

Metal nanoparticles incorporation during the photopolymerization of polypyrrole

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Abstract In this work we present a route to prepare intrinsically conducting polymer (ICPs)/Silver nanoparticles composite through the photon polymerization process. The method consists to use the transition metals ions assisted by UV light to polymerize the pyrrole monomer. At the same time that the monomer is polymerized the silver ions are reduced and the silver metal particle are produced and incorporated to the polymer matrix. The composite films were characterized by conductivity measurements, UV/vis and FTIR spectroscopy, X-ray diffraction, and scanning electronic microscopy. The morphological properties of incorporated silver nanoparticles were examined with respect to the nature of substrates, exposure time and monomer ratios. Soon after a silver nitrate solution containing Pyrrol is excited by an UV light, a black deposition appears on glass walls or other substrates, such PET (poly(ethylene terephthalate) immersed in the solution, however if the solution is set aside and protected from light, the same black films takes more than 48 h to form. The UV-visible absorption, X-ray

diffraction, infrared analysis and conductivity measurements confirm the formation of silver particles and pyrrole polymerization with composite conductivity in the order of 10^{-3} S cm^{-1} .

Introduction

Polypyrrole (PPy) belongs to a class of intrinsically conducting polymers (ICPs) and is one of the most widely studied polymers among ICPs because of its attractive inherent conductivity, redox and optical properties and its relatively simple synthesis process [1].

Although extensive studies have been published on chemical [2] and electrochemical synthesis of PPy [3], there are few reports about photopolymerization [4, 5]. In photosensitizing systems, including photopolymerization, photoinduced electron transfer plays an important role [6]. As a matter of fact ruthenium, cobalt and copper complexes have been used as photosensitizers and electron acceptors in the photopolymerization process of pyrrole [5, 7]. Using visible light the conductivity of the photopolymerized polypyrrole was found to be 3×10^{-4} S cm^{-1} a quite low value when compared to the chemical polymerization process. However, when UV light (254 nm) is used in the photopolymerization process in halogenated solvent with pyrrole and ferrocene or iron-arene salts [8], the result seems to be worst, and the reason for that is the fact that the photo generated halogen attack the growing chain, resulting in the loss of π -conjugation of the polypyrrole obtained, as a

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consequence, a low conductivity (10^{-5} S cm $^{-1}$) and low electrochemical activity were obtained. The polypyrrole was also obtained by photopolymerization without photosensitizer, the process consist to excite an acid aqueous solution of pyrrole with sunlight. The disadvantage of this method is the fact that its takes a long time to obtain the polypyrrole films (100 nm after 15 h).

The incorporation of metal nanoparticles in ICPs matrix has attracted considerably attention of the scientific community, mainly due to the possibility to develop suitable materials for electrocatalysis, chemical and microelectronic sensors [5, 7]. Usually electrochemical methods are used to prepare PPy films on electrodes, such as inert metals, carbon and semiconductor surfaces [9, 10, 11]. However, they are limited to the use of conducting substrates employed. On the other hand, using photopolymerization process, insulating substrates, such as glass or PET can be used as modified electrode. In this work we apply the recent synthesis route developed in our laboratory [12, 13], to prepare conducting polymer composites through the photopolymerization of pyrrole assisted by transition metals ions. In this process, the pyrrole monomer is polymerized and consequently the silver ions are reduced and the nano metals particles are produced.

Experimental

Materials

Pyrrole (Vetec) was distilled twice under atmospheric pressure and stored in the dark and at a low temperature prior to synthesis. Dichloromethane (Merck, p.a.), AgNO₃ (Plat-Lab, p.a.), methanol (Merck, p.a.), amorphous PET films (Rhodia Ster SA) were used as received and in some experiments treated with CH₂Cl₂ solvent. The glass substrate (boron silicate) employed was treated with “piranha solution” (3H₂SO₄:1H₂O₂) during 30 min, and afterwards washed with distilled water and dried a room temperature.

Photopolymerization proceedings

The pyrrole solution was prepared by dissolving 0.5 M of pyrrole in methanol, and 0.2 M of AgNO₃ in methanol and deionised water. Next step the solution was mixed together in the ratio 1:1 (Py:AgNO₃) and excited with a Hg lamp (UV irradiation) for times interval from 30 min to 2 h.

Characterization of PPy–AgNO₃ solution and composites

The UV–vis spectral characterization of PPy/AgNO₃ solution, before and after UV irradiation was performed using a Perkin-Elmer Spectrophotometer model Lambda-6. At regularly time interval, a small portion of the supernatants PPy/AgNO₃ solutions were taken from the experiment diluted in methanol and analyzed. The infrared spectra analyses of the PPy/Ag composite were recorded using Perkin-Elmer FT-IR 1600 spectrophotometer, where the composite analysis were done in KBr *pellets*. The sample was carefully scratched from the glass or PET support with a spatula mixed with KBr powder. Wide-angle X-ray diffraction (WAXD) patterns were recorded at a scanning rate of 2.0° s $^{-1}$ in the 2θ range from 2° to 60° using a Rigaku DMAX model 2400 X-ray diffractometer with a Cu target ($\lambda = 0.154178$ nm). The diffractometer was operated at 40 kV and 20 mA. The conductivity measurements of PET/ PPy/Ag composites was measured using a Cascade Microtech C4s-64 four probe system coupled to a Keithley 617 electrometer and a ET-2500 multimeter [14]. Scanning electron microscopy (SEM) analysis of the PPy/Ag and PET/ PPy/Ag composites was done using a JEOL microscopy Model JSM 6360, where the samples was gold-sputtered prior to measurements.

Results and discussion

The substrates used in this work to prepare the PPy/Ag composites was glass and poly (ethylene terephthalate) film. The concentration of Py and silver nitrate solution used in this work varied from 0.125 to 0.5 M and from 0.05 to 0.2 M respectively. The solutions were mixed together in a beaker containing glass or PET films and the photo polymerization process was analyzed from 30 min to 2 h. Soon as the silver nitrate solution containing pyrrole is excited by UV light, a black deposition appears on the beaker walls and in the top of the substrates immersed in the solution. It is interesting to mention here that, if the solution is set aside and protected from light, polymerization takes more than 48 h to occur.

Spectroscopic analysis

UV–vis spectroscopy

The UV–vis absorption spectrums of supernatant solutions of PPy/AgNO₃ are shown in Fig. 1 (b–d). It is

interesting to note that at the beginning, when there is no UV interaction, the solution is transparent as observed in Fig. 1a, where we can see only the solvent absorption and a shoulder around 320 nm which can be attributed to silver ions or/and to pyrrole monomer. As the UV light interacts with the solution and the interaction time increase, the color of the solution change first to blue Fig. 1b and subsequently to green Fig. 1c. The absorption spectra now presents 4 absorption peaks one at 320 nm attributed probably to silver ions and pyrrole monomer and the others at 462, 534, and 618 nm, attributed to absorption band of small silver particle, pyrrole dimer or oligomers respectively. It is interesting to note that when the polymer starts to grow on the glass walls the solution changer it color again to intense yellow as shown in Fig. 1d, where we can observe that all absorption bands decreases its intensity, remaining only the absorption at 462 nm which we attribute it to small silver particle, comparing the peak position of this band with silver particle size distribution in the literature [15], which we can conclude that the silver particles produced in this experiment is in the range of 40 nm.

FT-IR characterization

The FT-IR spectra of PPy/Ag composite in the range from 400 to 2000 cm^{-1} , is shown in Fig. 2. The spectra present strong absorbance at 1541, 1456, 1294, 1176, 1040, 964, 916 and 794 cm^{-1} . Which are characteristic of polypyrrole IR absorption modes, in agreement with literature results [16]. The IR peak at 1384 cm^{-1} is assigned to absorption band NO_3^- ion [17].

X-ray analysis

Figure 3 shows the X-ray diffraction patterns of pure PET film and PPy–Ag deposited on glass and PET films. The presence of the intense and broader peak in the range of 2θ from 10° to 30° in Fig. 3(a) can be assigned to the semi crystalline structure of PET polymer [18]. This observed effect seems to be related to extrusion process employing in the production of PET films, when not lateral stretching process is applied amorphous PET film is produced [18]. Figure 3(b) shows the reduction in the structural disorder, which are attributed to the treatment of PET film in CH_2Cl_2 solvent and photopolymerization process, indicating the presence of conductive polymer in the composite [19, 20]. The presence of silver metal particle is also

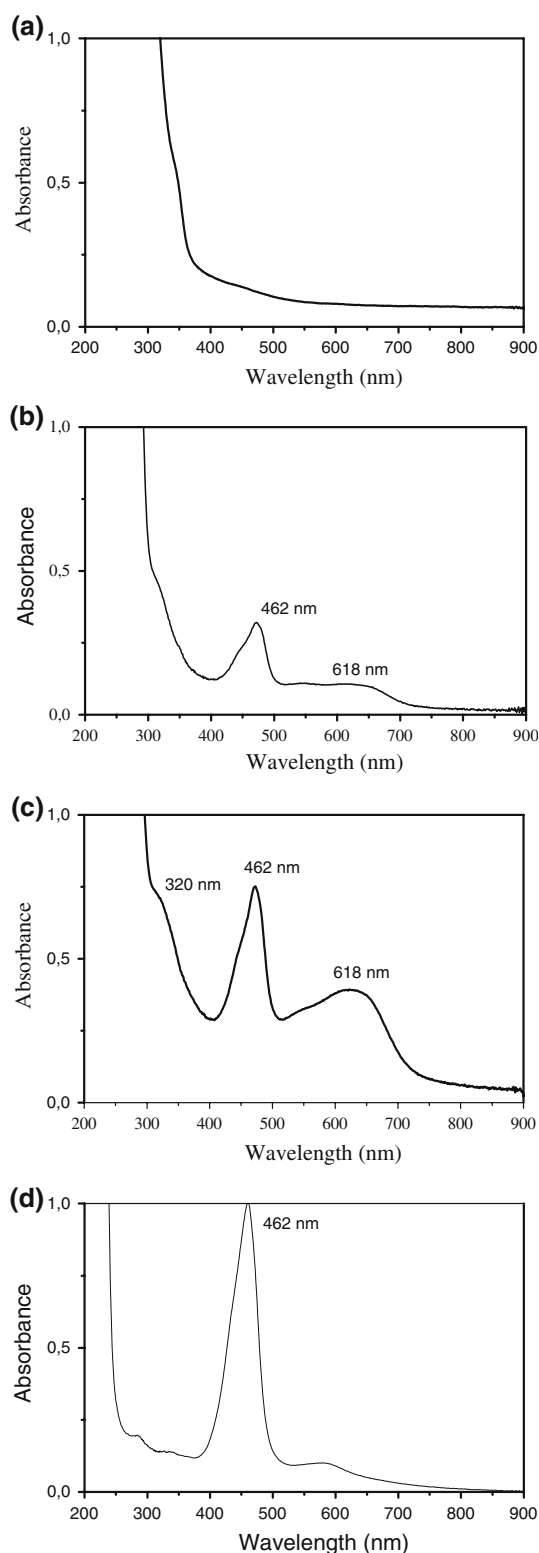


Fig. 1 UV-vis absorption spectra of Py/AgNO₃ solution, before UV irradiation (a) and after UV irradiation at different times (b) 30 min, (c) 2 h, and (d) after 1 week stocked without light

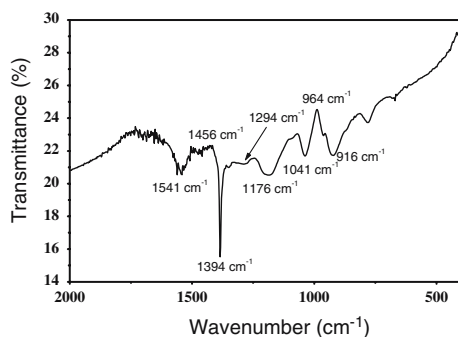


Fig. 2 Infrared spectra of PPy/Ag composite

observed in both Fig. 3(b) and (c), where the peaks at $2\theta = 38,10^\circ$ and $44,2^\circ$ is assigned to [111] and [200] planes of the silver crystalline structure [21].

Electrical conductivity characterization

The electrical conductivity of the PET/PPy/Ag composites measured with a four probe technique was found to be $10^{-3} \text{ S cm}^{-1}$, this result represent an increase in the conductivity of PET film of 11 orders of magnitude. When compared with literature results we observe that our results are consistent with the expected enhancement provided by the metal incorporation [4, 7].

Morphological characterization

Figures 4 and 5 shows the SEM images of PPy/Ag composites in PET films and glass substrate respectively. These analyses were performed in order to verify the effect of the synthesis parameter (swelling of PET substrate with CH_2Cl_2 and exposure times of the monomer solution before to UV radiation) on the composite morphology during a photopolymerized process. Figure 4 show that the morphology of polypyrrole films differs significantly from the results presented in the literature. The polymer films prepared without solvent presents a continuous globular structure while in CH_2Cl_2 solvent presents a planar sheet structure (Fig. 4a), probable due to the particle fractal grown assisted by silver particles and the solvent used, this kind of fractal structure has been already observed in the polypyrrole electrochemical synthesis [22]. For each analyzed composite, it was found that bright silver particles of the order of 40 nm are dispersed on the polymer surfaces (Fig. 4c), as confirmed by X-ray analysis, and absorption measurements, also if the polymer is left into the solution for long time, bigger silver metallic structure of the order of 100 μm starts to grow on the polymer surface as shown in Fig. 4b.

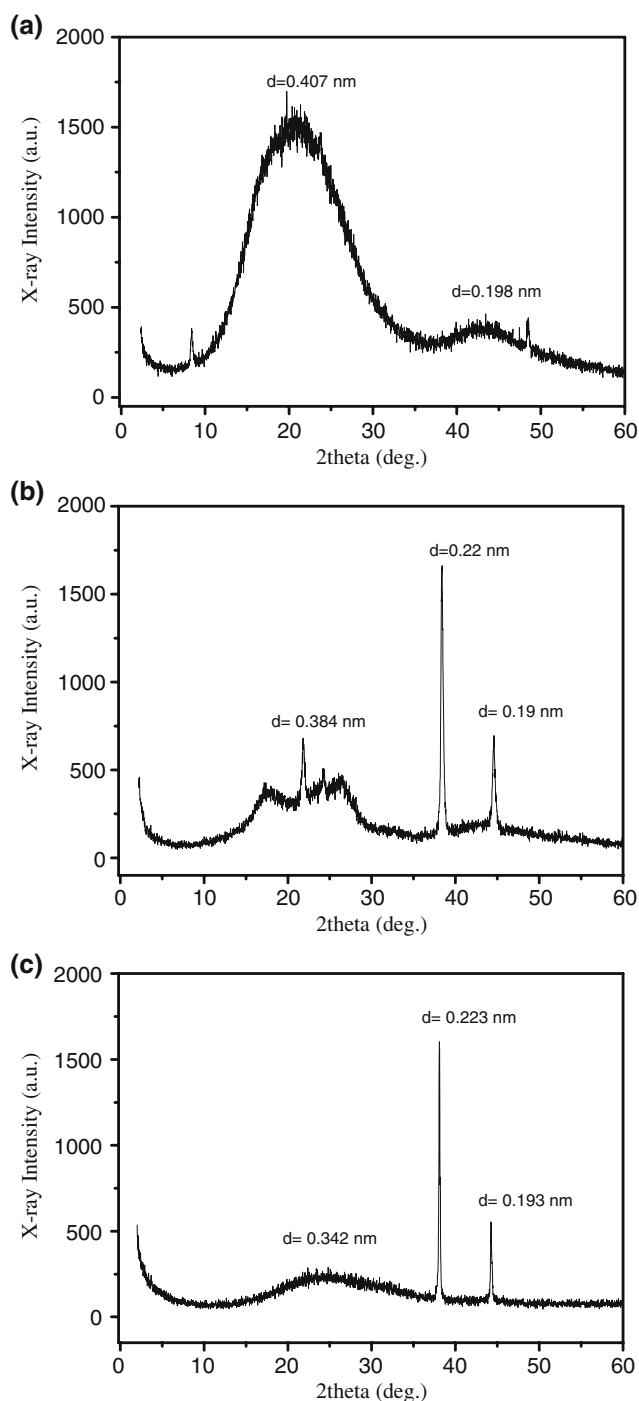


Fig. 3 X-ray diffraction pattern of pure PET film (a), PET/PPy/Ag (b) and (c) PPy/Ag deposited in glass substrate

Figure 5 shows the effect of exposure time on the morphology of the polymer grown on glass surface. As the exposure time increases, different growing patterns of polypyrrole are produced, at the beginning, Fig. 5a, we can see, globular morphology and few thin planar sheet structure which are consistent with films growth on hydrophilic surface [23], while for longer time Fig. 5c the sheet became thicker about 0,5 μm and more dominant.

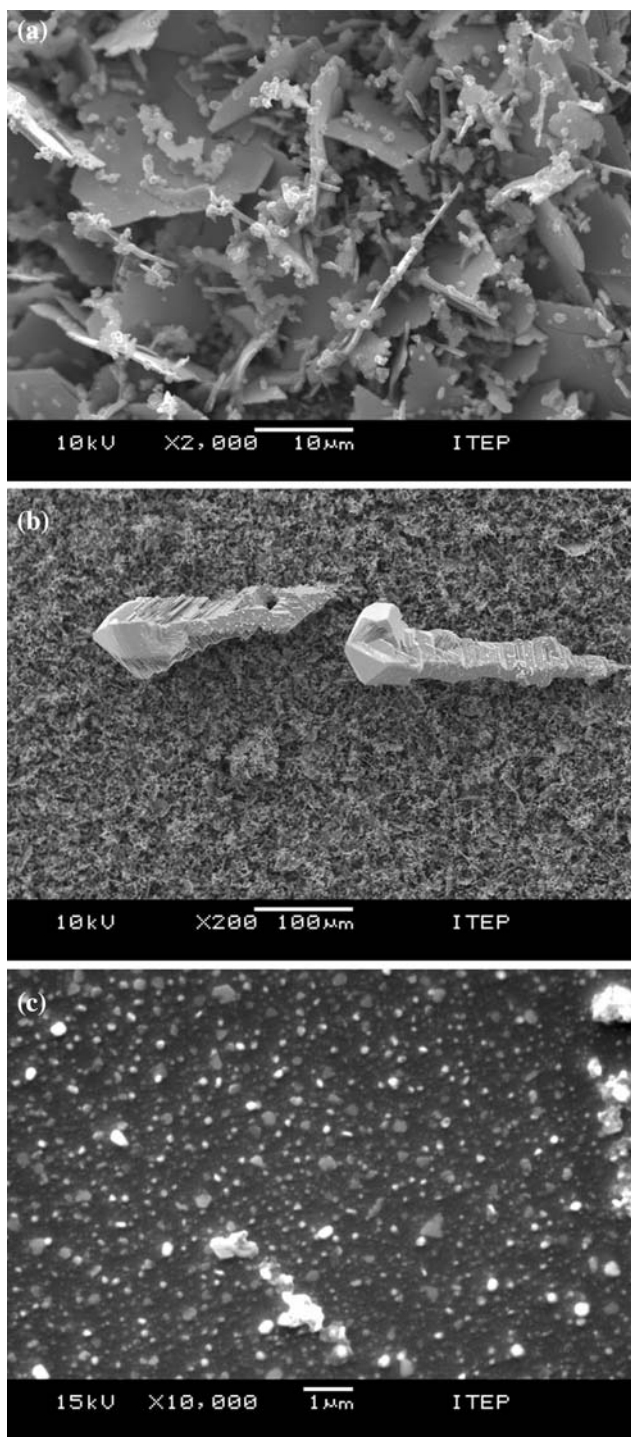


Fig. 4 SEM of polypyrrole film on amorphous PET films, treated with CH_2Cl_2 solvent (a and b), and without solvent (c)

Conclusions

We have succeeded to prepare polypyrrole onto non conducting substrate such as glass or PET films, by photopolymerization process assisted by transition metal ions. In the process the pyrrole monomer is polymer-

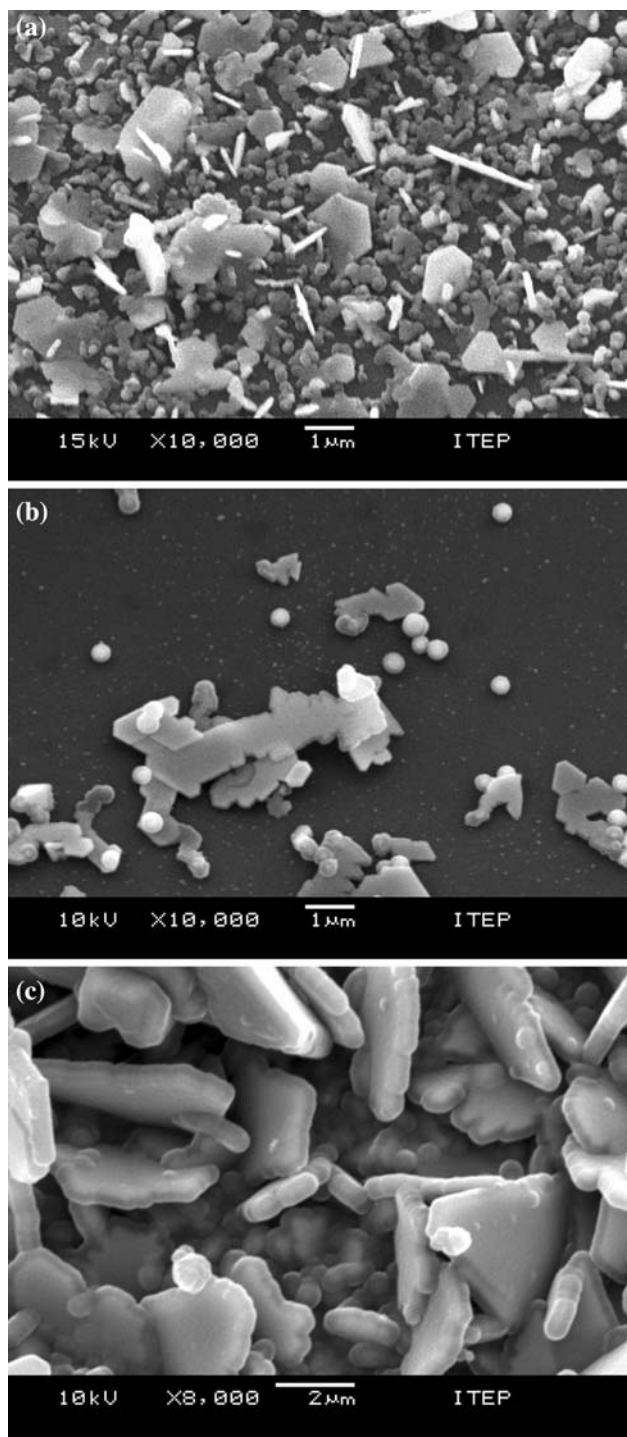


Fig. 5 SEM of polypyrrole film on glass substrate for different times of exposure of the monomer solution, (a) 24 h, (b) 48 h and (c) 72 h

ized and simultaneously the silver ions are reduced and the metal particles are produced and incorporated to the polymer matrix. The photopolymerization process using transition metal ions is a new and fast technique to prepare intrinsically conducting polymers/metal doped composites. The spectroscopic analysis, X-ray

diffraction and SEM measurements confirm the pyrrole polymerization and the formation of silver particles from nano to micrometer diameter, where the length of the particles depends on the time preparation of the sample.

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