crystallinity phases and physical properties arising from the various synthesis techniques. Thermal decomposition of silver oxide into oxygen and silver is the unique characteristics which become promising material for various technological applications.

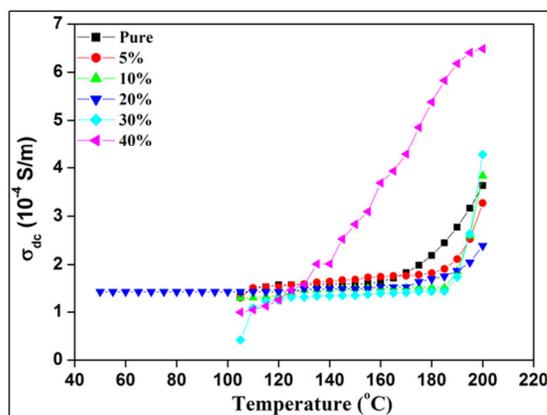


Fig. 4. DC Conductivity of Pure Polyaniline and doped Ag₂O (5%, 10%, 20%, 30%, 40%).

IV. CONCLUSIONS

The present work was an attempt to synthesize pure polyaniline and Ag₂O doped polyaniline with different concentrations (5%, 10%, 20%, 30% and 40%) and are characterized by various techniques such as structural (XRD), microstructural (SEM), Fourier transform infrared spectroscopy (FTIR) and electrical characterization (DC). We have reviewed more number of literatures of pure polyaniline and doped polyaniline in that Ag₂O is finalized for the substitution in polyaniline. Stoichiometric amount of aniline, hydrochloric acid, ammonium persulfate, Ag₂O are weighed and mixed in a proper proportion like 0.2M aniline, 0.2M ammonium persulfate, 0.1N hydrochloric acid, 5wt%, 10wt%, 20wt%, 30wt% and 40wt% Ag₂O. Structural analysis of polymer samples were carried out by X-ray diffraction, amorphous peak of polyaniline was found at 25 degree and sharp prominent peaks of Ag₂O doped polyaniline was obtained at 32.7, 54.7, 58.9 degree. This shows the crystallinity of polyaniline. Microstructural analysis by SEM shows agglomeration and irregular shapes of pure polyaniline and Ag₂O doped polyaniline. Chemical compositions of synthesized polymer samples are confirmed by the analysis of EDAX. It is seen that all the peaks of pure and Ag₂O doped polyaniline are seen in the graph. Fourier transform infrared spectroscopy study reveals the bonding and vibrations of sample. Electrical characterization of samples were carried out by DC conductivity measurement this shows conductivity of doped sample is higher than pure polyaniline.

REFERENCES

- [1]. Morrin A, Wilbeer F, Ngamna O, Moulton SE, Killard AJ, Wallace GG, et al. Conducting polyaniline nanoparticles. *Electrochem Commun* 2005; **7**: 317–22.
- [2]. Jang J, Bae J, Lee K. Synthesis and characterization of polyaniline nanorods as curing agent and nanofiller for epoxy matrix composite. *Polymer* 2005; **46**: 3677–84.
- [3]. Plesu N, Ilia G, Pascariu A, Vlase G. Preparation, degradation of polyaniline doped with organic phosphorus acids and corrosion essays of polyaniline–acrylic blends. *Synth Met* 2006; **156**: 230–8.
- [4]. J. Bernosconi, *Phys Rev. Lett.*, **28**(1972) 1452.
- [5]. R. H. Bughmass and L. W. Shacklette, *Phys. Rev. B*, **29**, (1989), 5872.
- [6]. M. Biemann, P. Schwaller, P. Ruffieux, O. Gröning, L. Schlapbach, and P. Gröning, “AgO investigated by photoelectro spectroscopy: evidence for mixed valence,” *Physical Review B*, vol. **65**, no. 23, Article ID235431, 5 pages, 2002.
- [7]. W. E. Garner and L. W. Reeves, “The thermal decomposition of silver oxide,” *Transactions of the Faraday Society*, vol. **50**, pp.254–260, 1954.
- [8]. E. Fortui and F. L. Weichman, “Photoconductivity in Ag₂O,” *Physica Status Solidi A*, vol. **5**, no. 3, pp. 515–519, 1964.
- [9]. J. F. Dierson and C. Rousselot, “Stability of reactively sputtered silver oxide films,” *Surface and Coatings Technology*, vol. **200**, no.1–4, pp. 276–279, 2005.
- [10]. Y. C. Her, Y. C. Lan, W. C. Hsu, and S. Y. Tsai, “Effect of constituent phases of reactively sputtered AgOx film on recording and readout mechanisms of super-resolution near field structure disk,” *Journal of Applied Physics*, vol. **96**, no. 3, pp. 1283–1288, 2004.