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Synthesis, Characterization and Electrical Property of Silver Doped Polypyrrole Nanocomposites

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ABSTRACT: Silver doped Nanocomposites ofpolypyrrole were successfully synthesized via in situ chemical oxidation polymerization of pyrrole. Ammonium Peroxodisulphate and Silver Nitrate were used as an oxidization agent and dopant, respectively. The molar ratio of monomer unit to oxidization agent and dopant was 1:1:1. The PPy-Ag Nanocomposites were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Visible spectroscopy. The electrical conductivity of chemically prepared polypyrrole in aqueous solution was found to be strongly dependent on the doping and oxidant used. It is probable apply for sensor and battery applications. Formation mechanism of the Ag/polypyrrole conducting polymer Nanocomposites is proposed.

KEY WORDS: Silver nanoparticles, Polypyrrole, electrical conductivity, Nanocomposites.

I. INTRODUCTION

Polymers are large molecule or macromolecule composed of many repeated subunits, known as monomer. Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life. Generally, polymers are insulators. In view of their properties they are considered as uninteresting and have limited applications from the point of view of electronic materials. However, in 1970s, the first polymer capable of conducting electricity, polyacetylene doped with iodine was reported [1]. The success proved that the polymer conductivity can be increased to as high as 15 orders of magnitude by oxidative doping effects.

It's simple synthesis process, used as coatings for corrosion protection [2-4], capable of exhibiting a significant level of electrical conductivity and have good environmental stability in the presence of oxygen and water has also given conducting polymer advantage over metal. Intrinsically conducting Polypyrrole (PPy) is one of the most widely studied conducting polymers because of its good environmental stability, in noxious characteristics, and easy synthesis. Therefore, PPy has the advantages of real applications in batteries, electronic devices, functional electrodes, electro chromic devices, optical switching devices, sensors and so on [7]. Due to the strong intermolecular and intramolecular interactions of PPy chains, they are not soluble in organic solvents and water. Because of its rigid ring structure, polypyrrole is very brittle and inflexible which produces a coating that can be easily broken leading to film defects wherein corrosion can initiate.

Conducting polymers can be easily synthesized by both chemical and electrochemical routes,[8][9] and preparation of various polymers in both aqueous and nonaqueous solutions has been reported [10][11]. Our aim was to prepare and characterize silver containing polypyrrole conducting composite materials in the presence of different oxidant. In this work, synthesis, characterization and electrical properties of conducting polypyrrole/silver composites are reported.



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II. EXPERIMENTAL WORKS

2.1 Materials

Silver nitrite (AgNO₃) was obtained from MERK and pyrrole was obtained from Sigma-Aldrich. Ammonium Peroxodisulphate purchased from LOBA Chemie which has been used as an oxidizing agent.

2.2 Synthesis of PPy/silver Nanocomposites

Polypyrrole powder (back) was chemically synthesized through the oxidation of the monomer by Ammonium Peroxodisulphate and Fe (III) salts of chloride in aqueous solutions.

The PPY/silver Nanocomposites are synthesized by following steps.

Pyrrole was freshly distilled under vacuum. FeCl₃ and $(NH_4)_2S_2O_8$ were used without further purification. All reagents were analytical grade. Water was purified by deionization. Dissolving (1M) Silver nitrite (AgNO₃) powder in deionized water at the 10^oC. After cooling down (1M) pyrrole solution added to the above Silver nitrite solution and stirring the mixture with the help of Magnetic Stirrer at one hour. Ammonium Peroxodisulphate was added drop wise to mixture with constant stirring. Reaction is exothermic hence temperature is minted between 0^oC to 10^oC. Similar processes were applied again with replacement of Ammonium Peroxodisulphate to Fe (III) salts of chloride in aqueous medium. The Black shiny powder obtained was filtered, washed with ethanol and water to remove the unreacted monomer, oxidant and ferric or ferrous contamination and dried at room temperature.

2.3 Characterization

The optical spectra of silver Nanocomposites of polypyrrole were record by UV-3600, Shimadzu spectrophotometer.Xray diffraction measurement was done by XRD 6000 Shimadzu diffractometer and by using Cu α (0.154 nm) radiation at the room temperature. The average size of the Nanocomposites Was recorded by scanning electron microscope (FE-SEM) operated at 10.0 kV.

III. RESULTS AND DISCUSSION

Fig 1(a) (b).shows that the UV-Vis spectra of PPy and PPy/Ag Nanocomposites respectively. PPy exhibit absorption peak at 446 nm which are in support with literature values [12].The UV-Vis absorption spectrum of the PPy-Ag Nanocomposites is shown in Figure1(b).



Two typical absorption bands at 465 and 545 nm, which correspond to the π - π * transition and bipolaron transition of the PPy chain, respectively. The absence of the strong surface Plasmon resonance of metal silver around 450 nm for the PPy-Ag Nanocomposites reveals that Ag is dispersed as very small particles of elementary silver within the PPy-Ag Nanocomposites.



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Figure 1. UV-vis spectra of PPy/Ag (b).

X-ray diffraction studies show that the PPy powder is amorphous in nature. Fig3. Indicate that the pure Polypyrrole broad peak presented by peak $2\theta = 20.530$ is due to PPY existence [13].



Figure 2.XRD patterns of Polypyrrole

The XRD patterns of the silver nanoparticles in polypyrrole matrix. Fig.3 can be seen clearly that the samples consist of crystalline phases presented by four main diffraction peaks at $2\theta = 38.110$, 44.290, 64.480, and 77.470that correspond to the lattice planes (111), (200), (220), and (311).



Figure 3. XRD patterns of PPy/Ag Nanocomposites

In addition, the XRD patterns show that the crystal structure of the sample is Face centered cubic.Synthesis of silver nanoparticles in PPy was confirmed by JCPDS file no.04-0783.

Fig.4 shows that the presence of a series of FT-IR characteristic bands for the PPy/Ag Nanocomposites and PPy. The peaks located at 1,540 and 1,454 cm-1 were related to the fundamental vibrations of the pyrrole rings in the protonated PPy [14]. Bands at 1,293 and 1,034 cm-1 were assigned to a combination C–H in-planering



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bending and the deformation of the five-membered ring that contains the C=C–N deformation [15]. The peak near 958 cm–1 may be attributed to the C–C out-of-plane ring deformation vibration. The peak at 1,163 cm–1 was related to C–N stretching wagging vibrations. In addition, the band at 1,655 cm–1 corresponded to the stretching vibration of the C=O group.



Figure 4.FT-IR absorption spectra of PPy (b) and PPy/Ag (a).

The morphology and size distribution of PPy particles and PPy/Ag Nanocomposites were determined by scanning electron microcopy (FE-SEM) shown in Fig5 and 6 respectively. SEM image of PPy/Ag composites are of spherical shape with diameter in the range of 155-256 nm.



Fig 5.SEM of Polypyrrole.

Fig 6(b).clearly represent that the average grain size is 214 nm. The sharp XRD peaks of Ag in the composite indicate that the silver metal nanoparticles are orderly distributed in the composite.



Fig 6. SEM of PPy/Ag Nanocomposites(a).

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Fig 6.SEM of polypyrrole/Ag Nanocomposites (b).

IV. ELECTRICAL PROPERTY

Fig7. Shows that the variation of electrical resistance as a function of temperature of pure PPy. In this work it was observed that as temperature increases the electrical resistance decreases and hence conductivity increases. Theses represent that the thermally activated property of conductivity has been confirmed. The conductivity of the PPy/Ag Nanocomposites prepared was found to be 14.4 S/cm, whereas that of the pure PPy was found to be 0.11 S/cm [16]. There was an increase of about two orders of magnitude in conductivity upon incorporation of silver in the PPy matrix was observed. The higher conductivity of the Nanocomposites should be depends upon concentration of silver in the Nanocomposites. Following Table 1 show that with the increase of AgNO₃ to pyrrole monomer, the conductivity of the Nanocomposites increased due to the increase of Ag content in the Nanocomposites.



Figure 7. Electrical resistance Vs.Temperature of pure PPy



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Ratio of AgNO ₃	Conductivity (S/cm)
0	0.11
0.1	1.3
0.2	2.9
0.3	4.8
0.4	6.7
0.5	8.4
0.6	9.2
0.7	10.2
0.8	11.9
0.9	13.2
1.0	14.4

Table 1.Different ratios of AgNO3 and Polypyrrole Conductivities

V. CONCLUSIONS

A simple and novel one-step chemical method has been introduced to prepare PPy-Ag Nanocomposites insitu chemical oxidation polymerization. The formation of metal silver and PPy has been characterized by XRD and UV-Vis absorption spectroscopy. The morphological scheme was visualized by SEM technique. It is observed that the electrical conductivity was increase in the increasing ratio of AgNO₃ hence it is strongly dependent on the doping and oxidant used. It is conclude that the Polypyrrole has thermally activated property of conductivity.

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