

Synthesis and Characterization of Ultrasonicated Silver Nanoparticles Embedded Conducting Polymer Nanocomposites

Y. B. Wankhede¹, B. M. Bahirwar², S. B. Kondawar³, P. G. Agone⁴

^{1,4}Department of Applied Physics, RCERT, Chandrapur, India

²Guru Nanak College of Science, Ballarpur, India

³Department of Physics, R.T.M. Nagpur University, Nagpur, India

Abstract: Silver nanoparticles were synthesized by colloidal route using silver nitrate (AgNO_3) as precursor and sodium borohydride (NaBH_4) as reducing agent. Conducting polymer polyaniline/silver (PANI/Ag), polyorthotoluidine/silver (POT/Ag) and polyorthoanisidine/silver (POA/Ag) nanocomposites were synthesized by chemical oxidation polymerization in the presence of ultrasonicated as-synthesized silver nanoparticles. Ultrasonication of as-synthesized silver nanoparticles provides the energy to speed up chemical reaction and helps for the interaction of Ag with the backbone of conducting polymers. The composition, morphology and structure of the nanocomposites were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). The XRD patterns indicated that the crystalline phase of Ag is cubic with crystallite size of 90 nm. FTIR confirms the existence of PANI/POT/POA and metal Ag in the composites. The SEM image shows that the Ag nanoparticles are well dispersed in the PANI/POT/POA matrix. The structural characterization of all nanocomposites was systematically investigated.

Keywords: Nanocomposites, conducting polymers, silver nanoparticles, ultrasonication

1. Introduction

Over past few decades polyaniline and its derivatives like poly(O-toluidine), poly(O-anisidine) have become the polymer of scientific and industrial importance as a remarkable properties. In today's world conducting polymers have attracted much attention due to high electrical conductivity, ease of preparation, good environmental stability and wide variety of applications in light-emitting, biosensor, chemical sensor, separation membrane and electronic devices. The most widely studied conducting polymers are polypyrrole, polyaniline, polythiophene etc. Additionally, PANI and its derivatives can coordinate with metal ions, such as silver, gold etc., giving the multi-metallic system and also preparation of nanocomposite materials with other polymers. Obtaining the silver nanoparticles has attracted particular attention due to their unique size-dependent properties, such as optical, electrical, chemical, catalytic, and septic properties with potential applications in nanotechnology, medicine, catalysis, and biomaterials [1-6].

Conducting polymers are characterized by a conjugated structure of alternating single and double bonds, the nature of their π -electron system, enhanced in oxidized or in reduced state and reversible redox activation in a suitable environment. The fundamental process of doping depends upon geometric parameters, such as bond length and bond angle. The charge is localized over the region of several repeating units. Conducting polymers have been found suitable for microelectronic device fabrication due to their excellent electric characteristics and ease of process ability. Polyanilines exist in a variety of protonation and oxidation forms. The most important form of polyaniline, green protonated emeraldine is produced by oxidation polymerization of aniline in aqueous acids. It is electrically

conducting due to the presence of cation radicals in its structure. Sonochemically synthesized silver nanoparticles also have number of applications for photocatalytic activity [7], coating on stainless steel plate [8] and surface enhanced Raman spectroscopy (SERS) [9]. It also has an extensive range of applications such microelectronics [10], optical devices [11], catalysis [12] and drug delivery systems [13].

In this paper, we report synthesis of PANI/POT/POA doped with ultrasonicated Ag nanoparticles using chemical oxidation method and structural characterization of PANI-Ag, POT-Ag, and POA-Ag nanocomposites.

2. Experimental

2.1. Materials and Methods

Aniline (99.5%), Ortho toluidine (99.5%), Ortho anisidine (99.5%), silver nitrate (99.5%), ammonium persulfate (99.5%) and sodium borohydrate (99.5%) were procured from E. Merck. Aniline and its derivatives were distilled prior to use. All supplementary chemicals were of analytical grade and solutions were prepared with double distilled water. FTIR characterization was done using a Shimadzu FTIR-8101A spectrophotometer via making pellet with KBr at 8 ton pressure. The XRD measurement was performed on a Philips PW1710 automatic X-ray diffractometer using $\text{Cu-K}\alpha$ wavelength ($\lambda=1.54059 \text{ \AA}$). SEM images were taken on JEOL JSM-6360 analytical scanning electron microscope.

2.2. Synthesis of Silver nanoparticles

Silver nanoparticles were synthesized separately by 0.001M solution of sodium borohydrate (NaBH_4) in ultrasonic bath, to which 0.01M silver nitrate solution was added drop by drop per second, till the colour of solution changes to pale

yellow. Ultrasonic bath was used for the sonication of solution. The sonochemical method for silver nitrate allows the formation of nanoparticles with a nonuniform dimensional distribution and a spheroidal shape.

2.3. Synthesis of PANI-Ag/POT-Ag/POA-Ag nanocomposites

0.1M aniline/o-toluidine/o-anisidine was dissolved in 1M HCl and the ultrasonicated silver nanoparticles solution was mixed vigorously. The solution was oxidized using ammonium persulphate (APS) with the same molar ratio to that of aniline/o-toluidine/o-anisidine. The reaction was carried out for 3 hrs, at room temperature (30°C). The dark green precipitate was dried at 80°C in vacuum oven and the samples were formed as PANI-Ag/POT-Ag/POA-Ag nanocomposites.

3. Results and Discussions

3.1. X-ray diffraction (XRD)

XRD patterns of PANI-Ag/POT-Ag/POA-Ag nanocomposites are shown in Fig. 1. The sharp peaks of the XRD pattern indicate that the synthesized nanocomposite are well crystalline and confirms the formation of single crystalline Ag nanoparticles in PANI-Ag/POT-Ag/POA-Ag. Bragg's reflections at $2\theta = 24.693, 25.942, 25.254, 26.853, 28.08, 30.029, 42.219, 44.3, 64.5,$ and 77.4 degree corresponds to $\{111\}, \{200\}, \{220\},$ and $\{311\}$ lattice planes, respectively, for the face-centered cubic (FCC) structure of silver nanoparticles embedded in PANI/POT/POA. The broadening of peaks shows the formation of nanocomposites and the average crystallite size was estimated to be ~ 90 nm using Scherrer formula.

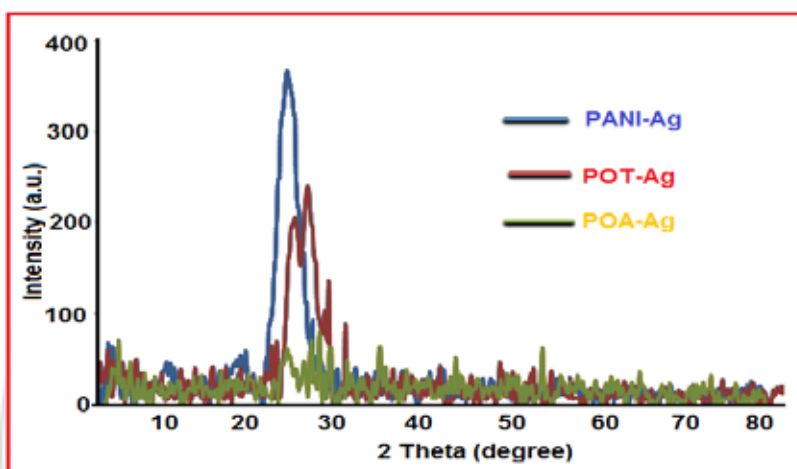


Figure 1: XRD patterns of PANI-Ag/POT-Ag/POA-Ag nanocomposites

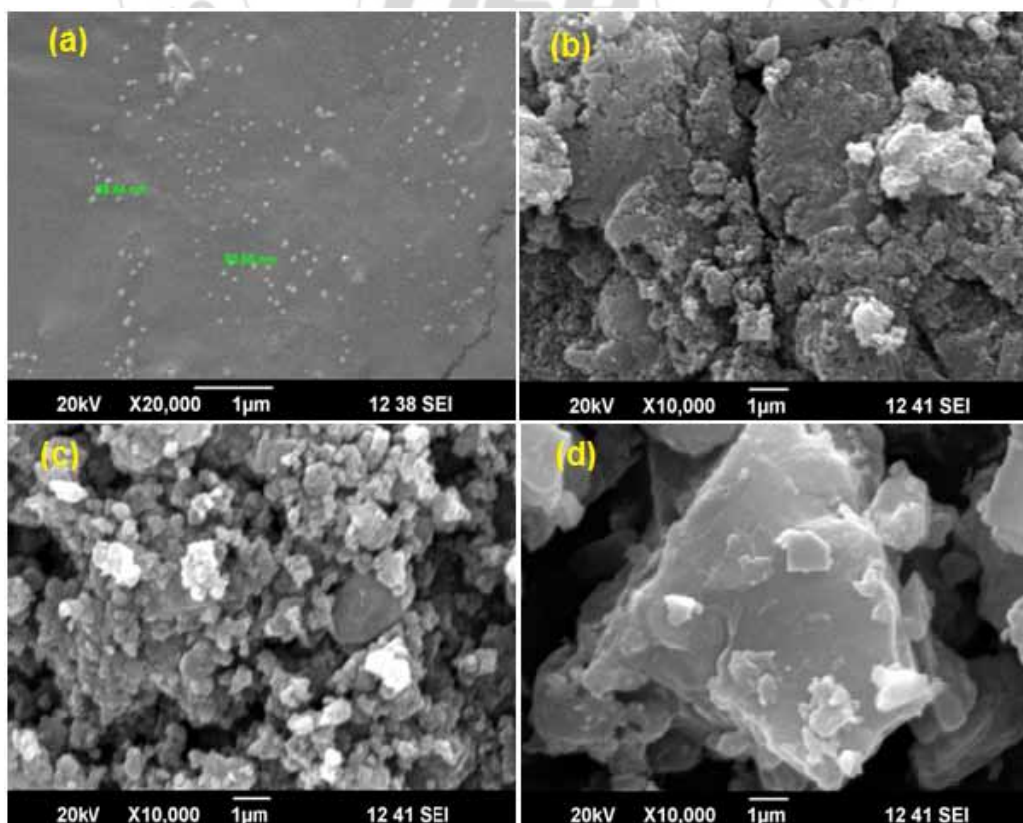


Figure 2: SEM images of (a) silver nanoparticles, (b) PANI-Ag, (c) POT-Ag, (d) POA-Ag nanocomposites

3.2. Scanning electron microscopy (SEM)

SEM images of silver nanoparticles, PANI-Ag, POT-Ag and POA-Ag nanocomposites are shown in **Fig. 2(a), 2(b), 2(c)** and **2(d)** respectively. The average particle size of silver nanoparticles was observed to 90 nm and matched with the size as determined by XRD. The fine structures of PANI-Ag/POT-Ag/POA-Ag nanocomposites are found to be slightly agglomerated and formed mostly wafer like structures indicating the formation of nanocomposites.

3.3 FTIR spectroscopy

The FTIR spectra of PANI-Ag/POT-Ag/POA-Ag nanocomposites are shown in **Fig. 3(a), 3(b)** and **3(c)** respectively. The characteristic peaks for PANI-Ag/POT-Ag/POA-Ag nanocomposites around 1580 and 1480 cm^{-1}

corresponds to the stretching of the benzenoid and quinoid units present in doped PANI respectively. The absorption peaks at 1300 and 1246 cm^{-1} , represents the C-H stretching vibration with aromatic conjugation. The spectra of PANI-Ag/POT-Ag/POA-Ag nanocomposites shows new bands at 3441, 3450 and 3316 cm^{-1} due to single bridge compounds polymeric association [14]. There is also a band at 2924 cm^{-1} showing the presence of chelate compounds. The C-H stretching vibration is represented by the band 2921 cm^{-1} . The band at 1481 and 1493 cm^{-1} may be due to aromaticity. Additional bands at $\sim 1250 \text{ cm}^{-1}$; $\sim 1150 \text{ cm}^{-1}$; $\sim 1020 \text{ cm}^{-1}$ and $\sim 1000 \text{ cm}^{-1}$ could be assigned to vibrations of the C-O-C bonds of the ether group [15] and aromatic C-O [16] respectively, the band at $\sim 500 \text{ cm}^{-1}$ is due to Ag indicating the interaction of Ag and conducting polymer.

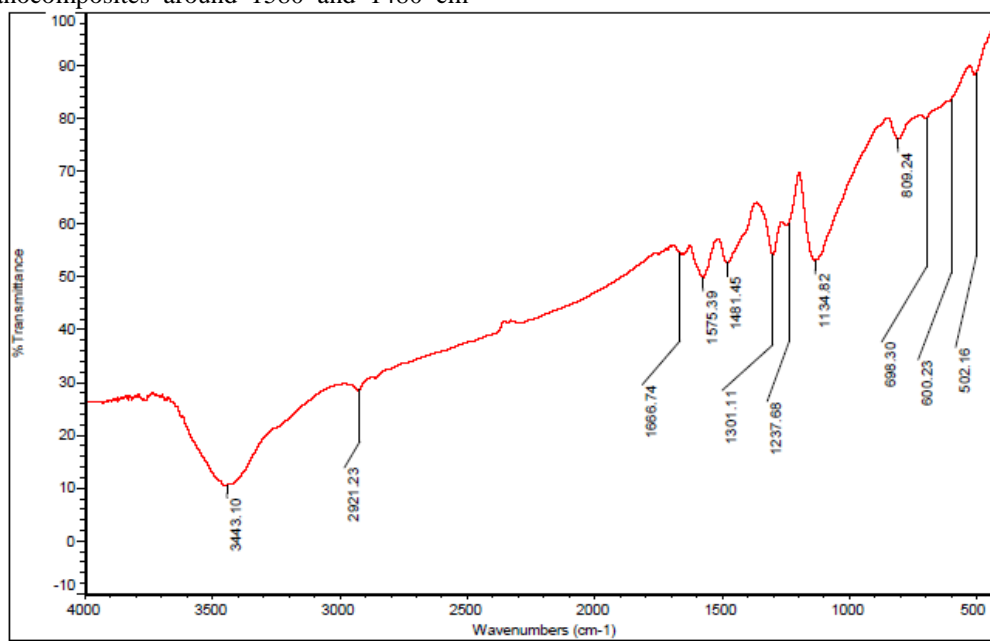


Figure 3(a): FTIR spectrum of PANI-Ag nanocomposite

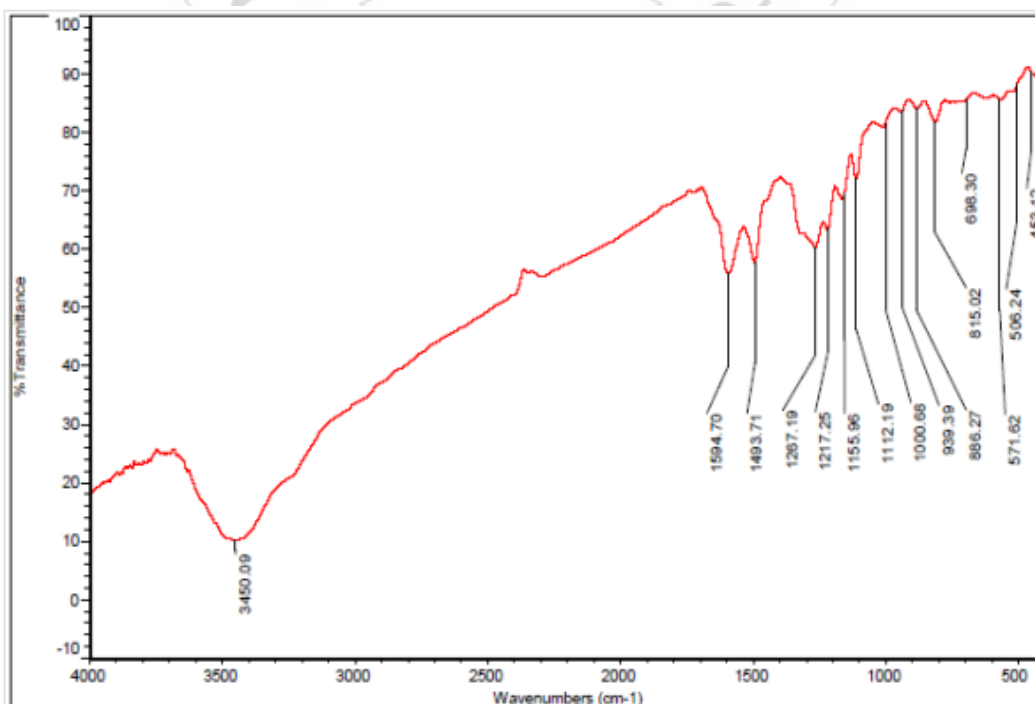


Figure 3(b): FTIR spectrum of POT-Ag nanocomposite

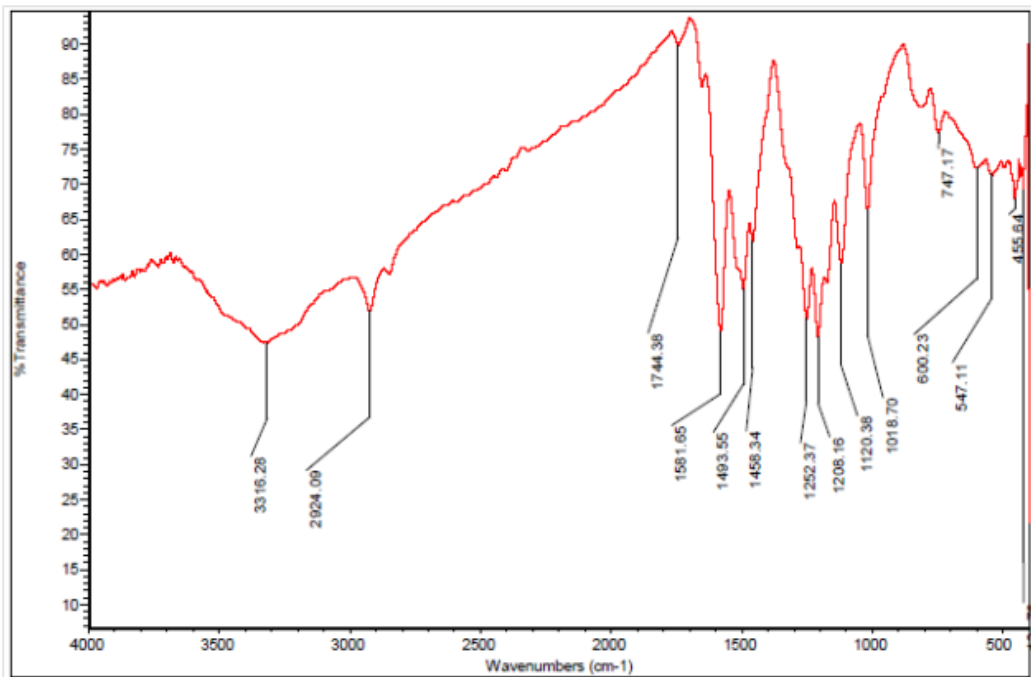


Figure 3(c): FTIR spectrum of POA-Ag nanocomposite

4. Conclusions

Silver nanoparticles and PANI-Ag/ POT-Ag/ POA-Ag nanocomposites were successfully synthesized by simple colloidal route and in-situ polymerization techniques respectively. PANI-Ag/POT-Ag/POA-Ag nanocomposites were found to be well crystalline with average crystallite size of embedded silver nanoparticles ~90 nm. FTIR confirms the existence of Ag nanoparticles in PANI/POT/POA matrix. SEM images show the fine structures of PANI-Ag/POT-Ag/POA-Ag nanocomposite with agglomerated and mostly wafer like structures.

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