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Nanoparticle-Embedded Polymer: Preparation and Characterization of PVA-PPy-Au Nanocomposite Free Standing Films

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ABSTRACT:

In this work, we report successful synthesis of novel nanocomposite films based on Polyvinyl Alcohol-Polypyrrole-Gold nanocomposite (PVA-PPy-Au NC). The films were synthesized by the in-situ chemical oxidative polymerization of pyrrole with iron (III) chloride as an oxidant, with variable loading of gold nanoparticles. The conducting films prepared from the nanocomposite solution were free standing, flexible and light weight. Citrate reduction method was used for the synthesis of gold nanoparticles (Au NPs). The structure and morphology of the novel nanocomposite films were characterized by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). According to TEM analysis, the size of nanoparticles was found to be about 20 nm. SEM studies of the nanocomposite films showed that the Au nanoparticles were well conjugated in the PVA-PPy matrix. The structures of PPy as well as nanocomposite films were confirmed from the XRD patterns and the FTIR spectra were used to examine the chemical structure of the obtained PVA-PPy-Au nanocomposite films. TGA showed the improved thermal stability of the polymer nanocomposite films.

KEYWORDS: Polypyrrole, Gold nanoparticles colloid, Polyvinyl alcohol, Nanocomposite

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INTRODUCTION

In last two decades, inorganic-organic nanocomposites, in particular, metallic nanoparticles (NPs) embedded in a conducting polymer matrix, have attracted much attention of investigators owing to a wide range of potential use of these materials[1-2]. Conducting polymers nanocomposites are increasingly significant due to their potential to combine the features of polymeric materials with those of inorganic materials, leading to more efficient applications than their bulk counterparts[3-5]. Conducting polymer with polyaromatic backbone including polypyrrole (PPy), polythiophene (PTh), Polyaniline (PANi), etc. are well known for their excellent electronic properties, due to which they received a great deal of attention [6-8]. On the other hand, the metal nanoparticles, such as platinum, silver, gold and copper, have attracted much attention in recent years due to their interesting properties and potential applications in technological fields viz. electronic, optical, textile industries, food packaging, waste water, air treatment, cosmetic, medicine and drug delivery[9-12].

Polymers are preferred host materials for stabilizing and capping of nanoparticles of metals. Polyvinyl alcohol (PVA) is an important non-toxic water-soluble transparent polymer. PVA is biocompatible, biodegradable, shows hydrophilicity and ability to form fiber. Because of these features, PVA has various applications in the food industries as a binding and coating agent[14,15]. PPy is the most widely used conducting polymer amongst the known conducting polymers because of its advantages such as high conductivity, improved stability, mechanical properties, and simplicity in its preparation[16]. PPy has high mobility of charge carriers along and across the polymer chains with highly delocalized π- bond structure[17]. PPy possess some unique chemical and electrochemical properties leading to the wide range of technological applications in sensors, actuators, anticorrosion coatings, rechargeable batteries, supercapacitors, EMI shielding, light emitting diodes, etc.[18-24]. Gold nanoparticles (Au NP) are of current importance because of their unique excellent optical properties. Among the wide range of hybrid nanocomposite materials, particularly gold–polymer nanocomposite is the subject of increased interest[25-28].

Therefore, in the present work, we have reported successful synthesis of gold nanoparticles homogeneously dispersed within the (PVA-PPy) polymer matrix. The Au NPs are prepared using the Citrate reduction method. Different characterizations including morphological (TEM, SEM) and spectral properties (FTIR, XRD) of the nanocomposite were performed and the results of the study are discussed. To the best of our knowledge, this is the first work on the synthesis of PVA-PPy-Ag NCs by in situ polymerization of PPy in the presence of PVA and Au NPs.

EXPERIMENTAL TECHNIQUES

Materials and Reagents

The monomer pyrrole was purchased from Spectrochem Pvt. Ltd, Mumbai. It was double distilled prior to use for synthesis. Chloroauric Acid was obtained from Molychem, Mumbai. Polyvinyl alcohol (PVA), Iron (III) chloride($FeCl_3$) and Trisodium citrate were procured from S. D. Fine Chem. Ltd., Mumbai. PVA was used as host polymer during the preparation of nanocomposite. $FeCl_3$was used as oxidizing agent during polymerization. Trisodium citrate here acts both as a stabilizing and a reducing agent. All chemicals were of analytical reagent grade (AR) and were used without further purification. Double distilled water was used for the preparation of solutions.

Preparation of PVA solution

Aqueous solution of polyvinyl alcohol (4% weight to volume) was prepared by dissolving 4.0g PVA powder into 100ml distilled water. This mixture was then stirred vigorously at 70°C for 3 hours on a magnetic stirrer with hot plate so as to obtain clear homogenous PVA solution, which was then left to cool to room temperature.

Preparation of Gold (Au) nanoparticles

In short colloidal solution of Au nanoparticles were synthesized by the chemical reduction of Chloroauric Acid using trisodium citrate by Turkevich method[29]. The details of experimental method has been reported in our previous papers[30]. In a typical experiment, chloroauric acid solution (0.5 mM) was heated up to boiling temperature. Trisodium citrate (38 mM) was added in the above solution to initiate the reduction of chloroauric acid. Immediately after addition of trisodium citrate, the solution turned colourless from translucent yellow. After few minutes, the colour slowly changes to ruby red, indicating the formation of Nano sized gold particles.

Synthesis of PVA-PPy-Au Nanocomposites

The PVA-PPy-Au Nanocomposite was synthesized by in situ chemical oxidative polymerization of pyrrole in the presence of PVA and Au nanoparticle colloidal solution. Aqueous solution of PVA (50ml) and Au NPs colloidal solution (100 ml) was stirred by a magnetic stirrer (~ 0^0C) for few minutes. 2 ml of pyrrole was then added to this solution via syringe. The mixture was stirred until pyrrole was thoroughly dissolved. Polymerization of pyrrole was carried out using iron (III) chloride as the oxidizing agent. The precooled aqueous solution of $FeCl_3$ (1 M) was added dropwise to the above solution. The mixture was allowed to react for 5 hrs under constant stirring at ~0^0C so that the pyrrole fully polymerizes. The obtained solution was gently stirred for 24 hrs. A homogeneous black coloured solution was obtained. Another two different samples were prepared following the same procedure using two different concentrations of gold nanoparticles. Samples were labeled as S_0 (PVA-PPy), S_1 (PVA-PPy + 50 mL 0.5 mM Au NP), S_2 (PVA-PPy + 100 mL 0.5 mM Au NP) and S_3 (PVA-PPy + 150 mL 0.5 mM Au NP)

Film fabrication

Films were formed by solvent casting method, by pouring a certain small portion on to a flat polypropylene clean petri-dish. The solvent got evaporated on its own when left to dry at room temperature under vacuum. The thickness of the films was controlled by the volume of the solution poured in petri dishes. Films of approximately 40 μm were prepared. The dried black coloured nanocomposite free standing films were peeled off from Petri dish. All the films were stored in a vacuum desiccator for further investigation.

Instruments and Analysis

UV-Visible absorption spectrum of gold nanoparticles was recorded over the wave length range of 200-800 nm using UV-Visible spectrophotometer UV-EQ-825 (Equiptronics). Scanning electron microscope (SEM) images of gold nanoparticles and PVA-PPy-Au NCs were taken on FEI Quanta 250, operated at 10 kV. Morphology was assessed with a transmission electron microscope Philips TEM CM200 operating at a voltage of 200 kV. Fourier Transform Infrared (FTIR) spectra of the samples were recorded on a Perkin-Elmer FTIR (Model Frontier) in the range of 400–4000 cm^{-1}. The X-ray diffraction (XRD) patterns were recorded on BRUKER D8 Discover with Cu Kα radiation ($\lambda = 0.154056$ nm) in the range of $2\theta = 20^0$ to 80^0. The thermo gravimetric analysis of the nanocomposite was carried out on Mettler Toledo, star system.

RESULTS AND DISCUSSION

UV-Vis Spectroscopy

Gold nanoparticles interaction with light is dependent on their nanometer-sized dimensions. Au NPs exhibit an optical feature known as surface plasmon resonance, which is responsible for the distinctive ruby red colour of colloidal gold. Plasmon resonance of the electrons in the conduction bands of gold nanoparticles results in a strong absorbance band in the visible region[31], which can be measured by UV-Vis spectroscopy. Fig. 3 exhibits the UV–Vis spectrum of colloidal solution of Au NPs. The appearance of a plasmon peak at 524 nm confirms the formation of Au NPs[32]. TEM and SEM images confirmed the size of nanoparticles.

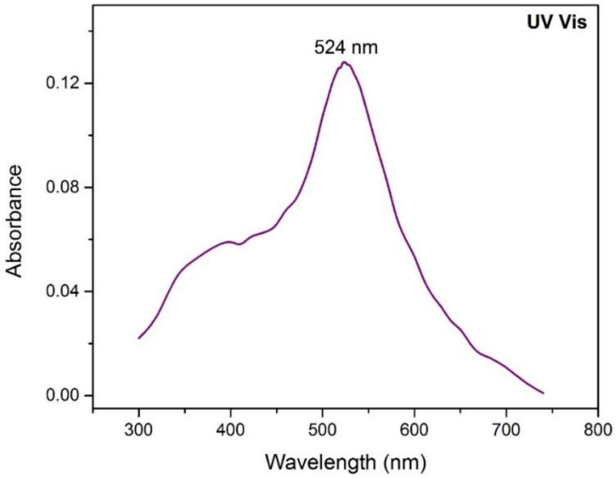
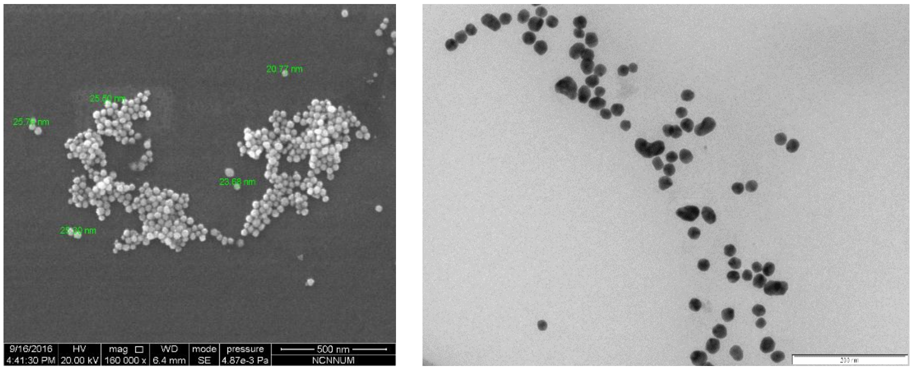


Fig. 3. UV–vis absorption spectra of Au colloidal solution

Morphology (SEM and TEM analysis)

Gold Nano particles

The morphological features of the bare gold nanoparticles prepared by citrate-induced reduction method are studied by SEM and TEM. The obtained micrograph of pure Au nanoparticles is shown in Fig. 4 make it very clear that nanoparticles are highly uniform in size, uniformly dispersed. The size of Au NPs was measured to be in the range of about 20-25 nm with spherical shape.

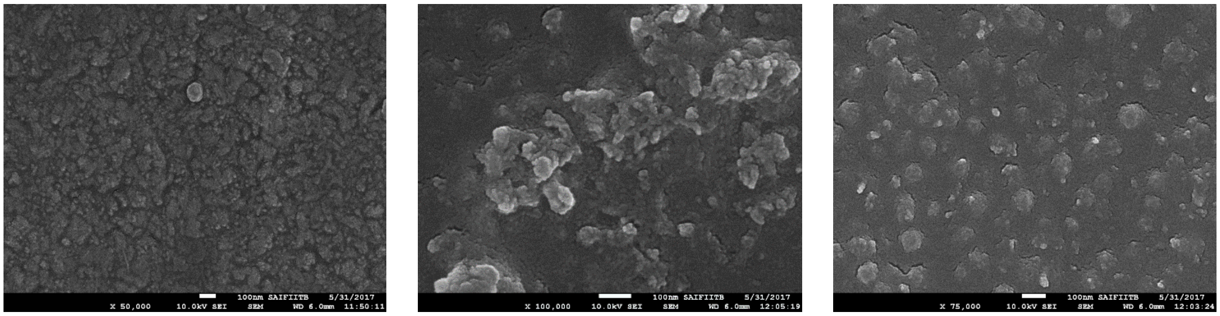


(a) **(b)**

Fig. 4. (a) SEM (b) TEM images of gold nanoparticles

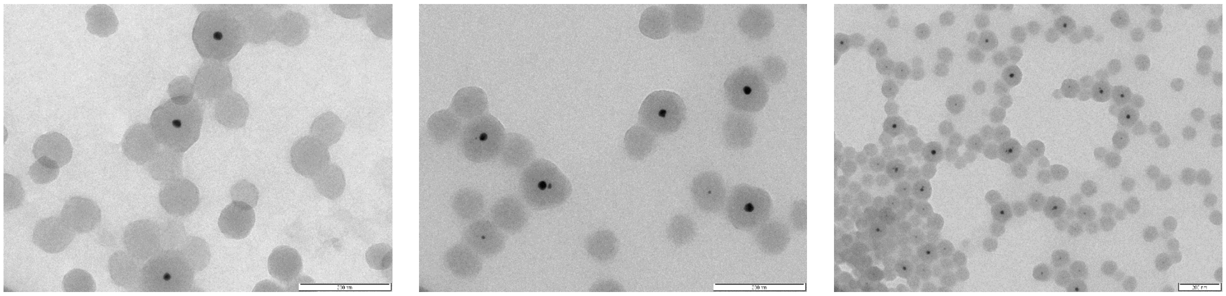
PVA-PPy-Au NC

The morphology of the prepared PVA-PPy-Au nanocomposites are studied by SEM and TEM, the obtained micrographs are shown in Fig. 5 and 6. The micrograph reveals the formation of conducting Au NPs distributed almost uniformly in PPy-PVA matrix composite film. These images clearly showed the porous and crystalline structure of coated nanoparticles. TEM results (Fig. 6 d-f) show the presence of nanoparticles. At lower concentration of Au (S_1), the small particles are widely spread across the matrix; however, as the Au concentration is increased (S_2 and S_3) agglomeration of particles is more prominent.



(a) **(b)** **(c)**

Fig. 5. SEM images of PVA-PPy-Au NC synthesized under different concentrations of gold nanoparticles (a) Sample S_1 (b) Sample S_2 (c) Sample S_3



(d) **(e)** **(f)**

Fig. 6. TEM images of PVA-PPy-Au NC synthesized under different concentrations of gold nanoparticles (a) Sample S_1 (b) Sample S_2 (c) Sample S_3

FTIR spectroscopy Result

Fig. 7 shows the FTIR spectra of prepared samples. The Spectrum of the PVA-PPy-Au-nanocomposite clearly exhibit some shifts and decreases in the peak intensities of the vibrational frequencies as compare to the characteristic absorption peaks of PPy and evidence the loading of Au NP in PVA-PPy matrix. The bands appear in the region 3250 - 3400 cm^{-1} due to O-H stretching of PVA and N-H stretching of pyrrole ring[33,34] The presence of C-H stretching and CH_2 bonds in alkanes which are in the PVA structure, was confirmed with the absorption peaks around 2850–3000 cm^{-1} and intense bending peaks around 1465-1480 cm^{-1}, respectively[35]. The characteristic absorption peak for polypyrrole at around 1530 and 1578 cm^{-1} can be assigned to typical polypyrrole ring vibration[36]. The shift in position of the peaks around 725-1110 cm^{-1} represent the C-H in plane and C-H out of plane deformation in polypyrrole units to higher wave numbers in the spectra, indicates an effective charge transfer between the Au and polypyrrole, as mentioned in previous reports[37].

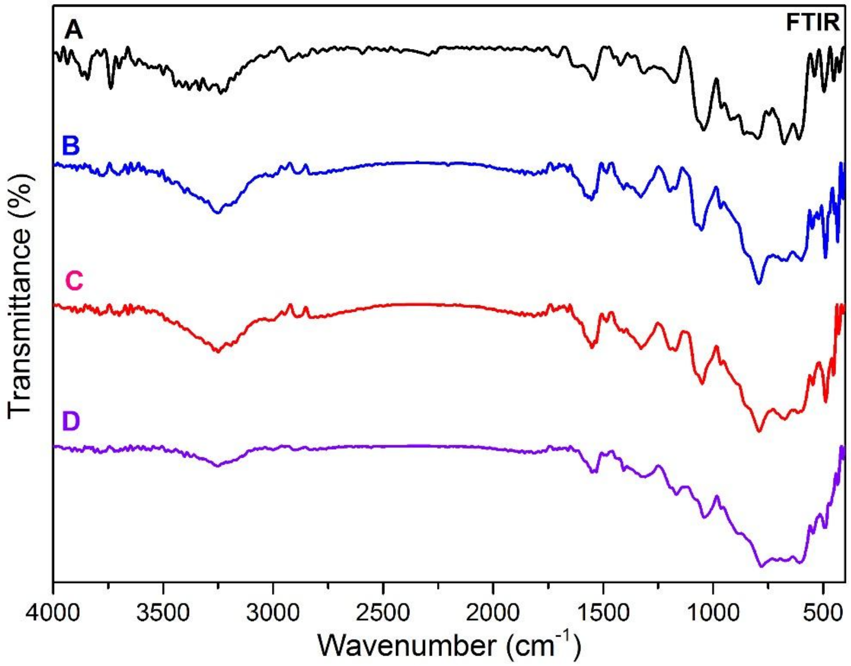


Fig. 7. FTIR spectra of PVA-PPy-Au NC synthesized under different concentrations of Au NPs. (A) Sample S_0 (B) Sample S_1 (C) Sample S_2 (D) Sample S_3

XRD Result

X-Ray diffraction patterns of synthesized PVA-PPy and PVA-PPy-Au NC films of different concentrations of Au NPs are shown in Fig. 8. Broad peak was observed at $2\theta = 19.7^0$ for PPy–PVA composite film, which is characteristic of amorphous nature[38] and indicates short range arrangement chains of polypyrrole[39]. The diffraction patterns for Au supported on PVA-PPy are observed at 2θ values of 38.22^0, 44.42^0, 64.68^0 and 77.68^0 correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystallographic planes, respectively. These peaks match well with the standard value of XRD of face centred cubic crystal structure of gold metal[40].

The average crystallite size was estimated by fitting the (1 1 1) diffraction peak (2θ = 38. 22°) width using Scherrer equation

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where D is the average size of the crystallite, K is the shape factor (equals 0.89 for unknown shape), λ is the wavelength of the X-ray radiation, β is the peak full line width at half of maximum (FWHM) in radian and θ is the diffraction peak position[41]. The average crystallite size of the gold is found to be about 25 nm, which is consistent with the result of the TEM**.**

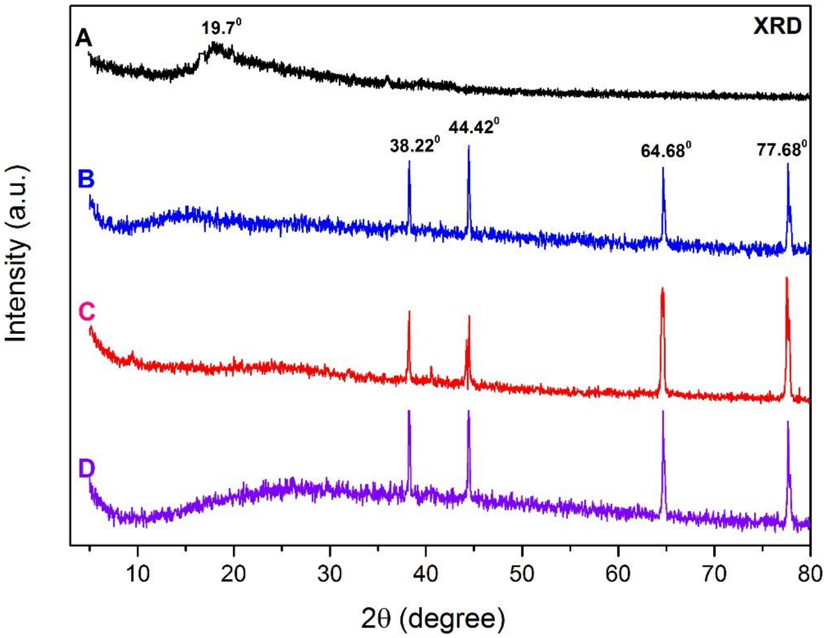


Fig. 8. XRD of PVA-PPy-Au NC synthesized under different concentrations of gold nanoparticles (A) Sample S_0 (B) Sample S_1 (C) Sample S_2 (D) Sample S_3

Thermogravimetric analysis:

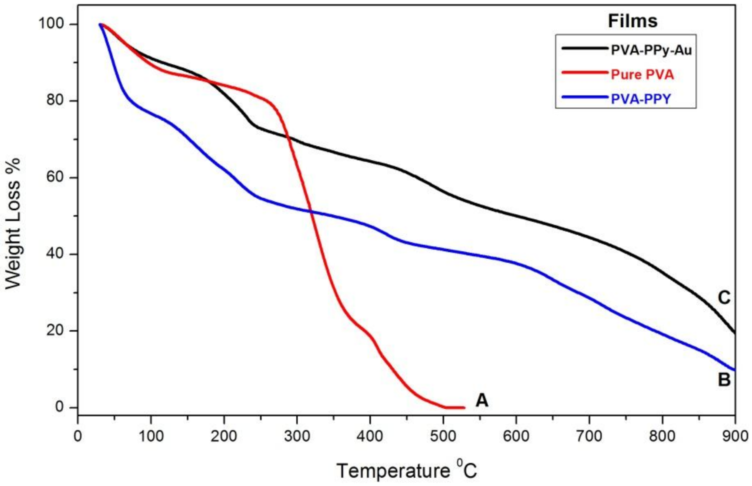


Fig. 9. Thermogravimetric analysis (TGA) curves of (A) Pure PVA (B) PVA-PPy (C) PVA-PPy-Au

Thermal degradation behavior of the synthesized films viz. Pure PVA, PVA-PPy, PVA-PPy-Au was studied by thermo gravimetric analysis (TGA). The thermal stability of prepared samples have been investigated up to a temperature 900^0C with heating rates 10^0C min^{-1} under a dynamic nitrogen flow and presented in Fig. 9. The following features are observed with the increasing temperature. For the PVA(curve A), there are three stages of weight loss, owing to the release of moisture, around 12% weight loss (first stage) within the temperature range of 45-110^0C. No considerable change in weight loss is observed from 110°C. Rapid degradation is observed within the temperature range 265^{0}C to 500^{0}C (third stage) weight loss, around 77%. This weight loss is attributed to the decomposition as well as degradation of the PVA film. The PVA-PPy (curve B) and PVA-PPy-Au nanocomposites (curve C) show a better thermal stability without rapid degradation. It is observed that the PVA-PPy and PVA-PPy-Au samples follow similar trend throughout the thermal treatment. The 20% weight loss of PVA-PPy starts around 68^{o}C while the nanocomposites show a better thermal stability with a 20% degradation temperature around 202^{o}C. On the addition of Au-NPs the decomposition stability of PPy increases by around 134^{o}C. The thermal stability of the polymer is improved due to incorporation of Au particles to polymer. The Au nanoparticles act as 'mass transport barrier' within the polymer matrix which suppresses the degradation of PVA-PPy leading to the higher decomposition temperature

CONCLUSION

In this study, we have synthesized PVA-PPy and PVA-PPy-Au NC films by the in-situ chemical oxidative polymerization method. The films were made using solvent casting method. Citrate reduction method was used for the synthesis of gold nanoparticles (Au NPs). The UV-VIS spectroscopy and SEM, TEM analysis confirmed the formation of gold nanoparticles. Confirmation of the presence of gold nanoparticles in PPy-PVA films is obtained by SEM, TEM, XRD and FTIR analysis. The improved thermal stability of the nanocomposites films has been confirmed by TGA. This novel nanocomposite films due to their unique structure can be suitable for gas sensing and antibacterial applications.

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