

Synthesis and characterization of Polyvinyl Alcohol-Polypyrrole-Silver nanocomposite polymer films with core-shell structure

Dattatray Nerkar^{1*}, Madhav Rajwade¹, Suryakant Jaware¹, Milind Jog²

¹Sathaye College, Dixit Road, Vile Parle (East), Mumbai 400057, India

²Kirti M. Doongursee College, Dadar (West), Mumbai 400028, India

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Abstract

The present paper describes the preparation and characterization of Polyvinyl Alcohol-Polypyrrole-Silver Nanocomposite (PVA-PPy-Ag NC) films. The prepared films were conducting, freestanding, flexible, and robust. Silver nanoparticles (Ag NPs) were synthesized from an aqueous solution of silver nitrate using trisodium citrate as a reductant. The casting solution for the films was prepared by in-situ chemical oxidative polymerization of pyrrole. This was done in the presence of Polyvinyl Alcohol and suspension of pre-synthesized silver nanoparticles. The absorption band at 424 nm in UV-Visible Spectroscopy of silver nanoparticles confirmed the formation of Ag nanoparticles. Scanning Electron Microscopy (SEM) studies revealed that spherical Ag NPs were produced with an average size of ~ 25 nm. The morphological analysis of the synthesized PVA-PPy-Ag nanocomposite films was carried out using Transmission Electron Microscopy (TEM). It was observed in the TEM images that Ag nanoparticles were well dispersed and conjugated in the PVA-PPy matrix. The structure of the produced films was studied by Fourier transform infrared (FTIR) Spectroscopy and X-Ray Diffraction (XRD). X-ray diffraction analysis exhibited the crystalline nature of the silver nanoparticles with a face-centered cubic (*fcc*) structure. The synthesized PVA-PPy-Ag nanocomposite films can be further utilized as potential material for the fabrication of gas sensors.

Keywords: Freestanding Polymer Films; Nanocomposites; Polypyrrole; PVA; Silver Nanoparticles.

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INTRODUCTION

Composed of two or more phases of chemical constituents, nanocomposites are the materials in which at least one of the materials is chemically or structurally in the nanometric dimension. Due to a growing range of applications and potential uses of these materials, there has been a surge in the interest and development of inorganic/organic composite in recent years [1, 2]. Among these materials, a prevalent class is the one which is composed of part conducting polymers and part noble metal. Conducting polymers have been an attractive class of materials in nanoscience and nanotechnology because of their highly

π -conjugated polymeric chains, unique electrical properties, and controllable chemical as well as electrochemical properties. The polymeric host materials are often desired for device fabrication due to their easy processing and ability to distribute the nanoparticles within the matrix [3, 4].

Among the known conducting polymers, polypyrrole (PPy) has been extensively studied because of its high conductivity, stability, mechanical properties, and high flexibility in preparation [5, 6]. PPy also has the advantage of numerous applications ranging from biosensors, sensors, microactuators, polymeric batteries, anti-electrostatic coatings, electronic devices, functional electrodes, electrochromic devices,

* Corresponding Author Email:

dattatray.nerkar@sathayecollege.edu.in

optical switching devices, and so on [6, 7]. On the other hand, metal nanoparticles, particularly silver, gold, platinum, and copper, have been noted for a focus of great interest because of their unique optical, electronic and catalytic properties and their important applications in many fields [8-10]. Conducting polymer-based nanocomposites loaded with metallic nanoparticles provide exciting systems to investigate the possibility of designing device functionality [11]. Hence, the study and synthesis of nanocomposite materials evoke interest in many researchers [12-17]. Polyvinyl Alcohol (PVA) is an important water-soluble synthetic polymer and is available in the form of powders and fibers. It is used in industries for paper coatings, as a textile sizing agent, as adhesives, and even in eye drops [18]. The aforementioned reasons make the PPy and PVA composites intriguing to study. Jyoti Srivastava *et al.* [19] reported the fabrication of Polyvinyl Alcohol-Polypyrrole-Silver Nanocomposite freestanding film for EMI Shielding Material in X-Band. The same was analyzed by Sowmya Sankaran *et al.* [20] in their review article.

The present work aims to synthesize freestanding flexible Polyvinyl Alcohol-Polypyrrole-Silver Nanocomposite (PVA-PPy-Ag NC) polymer films with good electrical conductivity. The films were prepared by the solution casting method. Turkevich method has been used to obtain silver colloidal suspension of silver nanoparticles (Ag NPs). The particles were synthesized via the reduction of silver nitrate (AgNO_3) by trisodium citrate. The casting solution for films of PVA-PPy-Ag nanocomposite was successfully synthesized via *in-situ* chemical oxidative polymerization of pyrrole in the presence of a colloidal suspension of Ag NPs and Polyvinyl alcohol. The silver nanoparticles were characterized by UV-Visible spectroscopy. The synthesized films were characterized by TEM, SEM, FTIR, and XRD.

EXPERIMENTAL TECHNIQUES

Materials and Reagents

The monomer pyrrole was obtained from Spectrochem Pvt. Ltd. Mumbai (India). Pyrrole was double distilled and stored in a refrigerator. Ferric Chloride (anhydrous), trisodium citrate and Polyvinyl alcohol (PVA) were procured from S. D. Fine Chem. Ltd., Mumbai. The degree of hydrolysis of PVA powder was 86-89 % and M.W. was 85000 - 124000. Silver Nitrate was obtained from

Research Lab Fine Chem. Industries, Mumbai. These chemicals were of AR grade and were used without further purification. Deionized water was used for synthesis.

Preparation of PVA solution

The aqueous solution of polyvinyl alcohol (4% weight to volume) was prepared by dissolving PVA powder into deionized water. This mixture was then stirred vigorously at 70 °C for 3 hours with a magnetic stirrer on a hot plate which was then left to cool until it achieved room temperature. The completed polyvinyl alcohol solution was clear, nearly colorless, and rather viscous.

Preparation of Silver (Ag) nanoparticles

The silver colloid was prepared by using the Turkevich method. This experimental method has been reported in our previous paper [21]. In a typical procedure, silver nitrate is dissolved in deionized water to give a solution of 1 mM. Further, 500 ml of 1 mM silver nitrate solution is heated up to boiling temperature. 50 mL of 10 mM trisodium citrate is added dropwise to this solution, at about 1 drop per second. Gradually, the color of the solution turns golden yellow, indicating the formation of Ag NPs [22-25].

Synthesis of PVA-PPy-Ag Nanocomposites

The PVA-PPy-Ag Nanocomposite was synthesized by *in-situ* chemical oxidative polymerization of pyrrole in the presence of polyvinyl alcohol and a colloidal solution of silver nanoparticles. The aqueous solution of PVA and silver nanoparticles suspension was stirred with a magnetic stirrer (in an ice bath) for ten minutes. Freshly distilled pyrrole was then added dropwise to this solution. The mixture was stirred for half an hour in an ice bath. The pre-cooled aqueous solution of oxidant ferric chloride (1 M) was added slowly to the above solution for polymerization of pyrrole. The mixture was allowed to react for three hours under constant stirring (in an ice bath) so that the pyrrole was fully polymerized. This composite solution was gently stirred for another 24 hours. A homogeneous black colored solution was obtained.

Film fabrication

Films of this solution were prepared by the solvent casting method. A small portion of this solution was poured on to a flat glass petri dish

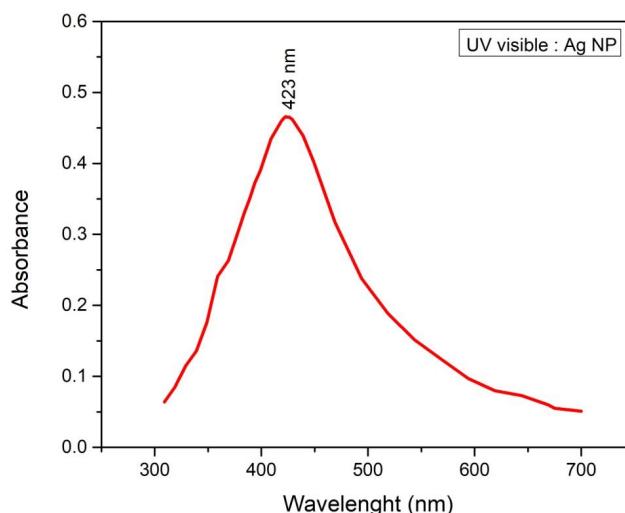


Fig. 1. UV-Vis absorption spectra of the colloid solution of Ag nanoparticles.

or polypropylene surface. The thickness of the film was controlled by the volume of the solution added. 5-6 ml of the stock solution was poured on to the petri dish each time to ensure that a film of ~30 to 40 micrometers thickness would be produced. The solvent evaporated when it was left to dry at room temperature. The dried nanocomposite films were peeled off from the petri dish or the polypropylene surface. The resulting composite films were black. All the films were preserved in a vacuum desiccator for further investigation.

Instruments and Analysis

UV- spectrophotometer UV-EQ-825 (Equiptronics) was utilized for recording the absorption spectrum of silver nanoparticles over the wavelength range of 200-800 nm. SEM images of silver nanoparticles and nanocomposite films were taken on JEOL, JSM-7600F, operated at an accelerating voltage of 10 kV. The morphology of nanocomposite films was assessed with a TEM JEM-2100F with 100 kV of accelerating voltage. The diffraction ring patterns (SAED) were examined in its HRTEM mode. Fourier transform infrared spectra (FTIR, Perkin-Elmer, Frontier) were obtained in the range of 400–4000 cm^{-1} . X-ray diffraction experiments were performed on Panalytical X'Pert Philips over the range of $2\theta = 5$ to 800. (Cu-K α radiation as X-ray source, generator voltage 40kV, tube current 30mA, $\lambda = 1.540598 \text{ \AA}$, step size $2\theta = 0.04^\circ$).

RESULTS AND DISCUSSION

UV-Vis Spectroscopy of Ag nanoparticles

UV-visible spectroscopy is the most widely used technique for the structural characterization of silver nanoparticles. The UV-visible absorption spectrum of the colloidal silver nanoparticles (Ag NPs) is shown in Fig. 1. The characteristic yellow color of the colloidal silver nanoparticles is due to a phenomenon known as plasmon absorbance [26, 27]. Here we observe broad surface plasmon absorption with a maximum of around 424 nm, which confirms the formation of silver nanoparticles [28]. UV-Vis spectroscopy was used to monitor the kinetics of nanoparticles synthesis; their size and morphology were confirmed by transmission electron microscopy (TEM). The color of the solution gives an approximate idea of the particle size [29]. To obtain a stable yellow colloidal silver solution, reaction conditions such as the stirring time, temperature, and the relative quantities of reagents must be carefully controlled. If the parameters are not controlled properly, aggregation begins. We observe that the yellow solution first turns a darker yellow, then wine red and eventually grayish, after which the colloid breaks down and particles settle out. These transitions are shown in Fig. 2 (a, b and c).

TEM analysis PVA-PPy-Ag nanocomposite films

Fig. 3 shows the TEM micrographs of the PVA-PPy-Ag nano-composites films with different magnification and selected-area electron



Fig. 2: The distinctive color of different sized silver Colloidal nanoparticles (a) yellow sol (b) darker yellow sol and (c) wine red sol.

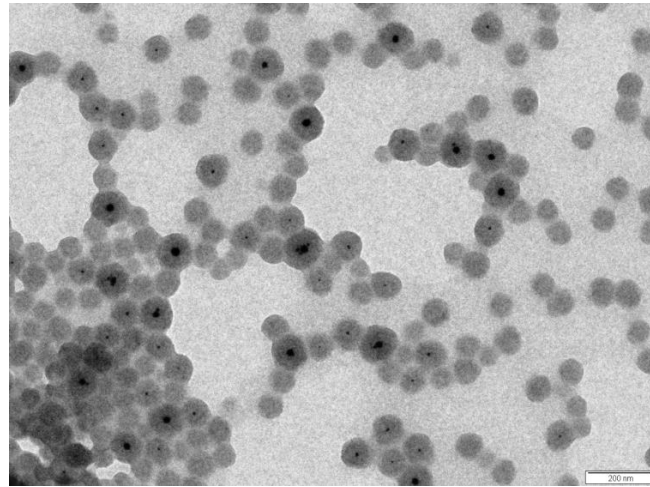
diffraction (SAED) patterns. Fig. 3(a) and (b) shows the small black particles are incorporated into the PVA-PPy matrix core-shell structure. The silver nanoparticles seem to be well conjugated in the PVA-PPy matrix. The present method produced spherical silver nanoparticles, as can be seen from Fig. 3(b) [30]. The TEM features reveal that Ag nanoparticles formed are not uniform. This is probably due to the aggregation of smaller particles or the clustering of silver nanoparticles. Moreover, the Ag nanoparticles have a little aggregation in the polypyrrole particles [31]. Fig. 3(c) shows the SAED pattern. The Electron diffraction pattern shows characteristic concentric rings as bright spots, which is associated with the crystalline nature of silver. The diffraction rings could be indexed based on the face-centered cubic (*fcc*) structure of silver. We observe that four rings arise due to reflections from (111), (200), (220), and (311) lattice planes of the face-centered cubic (*fcc*) silver nanoparticles [32].

SEM analysis of Silver (Ag) nanoparticles and PVA-PPy-Ag nanocomposite films

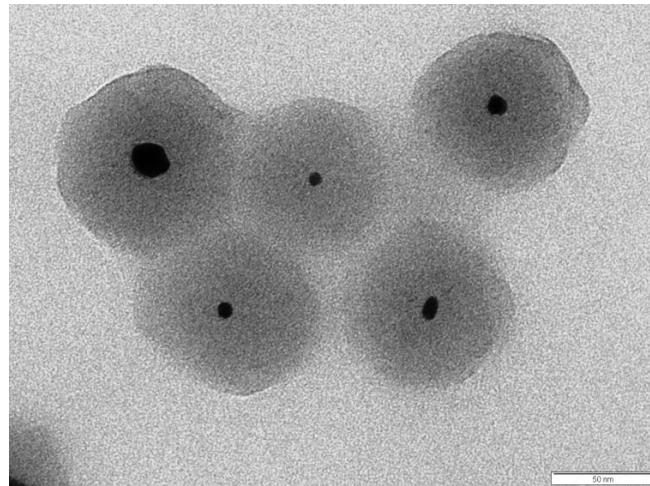
Fig. 4(a) shows the SEM image of pure silver nanoparticles. Spherical Ag NPs were produced with an average size of ~ 25 nm. Fig. 4 (b and c) shows SEM images of the PVA-PPy-Ag nanocomposite films. These micrographs prove that silver nanoparticles are distributed uniformly in PPy-PVA matrix composite. These images exhibit the porous structure of the nanocomposite films. For chemiresistive gas sensing applications, porous morphology is preferred as it promotes the adsorption of gas molecules [33, 34].

FTIR Spectroscopy Result

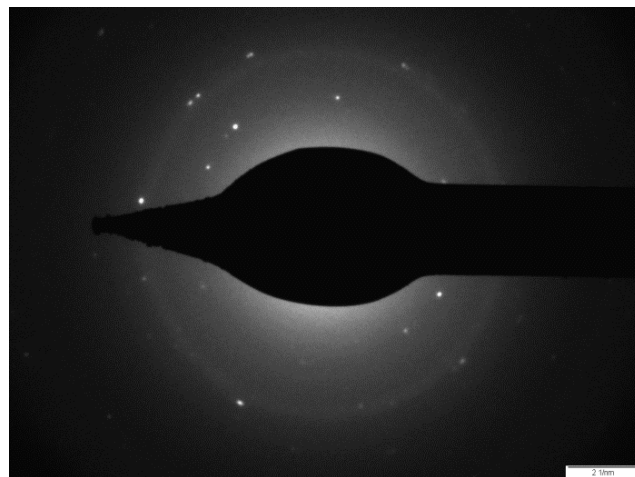
Fig. 5 shows FTIR spectra of (a) Polyvinyl Alcohol, (b) Polypyrrole oxidized by FeCl_3 , (c) Silver nanoparticles synthesized using trisodium citrate as a reductant and (d) PVA-PPy-Ag nanocomposite films. The characteristic bands for PVA were observed (Fig.5, curve a) at 3342 cm^{-1} (OH stretching), 2940 cm^{-1} (CH_2 stretching), 1735 cm^{-1} (C=O), 1433 cm^{-1} (CH_2 bending), 1096 cm^{-1} (C=O stretching), 919 cm^{-1} (CH_2 rocking) [35, 36]. The peak positions corresponding to most characteristic bands of PPy and their respective assignment are (Fig.5, curve b): 3427 cm^{-1} (N-H stretching vibrations), 2914 cm^{-1} (Absorbance of CH_2 group), 1537 cm^{-1} (Ring stretching mode C=C, C-C), 1446 cm^{-1} (C-H out-plane deformation), 1299 cm^{-1} (=C-H in-plane vibration), 1167 cm^{-1} (N-C stretch bending), 1043 cm^{-1} (= C-H in-plane deformation vibration), 779 cm^{-1} (C-C out of plane ring deformation) [37-40]. Important chemical bonds in Ag NPs are (Fig.5, curve c): 3424 cm^{-1} and 2926 cm^{-1} (C-H stretching vibrations of the primary and secondary amines, respectively), 1584 cm^{-1} (C=O stretching asymmetric in COO^-), 1395 cm^{-1} (C=O stretching symmetric in COO^-), 1030 cm^{-1} [41, 42]. The FTIR study of PVA PVA-PPy-Ag nanocomposite films is shown in Fig.5, curve d. The absorption bands observed in the IR spectra of the PVA-PPy-Ag nanocomposite films are compared with the spectra of PVA, PPy and Ag NPs. It is observed that all the characteristic IR absorption bands observed in the nanocomposite film are due to PPy, PVA and Ag NPs. The presence of OH stretching, C-H stretching and CH_2 bending present in the PVA structure was confirmed



(a)

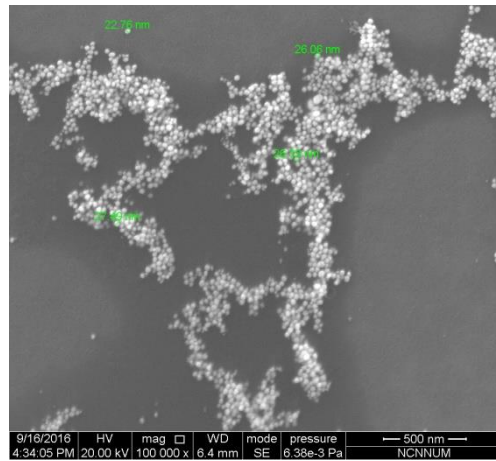


(b)

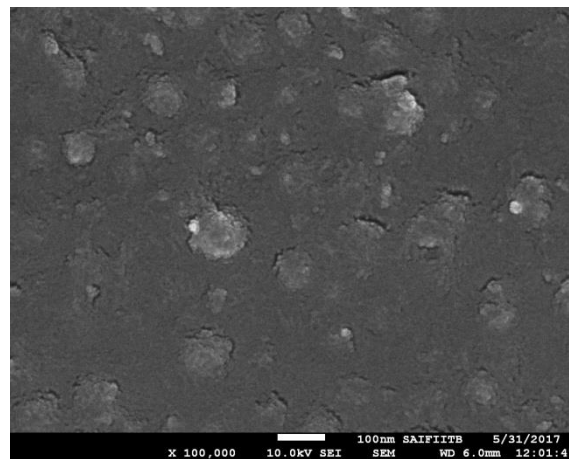


(c)

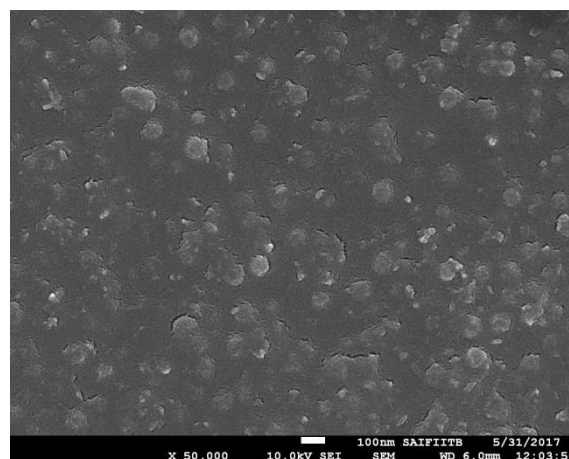
Fig. 3: TEM micrographs of the PVA-PPy-Ag films (a) with a magnification 200 nm (b) with a magnification 50 nm and (c) SAED pattern.



(a)



(b)



(c)

Fig. 4: SEM micrographs of (a) silver nanoparticles and the PVA-PPy-Ag films with a magnification (b) $\times 100,000$ (c) $\times 50,000$.

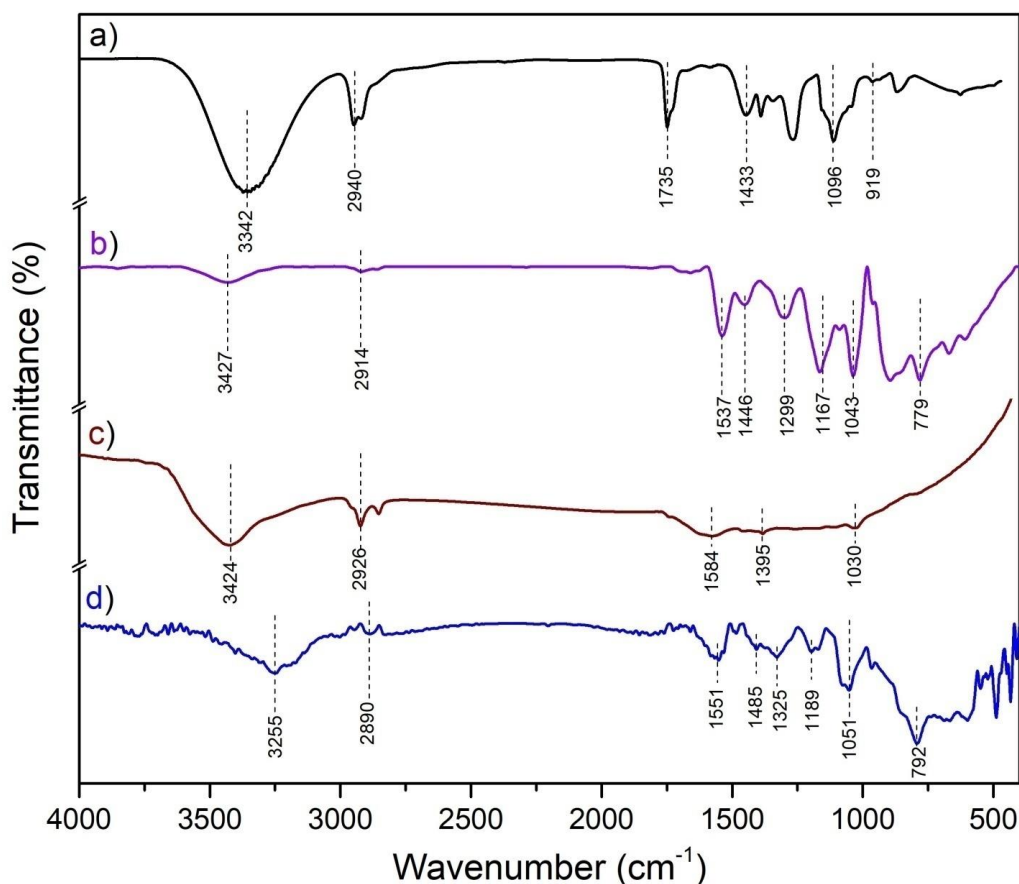


Fig. 5: FTIR spectrum of (a) PVA (b) PPy (c) Ag NPs, (d) PVA-PPy-Ag nanocomposite film.

with the absorption peaks at 3255, 2890 and 1485 cm^{-1} respectively in nanocomposite films. Nanocomposite films show peaks at 1551 and 1485 cm^{-1} , which correspond to the C-C and C=C stretching vibration in the pyrrole ring and C-H out-plane deformation respectively. The peak near 1185 cm^{-1} is assigned to the breathing vibration of the pyrrole ring. The peaks at 1051 and 792 cm^{-1} can be assigned to the =C-H in-plane deformation vibration and C-C out of plane ring deformation of pyrrole respectively. The band observed at 3255 cm^{-1} is associated with the N-H stretching vibrations in pyrrole. From the spectra, we can also find that the positions of the peaks of the nanocomposite film have a little shift to high wavenumber when compared with PVA and pure PPy. This may be attributed to the interaction of the incorporated silver on the PPy surface. This serves as evidence for the presence of Ag NPs in the composite polymer matrix. [43-46]

X-Ray Diffraction Analysis

The XRD pattern of the prepared PVA-PPy-Ag nanocomposite film is shown in Fig. 6 (a). The broad peak observed at 2θ ranges from 11° to 26° is related to the amorphous nature of polypyrrole [47]. Usually, the broad peak indicates short-range arrangement chains in polypyrrole [48]. Peaks with $2\theta = 38.22^\circ, 44.46^\circ, 64.65^\circ,$ and 77.68° , are related to (1 1 1) (2 0 0), (2 2 0) and (3 1 1) diffraction of Ag, respectively. These peaks are matched with the face-centered cubic (fcc) structure of silver (ICDD No. 04-0783) as shown in Fig. 6 (b), confirming the existence of metallic Ag in the PVA-PPy nanocomposite films [49, 50].

CONCLUSION

In the present study, PVA-PPy-Ag NC films were successfully synthesized by the in-situ chemical oxidative polymerization of pyrrole in the presence of polyvinyl alcohol and colloidal

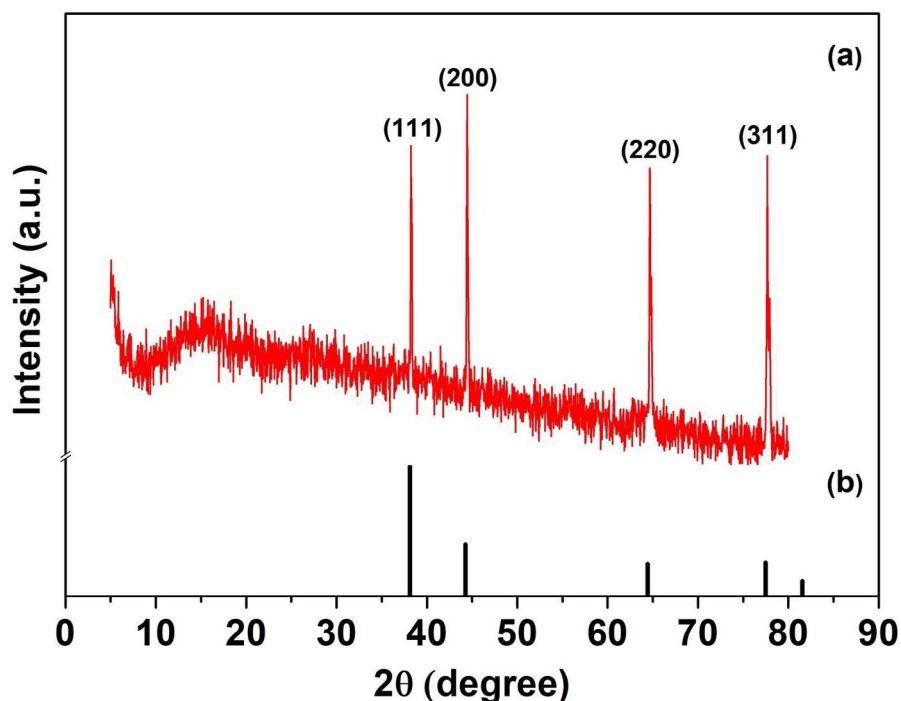


Fig. 6: (a) XRD pattern of the PVA-PPy-Ag nanocomposite film; (b) ICDD No. 04-0783.

suspension of silver nanoparticles. The films were developed by the solvent casting method. The silver nanoparticles (Ag NPs) were synthesized by the reduction of silver nitrate by trisodium citrate. The UV-VIS spectroscopy and SEM analysis confirmed the formation of silver nanoparticles. TEM, SEM, micrographs, XRD spectrum, and FTIR absorption spectroscopy confirmed the presence of silver nanoparticles in PPy-PVA films. Ag nanoparticles were in a broad size distribution from 20 to 40 nm with an average size of ~ 25 nm and were crystallized in the form of face-centered cubic (*fcc*) symmetry. Due to their unique morphological characteristics, these novel nanocomposite films could lead to gas sensors application.

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CONFLICT OF INTEREST

The authors declare that they have no competing interests.

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