

STRUCTURAL, OPTICAL AND ELECTRICAL CHARACTERIZATION OF POLYANILINE/ SILVER NANOCOMPOSITES

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Abstract-

Nanocomposites of conducting polyaniline with Silver (PAni/Ag) have been synthesized by in-situ polymerization of aniline monomer using ammonium persulphate as an oxidizing agent. The weight percentage of silver varied from 3% to 25%. The formation of PAni/Ag composites was assessed by X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and UV-Vis spectroscopy. The broadening of sharp peaks in the XRD pattern indicates the presence of nano phase of Ag. The crystallite size of PAni/Ag nanocomposite from XRD is found to be ~17.5nm. The FESEM image shows a nanoparticulate structure of silver and it is also seen that the Ag nanoparticles are well dispersed in the polyaniline matrix. UV-Vis spectrogram of composites shows three peaks at ~240nm, 450 nm and 700 nm respectively in addition to ~198 and ~324 nm peak of Pure PAni. The peak around 450 nm confirms the presence of radical cation or polaron transition. The peak around 700 nm is the characteristic peak of PAni Emeraldine base. The peak around ~240 nm could be assigned to the characteristic absorption of small metallic Ag cluster. The graph of $h\nu V_s$ ($ah\nu$)² was also plotted. The PL spectrum of PAni/Ag was excited with an excitation wavelength of 320 nm. Two peaks are observed at a wavelength of ~370nm and 600 nm. The DC conductivity of Pure PAni and its composites have been measured in the temperature range from 25°C to 150 °C. The DC electrical study of PAni/Ag nanocomposite clearly indicates that the Ag nanoparticles increase the electrical conductivity of polyaniline nanocomposites as compared to polyaniline.

Key words: XRD, Photoluminescence, Polyaniline, Differential scanning calorimetry

1. INTRODUCTION

During the last decade there has been a wide spread interest in conducting polymers. Polyaniline (PAni) is one of the most useful conducting polymers due to its high degree of stability [1]. It is one of the useful conducting polymers due to its ease of synthesis and simplicity in preparation [2, 3].

Conducting polymer has the electronic properties of semiconductors and at the same time it has got the mechanical properties of the polymer [2]. Due to global warming and the exhaustion of other fossil based fuels alternate renewable energies obtained by solar cells have attracted much attention. Thus the synthesis of novel conducting polymers and study of their physical properties has been of prime importance. There are many unresolved problem concerning the structure and properties of PAni because of the complexities in the molecular structure [4].

The conducting polymers are characterized by conjugated alternate single and double bonds. This feature originates from π -electron. Conducting polymers helped in understanding the fundamental chemistry and physics of π -bonded macromolecules. The π electron of conjugated polymers shows wide range of features in electrical and optical properties. [5]. The charge carriers in polyaniline are generally considered as polaron and bipolaron. The physical

properties of polyaniline depend on the choice of the counter ion called dopants [6]. The approach of chemical synthesis and the functional dopants in the polymer matrix eliminates the use of volatile dopants.

Generally PAni exists in four different forms (leuco-emeraldine base, pernigraniline base, emeraldine base and emeraldine salt (ES)). Among the different form of PAni only ES is electrically conducting and can be synthesized electrochemically or chemically in an acidic medium by means of oxidants [7]. The chemical oxidation polymerization is practically viable due to feasibility of synthesis mechanism for producing large scale PAni powder.

The inception of Nitrogen heteroatom in between Phenyl rings of PAni backbone chain results in the significant properties of PAni. The formation of polarons and bipolarons in the energy band led to the possibility of different types of charge conduction. Oxidation and protonation of amine nitrogen atoms causes the change in the electrical and optical properties of PAni [8].

The metal nanoparticles are prepared due to its unique physical and chemical properties. Stable silver nanoparticles are widely used as photosensitive components, photo catalysts and chemical analysis [9]. Silver nanoparticles also

possess many properties like electrical conductivity; antimicrobial activity etc., the incorporation of metal nanoparticles could effectively improve the electrical, optical properties of polyaniline composites. The electrical conductivity of such composites might also depend upon the molecular structure of polymer matrix [10]. To achieve nanoparticle dispersion is difficult because of high surface area to volume ratio.

In the present study, PANi/Ag nanocomposites with different Ag concentration were synthesized by in situ polymerization techniques. In this current work the structural, morphological, optical and electrical characterizations of nanocomposites are reported.

2. EXPERIMENTAL TECHNIQUE

Analytical grade Aniline monomer, Hydrochloric acid and Ammonium persulphate was purchased from Qualigens, and silver nitrate is purchased from Merck chemicals.

2.1 Synthesis of Pure Pani

The chemical polymerization of Aniline was carried out in the presence of hydrochloric acid. The prepared HCl solution is divided into two beakers. Appropriate amount of aniline solution is mixed in 3M HCl solution in first beaker and 2M of Ammonium per sulphate is added to 3M HCl in the second beaker. Then Ammonium per sulphate solution was added drop by drop to the prepared aniline solution which is maintained around 2 to 4° C till the colour changes to blue and then finally to dark green colour. Dark green colour indicates the formation of polyaniline. This solution is kept for stirring overnight to polymerize completely. Polymerized sample was purified by dialyzing against distilled water and the final solution is kept for drying at room temperature. Then the synthesised PANi is finally crushed to obtain a fine powder

2.2 Synthesis of Pani/Ag Nanocomposites

0.05 M AgNO₃ solution is prepared. Then the prepared AgNO₃ solution is added drop by drop to the prepared polyaniline solution. It is allowed for continuous stirring and the prepared solution is dialysed against distilled water. The final solution is purified as before and kept for drying. The samples of different compositions containing 0.01, 0.03 and 0.1 M AgNO₃ are also prepared by the same method.

3. CHARACTERIZATION TECHNIQUES

Structural characterization of the prepared PANi and PANi/Ag composites were carried out in Bruker X-ray diffractometer using Cu-K α radiation. The morphology of the sample was observed using FESEM in NEON 40 cross beam Carl Zeiss instrument. UV – Visible spectroscopy analysis was done using the Shimadzu 1800 UV – Vis spectrophotometer sweeping the incident wavelengths between 190 nm to 1200 nm. Photoluminescence study was carried out in a JY Fluorolog -3-11 Spectrofluorometer between the wavelength of 300 and 700 nm. DSC analysis is

done in the temperature range of 0 to 350°C using Mettler Toledo DSC1 instrument.

The polymer nanocomposites were ground in a mortar pestle to obtain fine powder form. The powder is pressed to form pellets of 1cm in diameter and thickness varies 1 to 3mm by applying pressure of 70 MPa in a hydraulic press. The prepared pellets are annealed for 2 hours. The mild annealing that the samples might receive will help the PANi to experience more ordering. The same sample was used to measure the electric conductivity (σ) using two probe technique from a temperature range of 25°C to 150°C.

4. RESULTS AND DISCUSSION

4.1 Xrd Studies

Fig. 1 shows XRD pattern of pure PANi and PANi silver nanocomposites. Pure PANi shows two peaks of 2θ at $\sim 20^\circ$ and 25° which correspond to (100) and (110) crystal planes [11, 12]. In addition to PANi Peaks, peaks corresponding to silver were also found at $\sim 32^\circ$ (101), $\sim 45^\circ$ (200), $\sim 65^\circ$ (220) and $\sim 78^\circ$ (311) plane [13]. All the reflections correspond to pure silver metal with face centred cubic symmetry. [14]. Degree of crystallinity of PANi/Ag composites were also calculated by X-ray diffraction analysis. The values were found to vary from 20% to 73%. Degree of crystallinity increases with increase in concentration of nano silver clearly indicating the homogeneous distribution of nanoparticles in the polymer matrix. The particle size of the crystalline particle can be determined using Debye Scherrer formula and it is found that the grain size of PANi/Ag nanocomposite is (~ 17.5 nm).

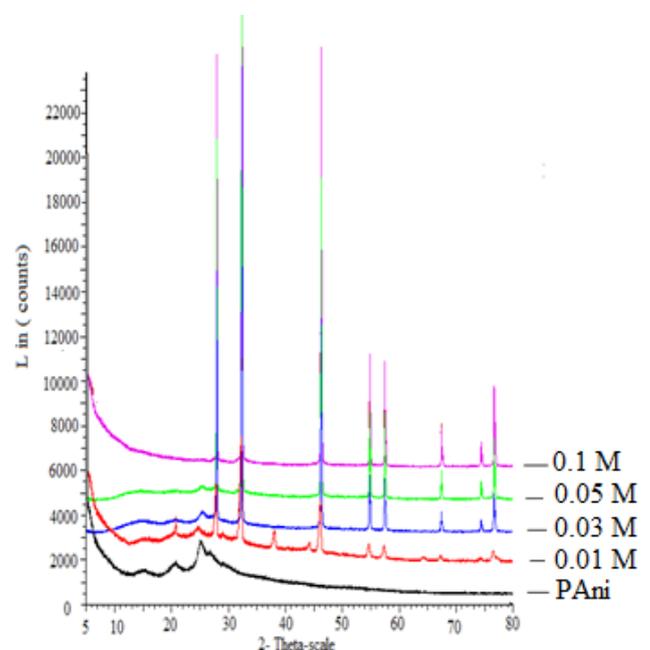


Fig: 1 XRD spectrum of PANi and PANi/Ag nanocomposites

4.2 Morphological Study

Fig. 2a and 2b shows FESEM images of PANi and PANi/Ag nanocomposites, respectively.

FESEM shows that the samples of pure PANi have a fibrillar structure. PANi chains are prepared in acidic media and exist in the form of poly cations [15]. In PANi/Ag nanocomposites, silver nanoparticles are well adhered on the PANi matrix, due to strong affinity of silver to nitrogen of PANi and it is also observed that Ag has a strong effect on the PANi's morphology; it shows a transformation in morphology of PANi particles from pure PANi to its nanocomposites. The formation of a relatively large cluster with Ag dispersion could be attributed to silver migration and aggregation. As the percentage of silver increases there is a change in morphology of PANi which helps in transportation through carbon backbone of PANi.

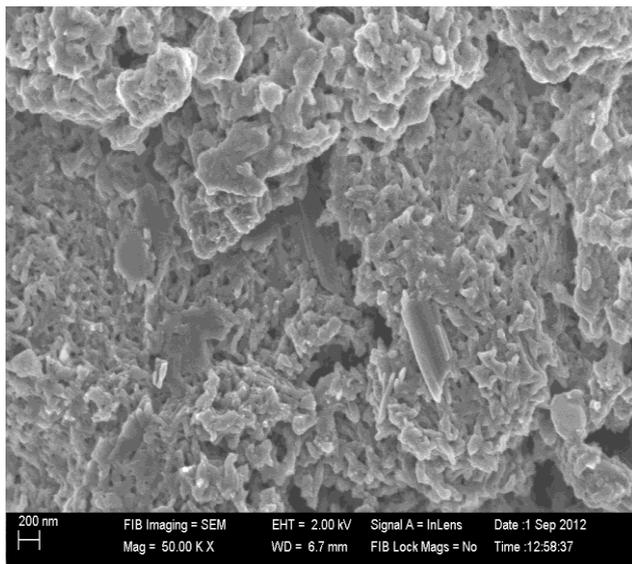


Fig. 2. a. FESEM image of pure PANI

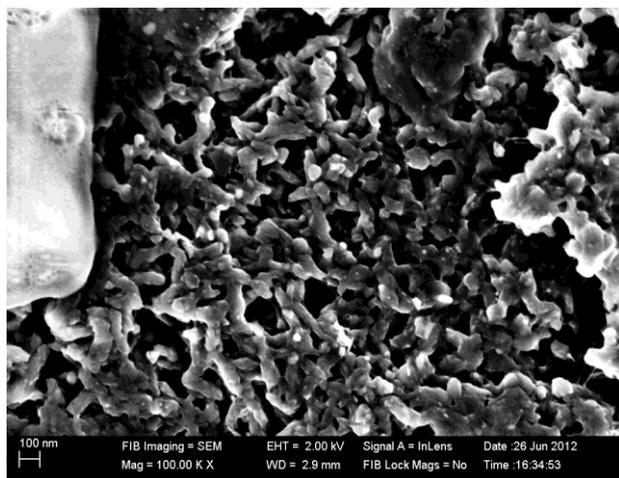


Fig 2.b. FESEM image of PANI/Ag nanocomposites

4.3 UV – Vis Study

Fig. 3 represents the UV-Vis graph of Pure PANi and its composites. UV-Vis spectrograph of the nanocomposites shows three peaks at ~240nm, 420 nm and a broad peak around 580 nm to 850 nm respectively in addition to ~198 and ~324 nm peak of Pure PANi. The peak at 324 nm is due to $\pi - \pi^*$ transition of benzenoid ring of PANi, which is related to the extent of conjugation bond between the

adjacent phenylene ring in the polymeric chain. The absorption band around 420 nm is attributed to the doping level of PANi which is predominant in lower percentage and the same is not significant at higher concentration. The peak also confirms the presence of radical cation or polaron transition. As the peak of PANi and the peak of silver gets superimposed at this position in the composites this peak can also be assigned to surface plasmon resonance absorption of the electrons in the conducting silver bands which indicates that the nanoparticles are present in the nanocomposites [16].

The intensity of polaron absorption band is related to the doping of PANi. Generally the absorption of polaron band decreases for PANi with higher doping level as the radical cation is distributed uniformly [17]. The broad peak in the range 580 to 850 nm might be due to the excitation like transition in quinoid units corresponding to the semiconducting phase of PANi [18]. This peak might be due to intermediate species, possibly a mixture containing major amount of conducting emeraldine salt. The peak around ~240 nm could be assigned to the characteristic absorption of small metallic Ag cluster.

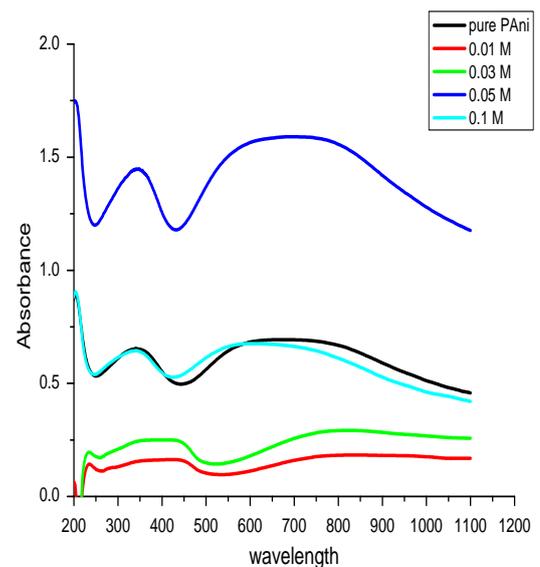


Fig.3 UV-Vis study of PANi and PANi/Ag nanocomposites

4.4 Photoluminescence Analysis

Fig. 4 shows PL spectrum of PANi/Ag was excited with an excitation wavelength of 320 nm. The excitation wavelength is taken as 320 nm to excite silver nanoparticle may be due to π^* transition of the benzenoid unit of polyaniline. Two peaks are observed at a wavelength of ~370nm and 600 nm in composites. Pure PANi reveals three peaks at ~370°, 580° and 610°. The peak of PANi and composites at ~370 nm attributed to the benzenoid groups causing the emission in polymers [19] and the peak ~610 nm is due fully protonated species, whereas, the composite peak at ~600 nm is the indication for the preceding cluster growth process and the appearance of nanoparticles.

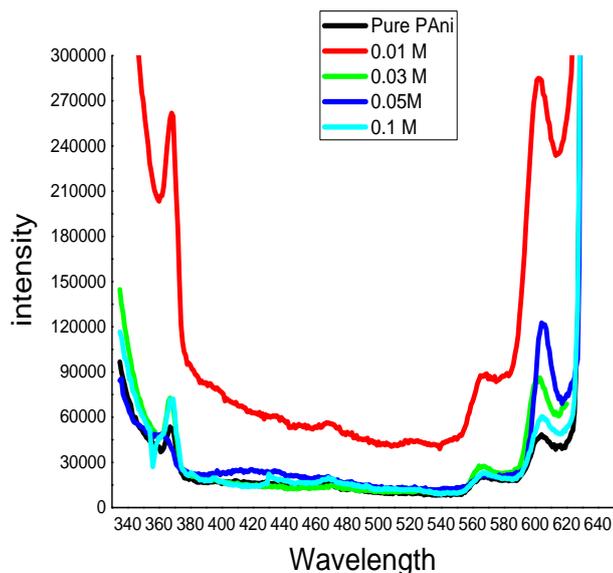


Fig.4 Photoluminescence of Pure PANi and PANi/Ag nanocomposites

4.5 DC Conductivity

To understand the DC conductivity effect of Ag nanoparticles on PANi, a comparison was made between pure PANi and its composites. Fig. 6 shows the temperature dependence of DC conductivity in the range 25°C to 150°C. From this figure it is evident that as the concentration of silver increases conductivity increases. As the concentration of silver is increased in the composites, minimum increase of 2 orders of magnitude and maximum of 6 orders of magnitude are inferred in composites compared to PANi. This increase in conductivity after doping may be due to increase in the number of polarons formed during the doping process. The electrical conductivity of conducting polymers results from mobile charge carriers that are introduced through doping.

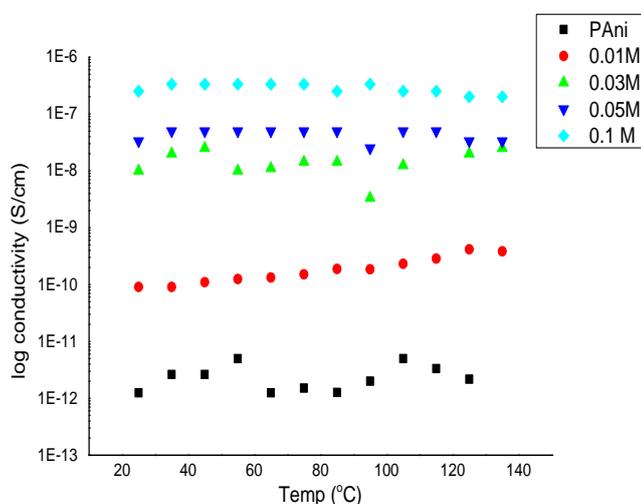


Fig.5 DC conductivity of Pure PANi and PANi/Ag nanocomposites

CONCLUSION

PANi/Ag nanocomposites were successfully synthesized by in-situ polymerization at different Ag concentrations. The formations of Ag nanoparticles in the nanocomposites were confirmed by XRD, FESEM and UV-Vis spectroscopy. The optical characteristic was confirmed by photoluminescence studies. The samples are thermally characterized by DSC. The electrical study was confirmed by DC conductivity. The fibrillar structure of PANi and the linkage of these PANi chains with silver nanoparticles incorporated in it could be the reason for the better conductivity in the PANi nanocomposites. The XRD patterns shows that as the concentration increases the intensity increases. It also indicated that the crystalline phase of Ag. FESEM analysis showed the uniform dispersion of Ag nanoparticles in the PANi matrix. UV-Vis analysis shows both the PANi and Ag peaks, and Photoluminescence analysis shows that composites shows a similar shape like PANi, indicates that it is an efficient way to modify the intensities. DC electrical conductivity of polyaniline/Ag nanocomposites was found to increase when compared to pure polyaniline. The DC conductivity of the samples was found to increase with temperature which is indicative of the metallic nature of the polymer composites. The activation energy of the samples is also calculated.

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