Synthesis of ZnO Nanoparticles and Electrodeposition of Polypyrrole/ZnO Nanocomposite Film

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Zinc oxide nanoparticles (ZnO NPs) were synthesized by simple and efficient method in aqueous media from zinc nitrate without any requirement of calcinations step at high temperature. The ZnO NPs are studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Then, a hybrid material of polypyrrole (PPy)/ZnO NPs were synthesized with electropolymerization of pyrrole in an aqueous media within dispersed ZnO NPs. The particulars of PPy growth properties have been considered by continuous voltammograms. PPy and PPy/ZnO NPs microscopic images were obtained by SEM and atomic force microscopy (AFM) techniques.

1. INTRODUCTION

Nanostructured materials have received much attention because of their novel properties, which differ from those of bulk materials [1,2]. Control of dimension and morphology of materials has aroused the interest of researchers in the design of functional devices due to the optical and electronic properties of nanometer- and micrometer-sized materials, which determine their applications, can be adapted by varying their size and shape [3].

Zinc oxide (ZnO), a versatile semiconductor material, has been attracting attention because of the commercial demand for optoelectronic devices operating at blue and ultraviolet regions [4]. ZnO is a wurtzite-type semiconductor with band gap energy of 3.37 eV and it has very large excitation binding energy (60 meV) at room temperature [5]. Recently, special attention has been devoted to the morphology, as ZnO can form different nanostructures [6-8]. Thermal stability, irradiation resistance and flexibility to form different nanostructures are the advantages that expedite its potential wide

applications in photodetectors [9], surface acoustic wave devices [10], ultravioletnanolaser [11], varistors [12], solar cells [13], gas sensors [14], biosensors [15], ceramics [16], field emission [17], and nanogenerator [18].

Since the discovery of conductance in conjugated polymers, a great interest has been paid to these materials and has been extensively explored as alternative to metals or inorganic semiconductors in fabrication of optoelectronic, microelectronic and microelectrochemical devices [19-21]. Polypyrrole (PPy), one of the important conducting polymers, have potential applications in drug delivery [22, 23], sensors [24], and corrosion protection [25]. Based on its semiconductor properties PPy has been exploited as the electronic component in electronic devices, e.g., photoelectrochemical devices [26], organic light-emitting diodes [27], and rectifying devices [28]. PPy also shows physicochemical properties which impart to various applications in DNA sensors [29], actuators [30], and immunosensors [31].
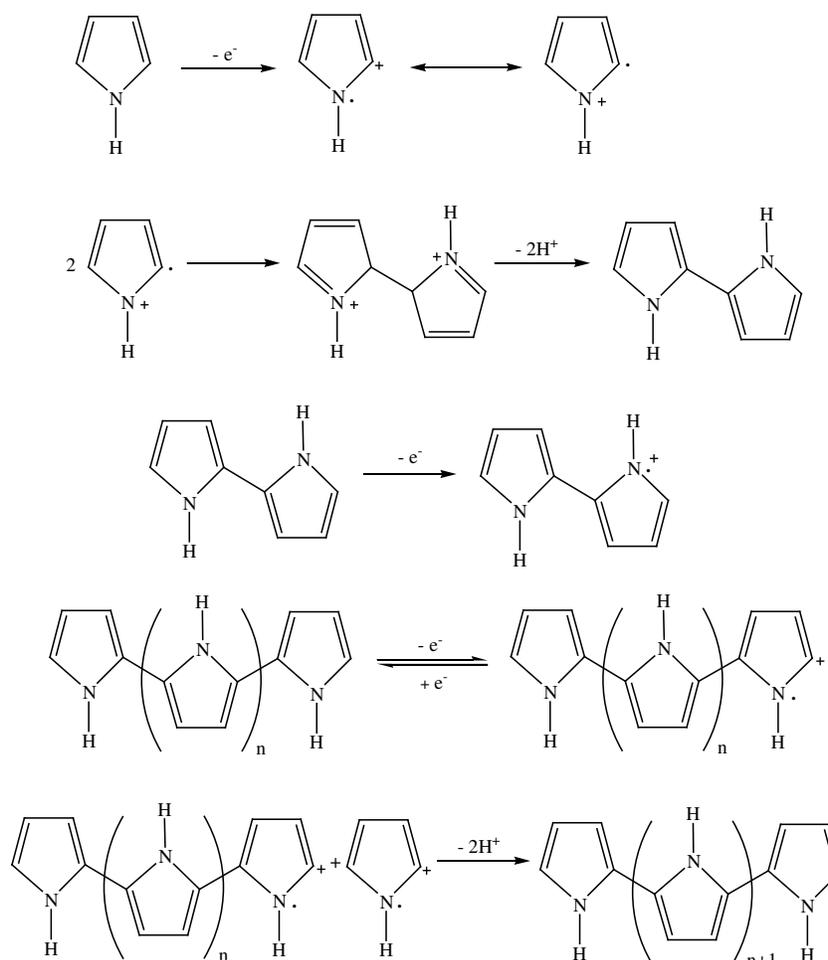
Figure 1. Mechanism of formation of PPy.

The chemistry of conducting polymers has been significant development since Diaz et al. [32] demonstrated in 1977 the depositing thin films of PPy using electro-oxidation. PPy have a linear structure and it linked only through α and α^1 positions of pyrrole ring. Pyrrole is oxidized to form radical cation which reacts with another pyrrole radical to form dimer. The dimer undergoes future oxidation and conjugation with pyrrole radicals. The procedure continues until PPy is formed (Figure 1).

Nowadays, an intensive attention has been paid to the design of nano-devices, due to the growing miniaturization of microelectronic devices. Some polymer/nanoparticle (NP) composites have already been reported in the literatures, such as polyaniline/metal oxide NP composites [33-35], PPy/TiO$_2$ [36], PPy/Ti [37], PPy/Au [38], PPy/Ag [39], PPy/Pt [40], and PPy/Pd [41].

This work focuses on the ZnO NP synthesis and formation of ZnO NP incorporated PPy film (PPy/ZnO) and characterization of the electrodeposited nanocomposite. Generally, the ZnO NPs use for the construction of conductive polymers may lead to improvements in material properties for specified applications.

2. EXPERIMENTAL PART

2.1. Materials

All chemicals used were purchased from Merck Company. Pyrrole was stored below 5 °C in the dark. Solutions were prepared by using distilled water.

2.2. Electrochemical polymerization and characterization

Aqueous electropolymerization was performed in three electrode system contained in a single compartment cell. A platinum (Pt) disk (3.14 mm^2) was used as working electrode. The counter electrode is comprised of a platinum wire. An Ag/AgCl/NaCl (3 M) electrode was used as reference electrode. All electrodes manufactured by Azar Electrode Company (Iran). An Autolab Potentiostat/Galvanostat Model PGSTAT 30 (Eco Chemie B.V., Netherlands) was used as the source of power supply. Polymerizations were carried out at ambient temperature (25 ± 2 °C). The SEM images were recorded using a ZEISS DSM 960 and TEM studies were performed use of a ZEISS CEM 902 A. Furthermore, AFM images were obtained using a DME atomic force microscope with a Dual Scope C-21 controller and DS 95-50 scanner.

2.3. Synthesis of ZnO NPs

To prepare of ZnO NPs, in a typical experiment, a 0.45 M aqueous solution of zinc nitrate (Zn(NO$_3$)$_2$.4H$_2$O) and 0.9 M aqueous solution of sodium hydroxide (NaOH) were prepared in distilled water. Then, the beaker containing NaOH solution was heated at the temperature of about 55 °C. The Zn(NO$_3$)$_2$ solution was added dropwise (slowly for 40 min) to the above heated solution under high-

speed stirring. The beaker was sealed at this condition for 2 h. The precipitated ZnO NPs was cleaned with deionized water and ethanol then dried in air atmosphere at about 60 ºC. Morphology of the sample was investigated using SEM and TEM. Parts (a) and (b) of Figure 2 show the typical SEM images of the sample. These images demonstrate that a bulk quantity of flower-like bunches exist. Each bunch is gathered of closely packed nanometer scale rods and forms radiating structures. Parts (a) and (b) of Figure 3 show TEM images of the sample. The flower-like nanostructure is observable from image of part (b). After treatment during the TEM sample preparation, flower-like nanostructures were not destroyed. This indicates that the formation of flower-like nanostructures is not due to aggregation.
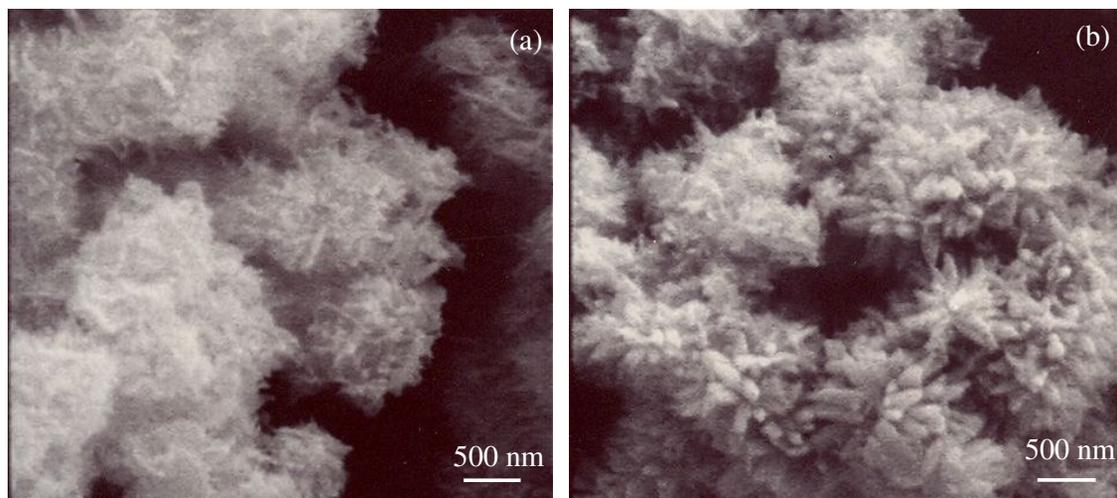
Figure 2. (a and b) SEM images of ZnO NPs.
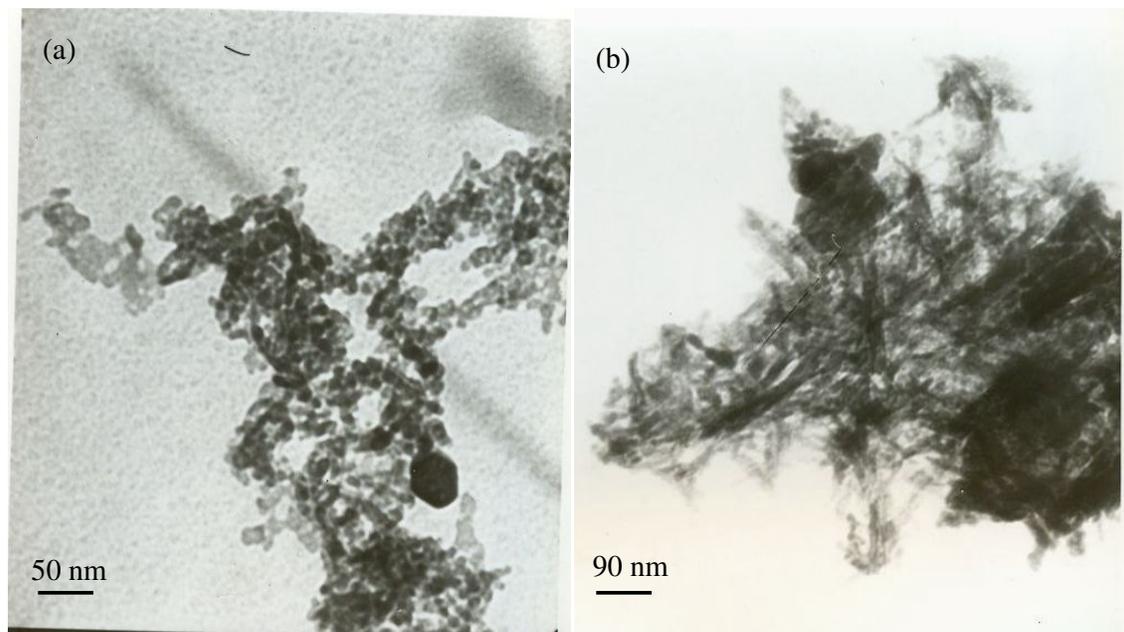
Figure 3. (a and b) TEM images of ZnO NPs.

2.4. Electropolymerization of PPy

Before electropolymerization, surface of the Pt electrode was mechanically polished successively by 1 and 0.05 µm of alumina slurry on a polishing cloth, followed by a thorough distilled water rinsing. The electrode was then successively sonicated in ethanol and distilled water to remove the adsorbed particles.

For electropolymerization of pyrrole, 50 mg ZnO NPs were added in 100 mM $NaClO_4$ containing of 30 mM pyrrole. Then PPy/ZnO NPs composite were electrochemically polymerized by applied potentials to Pt working electrode at 100 mV/s. For comparison, pure PPy was also polymerized in the same condition as mentioned above, but no ZnO NPs added in the polymerization electrolyte.

3. RESULTS AND DISCUSSION

It is well established that the supporting electrolyte nature and concentration used to synthesize a conducting polymer affecting its morphology and some of its properties. Otero *et al.* [42] reported the electropolymerization of PPy-polystyrenesulfonate on Pt substrate, the polyelectrolyte is firstly adsorbed on the Pt surface and thus delays the pyrrole oxidation process for PPy formation. However, once the pyrrole oxidation is initiated, this process is much faster for increased polyelectrolyte concentration. Demoustier-Champagne *et al.* [43] investigated the effects of various synthesis parameters (electrosynthesis method, monomer concentration, and electrolyte) on electropolymerization of pyrrole.
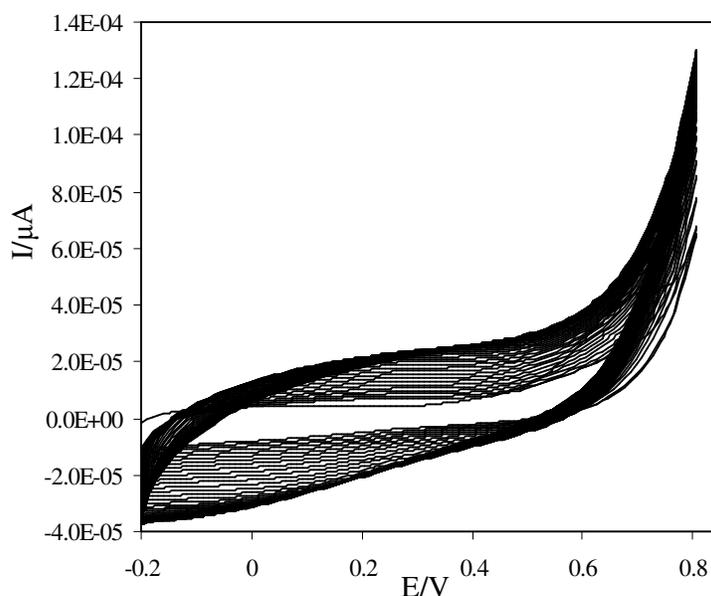
Figure 4. The growth of PPy film during continuous voltammograms (50 cycles) in a solution of 30 mM of pyrrole in 100 mM of $NaClO_4$ at 100 mV/s.
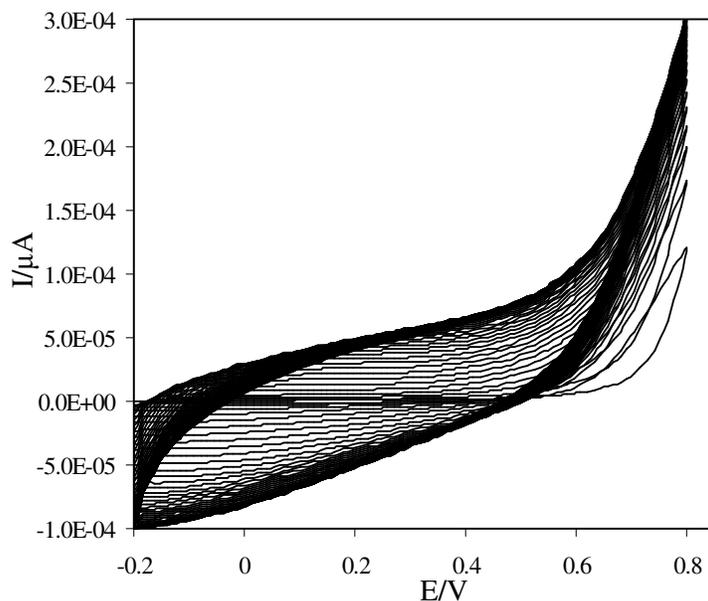
Figure 5. The growth of PPy/ZnO NPs composite film during continuous voltammograms (50 cycles) in a solution of 30 mM of pyrrole in 100 mM of NaClO₄ with ZnO NPs dispersed into the electrolyte solution at 100 mV/s.

Figure 4 shows the cyclic voltammograms (CVs) which were recorded during continuous voltammograms in a solution of 30 mM pyrrole in 100 mM NaClO₄ on a Pt substrate electrode. While, Figure 5 shows the CVs which were recorded during continuous voltammograms in a solution of 30 mM pyrrole in 100 mM NaClO₄ in the presence of ZnO NPs, dispersed in electrolyte solution. Here it is important to mention that addition of ZnO NPs into electrolyte solution affects the electropolymerization process. For this reason, a certain quantity of ZnO NPs (50 mg) was dispersed in the electrolyte solution (25 ml). After comparing Figures 4 and 5, influence of ZnO NPs in the electropolymerization of pyrrole can be observable. The consumed charge in electropolymerization of pyrrole in the presence and absence of ZnO NPs is different. The difference can be explored by the influence of ZnO NPs in electrodeposition of PPy. This phenomenon has become more evident from the parts (a) and (b) of Figure 6. This Figure shows the comparative voltammograms of PPy and PPy/ZnO NPs during the formation on Pt substrate, indicates that the addition of ZnO NPs significantly increase the recorded currents at the same applied potentials. So, the higher polymerization process takes place in the presence of ZnO NPs. It can be concluded that electropolymerization on the PPy/ZnO NPs composite initial layers is easier than the pure PPy initial layers.

To investigate the surface morphology of electrodeposited polymer films, the surface was examined by SEM and AFM techniques. Parts (a) and (b) of Figure 7 show the SEM images of PPy/ZnO NPs composite film and Part (c) of this Figure shows the SEM image of pure PPy film. Compare the morphology of PPy grown in the presence and absence of dispersed ZnO NPs in solution

shown that they are different. The nanocomposite film is accompanied by much micrometric and nanometric roughness. In fact, such structure has been produced from ZnO NPs presence during the electropolymerization process and film substrate is a result of polymer growth and special structure of ZnO NPs (Fig. 8). So, the film can be presents a large surface area. As is well known, properties of a broad range of materials and performance of different devices depend strongly on their surface characteristics.
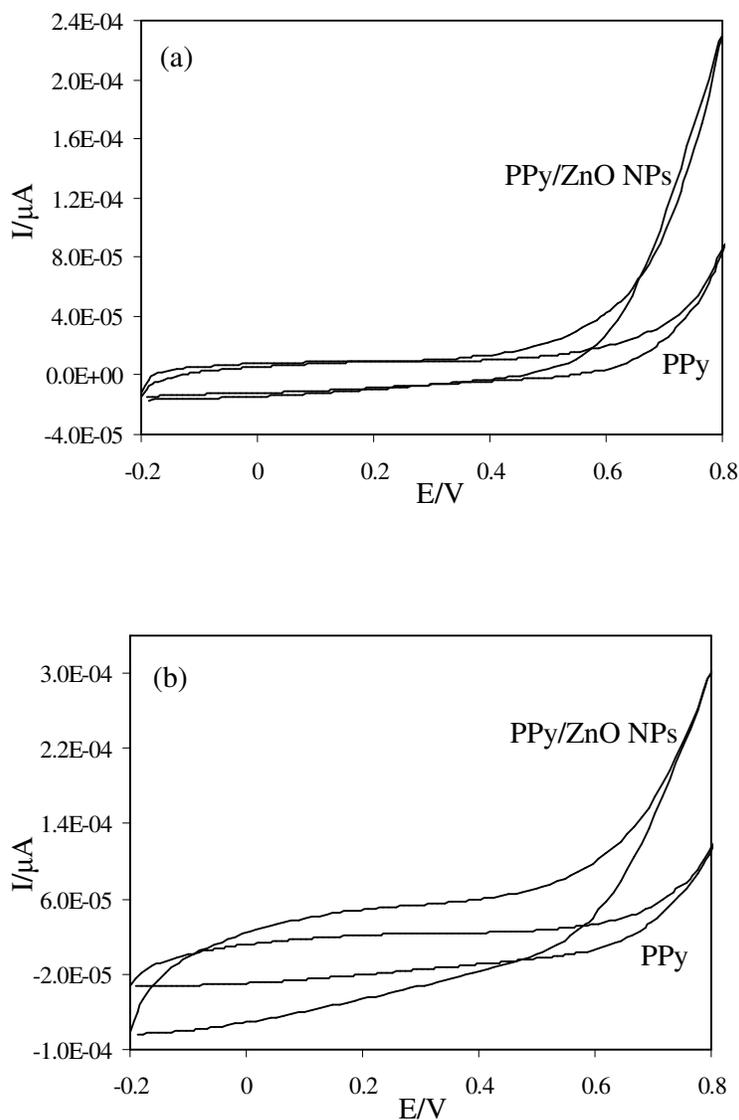
Figure 6. (a) 5th and (b) 20th comparative cyclic voltammograms during the growth of PPy and PPy/ZnO NPs films at 100 mV/s.
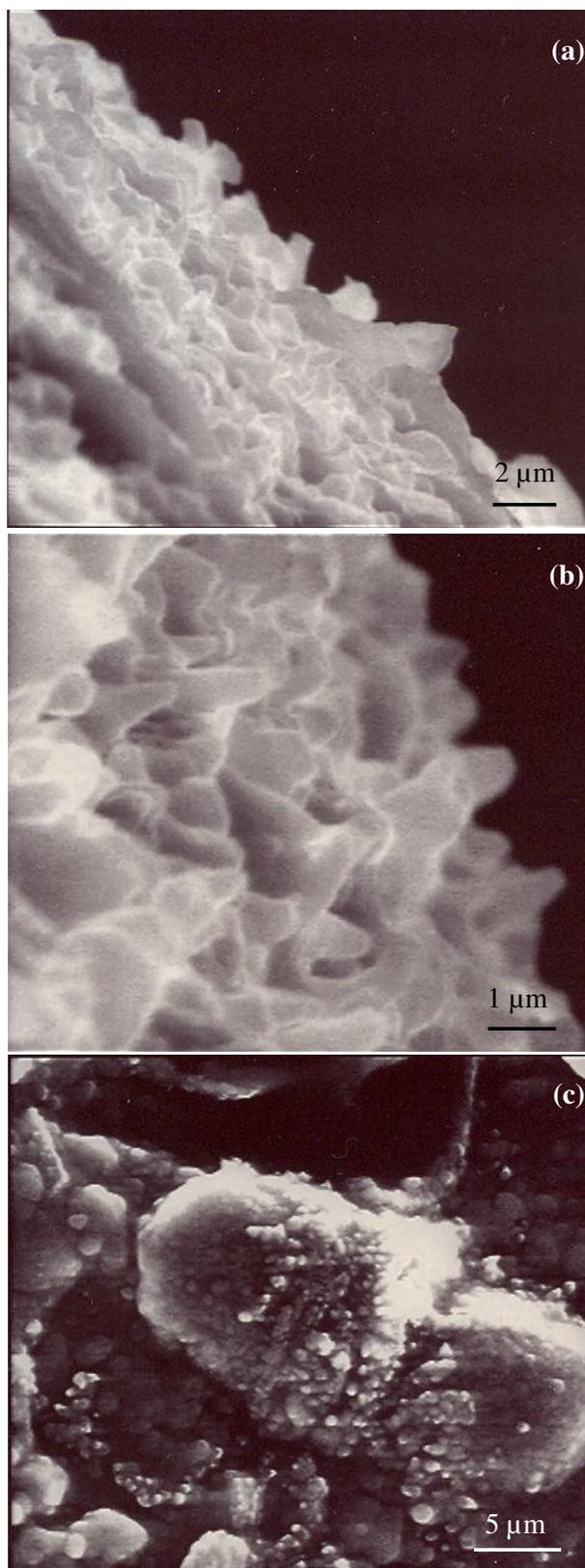
Figure 7. (a and b) SEM images of PPy/ZnO NPs composite film, (c) SEM image of pure PPy film.
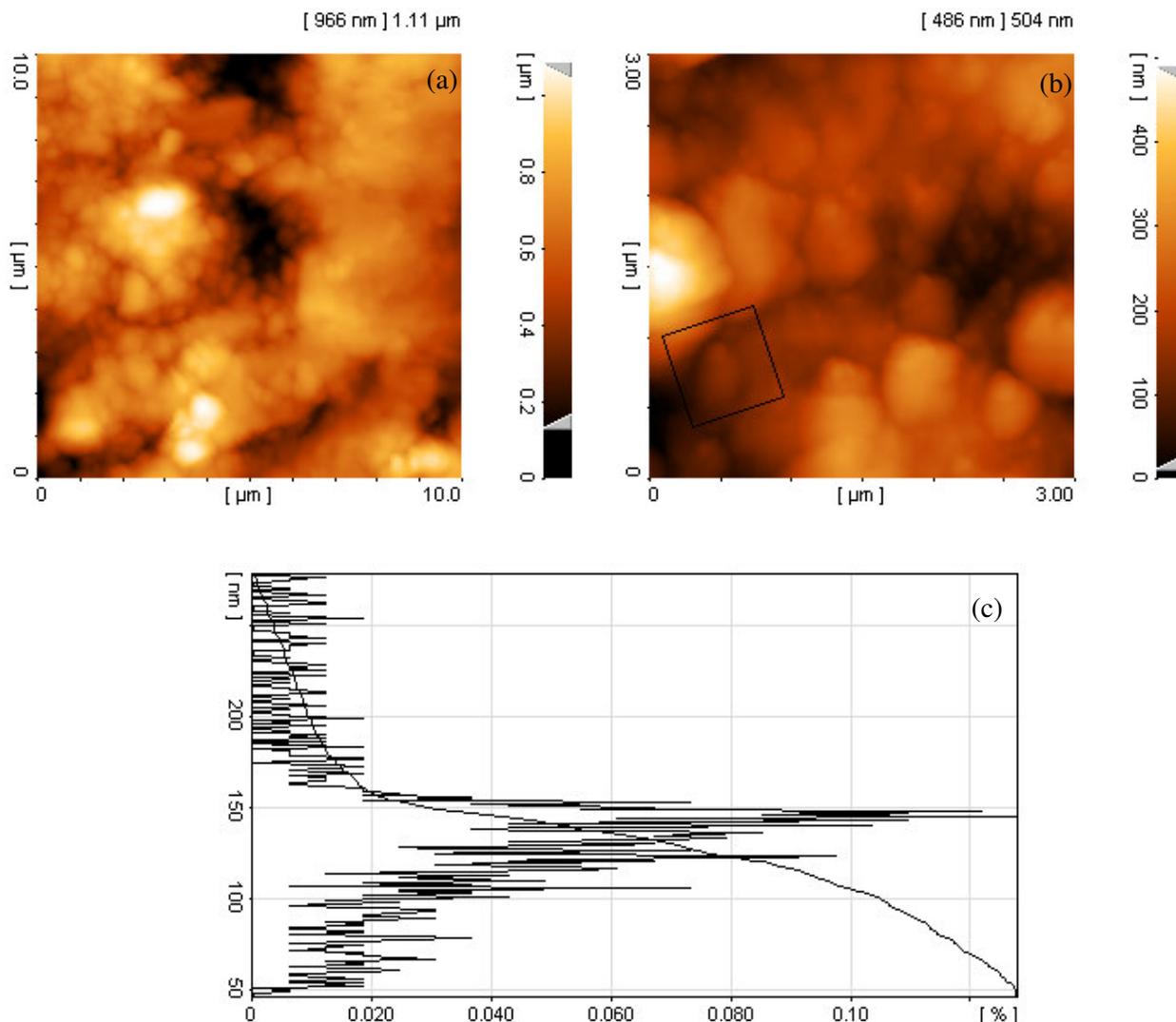
Figure 8. (a and b) AFM images of PPy/ZnO NPs composite film, (c) obtained image height distribution for selected area from part (b).

4. CONCLUSIONS

There is a great attention in processing polymer nanocomposites, both from the point of view of fundamental properties determination and the development of new applications. Synthesis of the nanocomposites of PPy with inorganic NPs is potential route to improve the performance of PPy, aiming to attain the materials with synergetic or complementary behaviors between PPy and the inorganic NPs.

PPy/ZnO NPs composite were synthesized by electropolymerization on the platinum substrate electrode. The results indicated that ZnO NPs presence can affect the electropolymerization process.

This effect happens when ZnO acts as incorporating agent. It is possible to control the composite structure using a variety of nanostructures. Since composites made from inorganic nanomaterials exhibit indispensable constancy, this design can be effectively employed for applicable functions.

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