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Synthesis and Characterisation of Poly (O-Toluidine) Silver Nanocomposites

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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 polyorthotoluidine/silver (POT/Ag) nanocomposites were synthesized by chemical oxidation polymerization in the presence of synthesized silver nanoparticles colloidal solution and the oxidant ammonium peroxydisulfate (APS). The presence of APS has a marked accelerating effect on the oxidation of toluidine with silver nitrate. The nanocomposite was characterized by XRD, FTIR and SEM to study the effect of silver nanoparticles. Oxidations in 1 M HCl acid produced composites in high yield. The XRD image shows a nanoparticular structure of silver which is well dispersed in the polytoluidine matrix. The broadening sharp peaks in the XRD pattern indicate that the synthesized POT/Ag nanocomposite is nanocrystalline. FTIR reveals the presence of silver metal ions uniformly embedded into POT. The molecular structure of the POT-Ag was confirmed by FTIR spectra. SEM reveals the size of nanoparticle and the structure surface morphology of POT-Ag nanocomposite.

Keywords: - Nanocomposites, Conducting Polymer, Poly-ortho-toluidine, Colloidal, Oxidation.

1. Introduction

In recent years, two classes of organic materials like conducting polymers have gained enormous interest for their attractive chemical – physical properties [1– 4]. Polyaniline (PANI) and its derivatives (POT, PMT, POAS…,) has become an important representative of the class of conducting polymers because of its excellent stability in air. The chemistry of polyanilines is generally more complex with respect to other conducting polymers. This fact is due to their dependence on both the pH value and the oxidation states, described by three different forms known as leucoemeraldine base (fully reduced form), emeraldine base (EB) (50% oxidised form), and pernigraniline base (fully oxidised form). The most important is the EB form and its protonation by means of H+ ions generated from protic acids gives the emeraldine salt form, responsible of the strong increment of the conducting properties [9]. This process is reversible and it is possible for the presence of amine groups basic sites located along the conducting polymer backbone [10, 11]. The doping process of polyanilines is always associated to conformational modifications of the polymeric chains, due to the local distortions created by the addition of H+ ions to the basic sites [12]. These distortions affect the morphology of the deposited films by varying their organisation and play an important role for the mere electrical properties of the conducting polymer. This simple method of synthesis is able to improve the chemical – physical properties of the conducting polymer.

Nano composites are a special class of materials originating from suitable combination of two or more nano particles in some suitable technique, resulting in materials having unique physical properties and wide application [5]. The field of nano composite materials is growing very rapidly. Metal –polymer nano structured composites are giving rise to a great deal of interest because of their possible applications in technologically relevant fields such as electro catalysis and sensors[6].Nobel metal NPs are particularly interesting due to their close lying conduction and valence bands in which electrons move freely which generate surface plasmon bands [15]. Among the different metals studied to date, silver NPs attract special attention due to their high electrical conductivity, antimicrobial effect, and oxidative catalytic functions and unique.

The properties of the poly (substituted anilines) depend on the type of substitution like electron withdrawing, electron donating groups or less affecting groups like alkyl groups [12−14]. This investigation reports that how different types of groups affect the synthesis and properties of poly (substituted anilines). The chemical oxidative method was used to synthesize POT (Poly-Ortho-Toluidine) and metal nanocomposites under similar conditions. It will be interesting to study how different types of groups affect the synthesis and properties of POT-Ag. We present here the preparation of conducting POT-Ag nanocomposite by in-situ polymerization of aniline in the presence of silver nitrate as precursor, using HCl acid by rapid stirring process and its characterizations. The effect of the polymer composition on polymer properties such as FT-IR, X-ray diffraction (XRD), Scanning electron micrographs (SEM), response were evaluated.

2. Materials and Methods:

***2.1 Materials and Methods*: -** All the chemicals used were of analytical reagent (AR) grade. Silver nitrate (99.5%) O-Toluidine(99.5%), and Ammonium persulphate (99.5%), HCl (99.5%) were procured from E. Merck. Ortho-Toluidine was distilled prior to use. All 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. FTIR absorption spectra of POT-Ag composites were performed on a FTIR spectrophotometer in the wavelength range 400-4000 cm^{-1}.The XRD measurement was performed on a Philips PW1710 automatic X-ray diffractometer using Cu-K_α wavelength (λ=1.54059 Å). The morphological were carried out by using SEM. SEM images were taken on JEOL JSM-6360 analytical scanning electron microscopes.

2.2. *Synthesis of Silver nanoparticles:* - Silver nanoparticles were synthesized separately by 0.001M solution of sodium borohydrate ($NaBH_4$) in a beaker, to which 0.01M silver nitrate solution was added drop by drop per second, with rapid mixing of solution, till the colour of solution changes to pale yellow. Thus the formed colloidal solution of Silver nanoparticles has a nonuniform dimensional distribution and a spheroidal shape.

2.3. *Synthesis of POT-Ag Nanocomposites:*- 0.1M POT was dissolved in 1M hydrochloric acid and the 0.2M silver nitrate was mixed. The solution was oxidised using APS with the same molar ratio to that of toluidine and the mixture was kept at room temperature (30°C). The mixture was rapidly stirred, for about 3hrs. Green

solid produced in the oxidation was collected by filter, rinsed with corresponding HCl and dried at room temperature.

3. Results and Discussion

3.1 X-Ray Diffraction (XRD) Study: XRD patterns of the synthesized POT-Ag nanocom-posite are shown in **Fig.1**. The diffraction peaks at 2θ = (145.282º), (23.189°), (25.653°), (31.930°) and (42.881°) to the (111), (200), (220) and (311) diffraction planes, respectively, ascribed to the cubic structure of Ag [7]. The average crystallite size of the polyorthotoluidine-silver nanocomposite was calculated using the Scherrer Equation [8]: $D = \frac{0.94\lambda}{\beta \cos\theta}$ where D is the crystal size of Ag, the wavelength of X-ray (0.154 nm), θ half diffraction angle of peak (in degrees) and β the true half peak width. The average size of the Ag determined through the (111) plane is ~5nm.

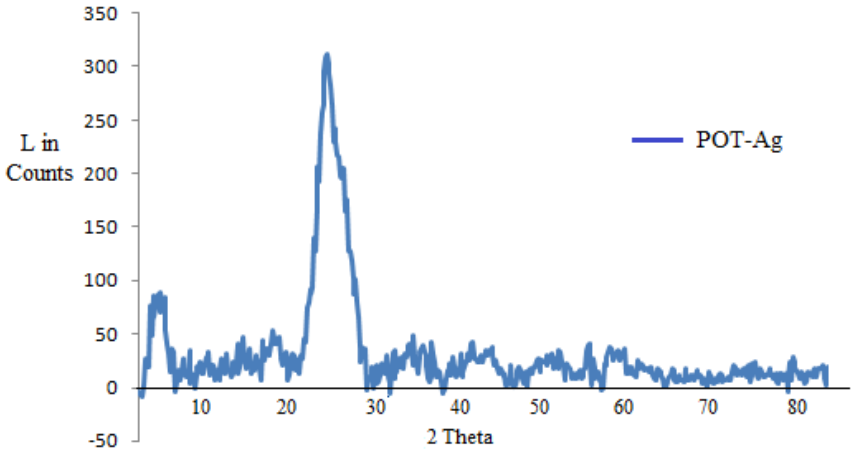

Fig.1XRD pattern of POT-Ag Nanocomposite

3.2Fourier Transform Infrared (FT-IR) Study: **Fig.2** shows the FTIR spectra of POT-Ag nanocomposite. The bands related to N-H stretching of an aromatic amine (N-H stretching) normally appear in the region 3157.45 cm^{-1} The band could be assigned to the asymmetric and symmetric stretching modes of –NH2 group, respectively.

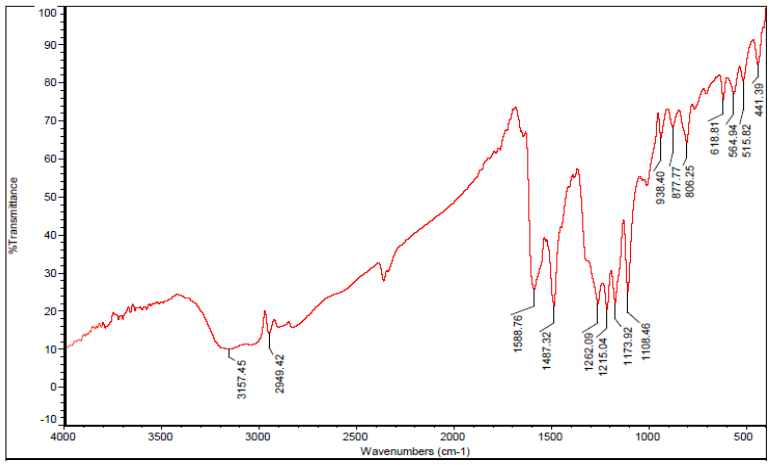

Fig.2. FT-IR spectra of POT-Ag Nanocomposite

The bands corresponding to quinoid (N=Q=N) and benzenoid (N-B-N) ring stretching modes were observed at 1588.76 cm^{-1} and 1487.32 cm^{-1} respectively. Another characteristic band in the infrared spectra refers to quinoic unit at about 1262.09 cm^{-1} arises due to protonation of POT. The peak appeared at 1215.04cm^{-1} corresponds to -N=Q-N+-B- which is characteristic of the protonated state. The bands at 1173.92 cm^{-1} correspond to polytoluidine in the composites. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C-N bond appear at 1215.04 and 1173.92cm^{-1}, respectively. The evidence of formation of polyanisidine with 1, 4-substituted phenyl rings occurred at around 1108.46cm^{-1}. The band corresponding to out of plane bending vibration of C-H bond of p-substituted benzene ring appears at 938.40cm^{-1}. The additional bands at 441.39 cm^{-1} belonging are due to Ag. The spectra of POT obtained with silver nitrate as an oxidant in HCl resembles the product of anisidine oxidation using APS. This product is composed of non-conducting oligomers containing phenazine like units and conducting POT-Ag.

3.4. Scanning Electron Microscope (SEM) Studies: SEM Photographs obtained at different magnifications are shown in **Fig.3**. It was confirmed from SEM that the material Particle size shows the nano range. It can be seen from the figure that the fine structure of POT-Ag nanocomposite is slightly agglomerated and form mostly wafer like structures.

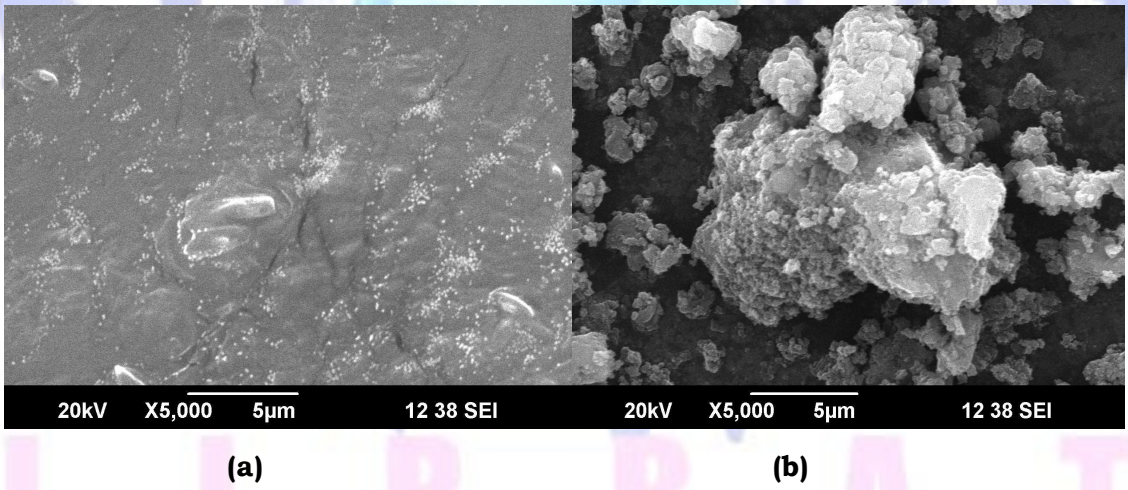

Fig.3 SEM images of (a) Ag Nanoparticles and (b) POT-Ag Nanocomposite

4. CONCLUSION

Interfacial polymerization is a general method to make bulk quantities of polyorthotoluidine nanocomponents. The synthetic conditions are very flexible and can be performed with a broad selection of solvents, doping acids, monomer concentrations, and reaction temperatures. We have synthesized POT-Ag nanocomposites by chemical oxidative method. The formation of Ag nanoparticles and their presence in the prepared nanocomposites were confirmed by XRD, FTIR and SEM on the basis of the analysis of results, conclusions drawn are:

i) From FT-IR, the presence of N=Q=N is confirmed by the bands absorbed at 1588.76cm^{-1} and N-B-N at 1487.32cm^{-1}. Homogeneous dark green

polymerized mixture is showing the presence of emeraldine salt which is confirmed by FT-IR.

ii) From XRD&SEM analysis the particles size of Poly (*O*-Toluidine)/Silver nanocomposite is found be in nano range. Ag nano particles can change the properties which are attributed to size effects.

iii) The XRD patterns indicated that the crystalline phase of Ag is cubic with average crystalline size of ~5nm.

iv) SEM analysis showed uniform dispersion of the Ag nanoparticles in the POT matrix. It reveals the wafer like structure morphology of POT-Ag nanocomposites.

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