



Synthesis and Characterization of Polypyrrole/TiO₂ Nanocomposite using Poly(vinyl alcohol) as a Surfactant

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In this study nanocomposites of polypyrrole (PPy) and TiO₂ were synthesized in aqueous media by polymerization of pyrrole using FeCl₃ as an oxidant in the presence of poly(vinyl alcohol) as a surfactant. The PPy/TiO₂ nanocomposites were characterized in terms of their particle size, morphology and chemical structure. X-Ray diffraction and fourier transform infrared spectra were used to characterize the structure of the obtained PPy/TiO₂ nanocomposites. The morphology of products was characterized by using scanning electron microscope. The results indicate that the morphology and particle size of products are dependent on the surfactant, the type and concentration of metallic oxide.

Key Words: Polypyrrole, Nanocomposite, Titanium oxide, Morphology, X-Ray diffraction.

INTRODUCTION

After the first preparation of the highly conducting polyacetylene (PA) in 1977, much effort has been devoted to the synthesis of other organic conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTh) and their applications in devices combining optical, electrochemical and conducting properties. Preparation of these polymer composites in the presence of insulating materials is useful in improving the electrical properties, morphology, stability and crystal structure of these composites which are the key factors in governing the device performance. One way of making these composites involves synthesizing the conducting polymers using chemical or electrochemical polymerization in the presence of such materials^{1,2}. These polymers possess good tunable electrical conductivity and are organic electrochromic materials with chemically active surface³⁻⁵. But they are chemically sensitive and have poor mechanical properties and thus pose a processibility problem. Thus nanocomposites formed by combining conducting polymers and oxides nanoparticles possess all the good properties of both the constituents. The properties of nanocomposite of such kind are strongly dependent on concentration of polymer. Polypyrrole, one of the conducting polymers, has received more attention in the preparation of nanocomposites due to its high stability in conducting oxidized form^{6,7}.

Polypyrrole is appealing because of its tuneable conductivity and stability in air⁸ that allow applications in electronic

displays⁹, electrode materials¹⁰, molecular electronic circuit elements¹¹, restoration of data¹², indicators of gasometers¹³ and biochemical analysis¹⁴. Different approaches have been studied to electrochemically synthesize polypyrrole¹⁵. The morphology and chemical/physical properties of the produced film particularly depend on the deposition conditions including the electrolyte nature, the deposition potential, the dopant properties and the monomer concentration. Various nanoparticles could be incorporated in conductive polymers to improve their conductivity and stability¹⁶⁻¹⁹. In this study polypyrrole/TiO₂ nanocomposite was prepared using poly(vinyl alcohol) as a surfactant.

EXPERIMENTAL

A magnetic mixer model MK20, digital scale model FR 200, scanning electron microscope (SEM) model XL30, X-ray diffraction and fourier transform infrared (FTIR) spectrometer model Shimadzu 4100 were employed.

Materials used in this work were pyrrole ($d = 0.97$ g/mL), poly(vinyl alcohol), $M_w = 72000$, titanium dioxide and ferric chloride, from Merck. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Pyrrole monomer was purified by simple distillation.

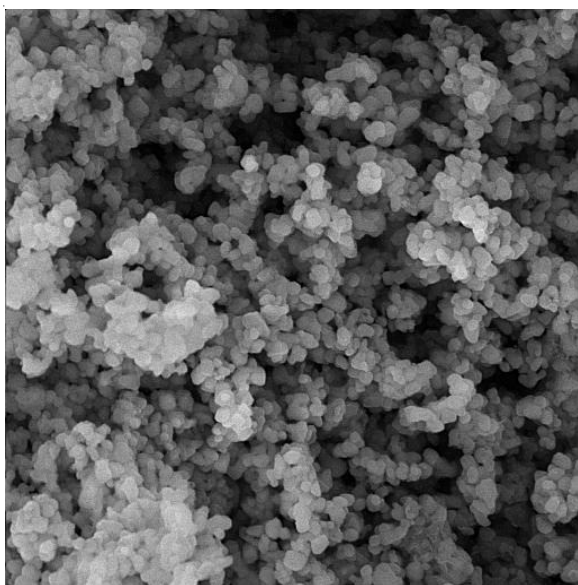
Nanocomposite preparation: The reaction was carried out in an aqueous media at room temperature for 5 h. In a typical experiment 1 mL of pyrrole monomer was added to a stirred aqueous solution (100 mL) containing 5.4 g of FeCl₃,

1 g of titanium oxide and 0.1 g of poly(vinyl alcohol). After 5 h the polymer was collected by filtration and in order to separate the oligomers and impurities, the product was washed several times in succession with deionized water. It was then dried at room temperature.

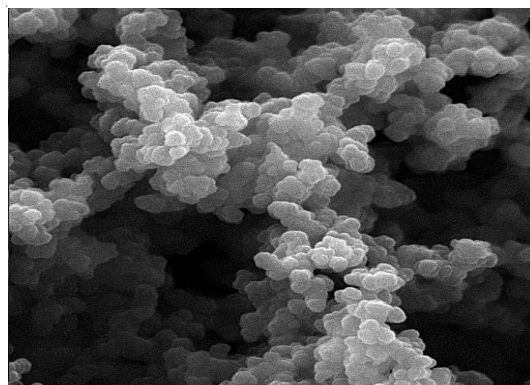
RESULTS AND DISCUSSION

The chemical method can be a general and useful procedure to prepare conductive polymer and its composites. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters²⁰. The yield, particle size and morphology are dependent on the presence of TiO₂ and surfactant, because the surfactant are adsorbed physically or bonded chemically to the growing polymer²¹. This is presumably due to the presence of adsorbed chemically surfactant to the polypyrrole particles. Surface active agents affect the physical and chemical properties of the solutions. Figs. 1(a) and 1(b) show the morphology of pure polypyrrole and TiO₂, respectively. As can be seen in Fig. 2(a) the polypyrrole obtained using TiO₂ exhibits spherical particles. By comparison between Fig. 2(a) and 2(b) particle size decreasing using poly(vinyl alcohol), because surfactant prevent from gross aggregation of particles.

Fig. 3 represents the FTIR spectra of the pure polypyrrole, TiO₂/polypyrrole composite and the TiO₂/polypyrrole composite with poly(vinyl alcohol) as a surfactant. As can be seen Fig. 3(c) the peaks related to pyrrole unit at 1554 cm⁻¹. The peaks are at 1325 cm⁻¹ (C-N stretching vibration), 1194 cm⁻¹ (C-H in-plane deformation), 1052 cm⁻¹ (N-H in-plane deformation), 917 cm⁻¹ (C-H out-of-plane deformation) and 674 cm⁻¹ (C-H out-of-plane ring deformation). An additional peaks which were observed. This indicate that polypyrrole is slightly over oxidized during the growth process²². As can be seen some peaks of the TiO₂/polypyrrole composite have a little shift to high wavenumber when compared with pure polypyrrole. This may be due to the interaction between polypyrrole and titanium oxide.

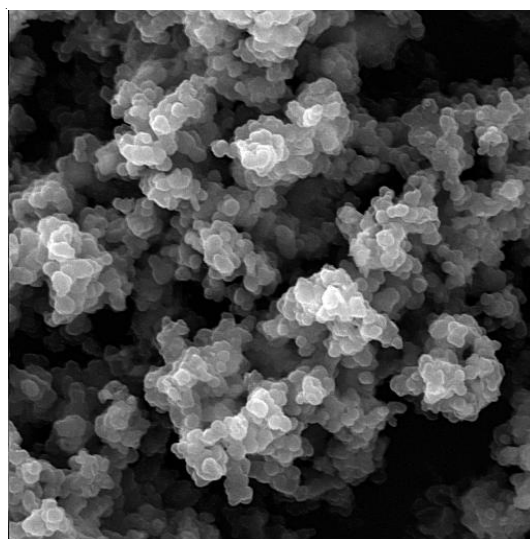


(a)

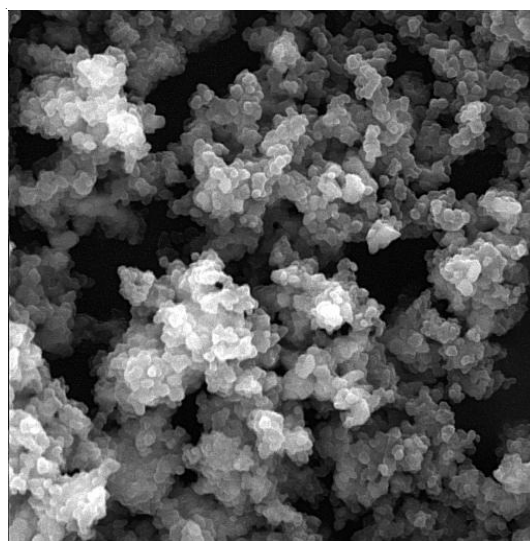


(b)

Fig. 1. Scanning electron micrograph of (a) pure TiO₂ and (b) pure polypyrrole generated in aqueous media. Reaction conditions of polypyrrole FeCl₃ = 54 g/L, pyrrole monomer 14.45 × 10⁻² mol/L, volume of solution 100 mL, reaction time 5 h at room temperature



(a)



(b)

Fig. 2. Scanning electron micrograph of (a) polypyrrole/TiO₂ and (b) polypyrrole/TiO₂ using poly(vinyl alcohol) as a surfactant generated in aqueous media. Reaction conditions: FeCl₃ = 54 g/L, pyrrole monomer 14.45 × 10⁻² mol/L, TiO₂ 1 g, poly(vinyl alcohol) 1 g/L, volume of solution 100 mL, reaction time 5 h at room temperature

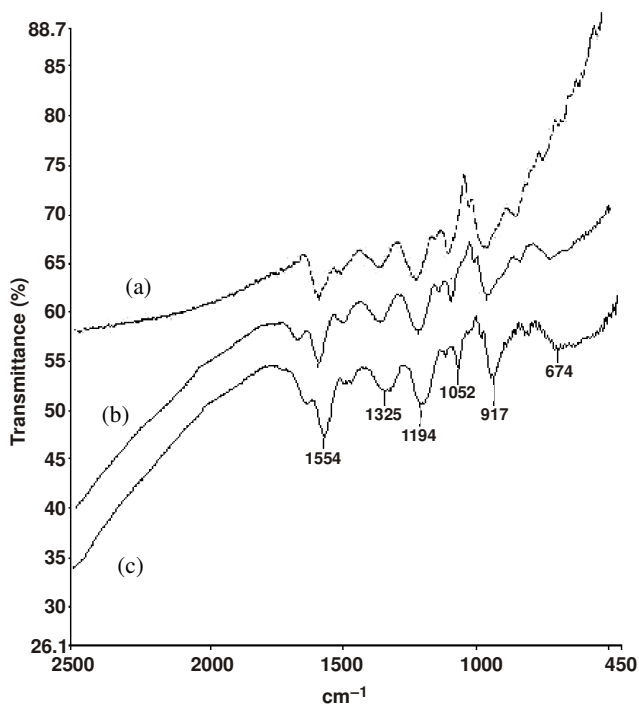


Fig. 3. FTIR spectra of (a) pure polypyrrole, (b) polypyrrole/TiO₂ and (c) polypyrrole/TiO₂ with poly(vinyl alcohol) used as surfactant in aqueous media

Figs. 4 and 5 show X-ray diffraction patterns of pure polypyrrole, TiO₂, polypyrrole/TiO₂ composite and polypyrrole/TiO₂ composite with poly(vinyl alcohol) as surfactant, respectively. As can be seen in Fig. 5(a), XRD pattern of polypyrrole/TiO₂ nanocomposite exhibit a predominant TiO₂ peaks than polypyrrole. The broad peak with 2θ around 25.4° is related to the diffraction of amorphous polypyrrole and the other peaks with 2θ at 27.4, 36.1 and 54.3° are related to diffraction of TiO₂, respectively. Crystallite size was calculated from the TiO₂ diffraction line using Scherrer's equation, $L = k\lambda/\beta\cos\theta$, where L is the mean dimension of the crystallite, β is the full width at half maximum of the diffraction peak, θ is the diffraction angle, λ is the X-ray wavelength and K is the shape factor and if the shape is unknown k is often assigned a value of 0.89²³. When the reflecting peak at $2\theta = 27.4^\circ$ are chosen to calculate the average diameter. The average diameter of the crystals of the pure TiO₂, polypyrrole/TiO₂ and polypyrrole/TiO₂ composite with poly(vinyl alcohol) are 48, 42 and 36 nm, respectively.

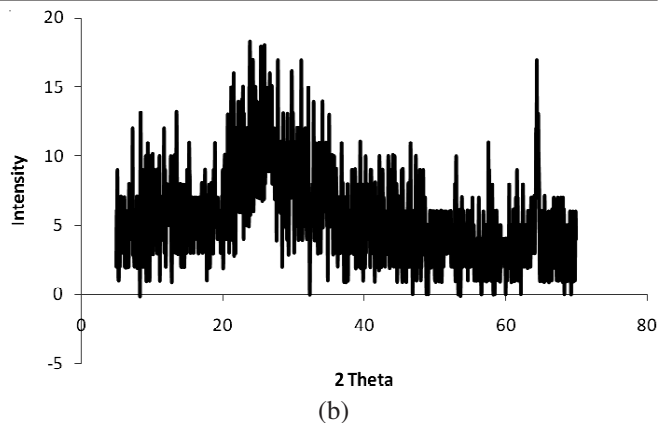
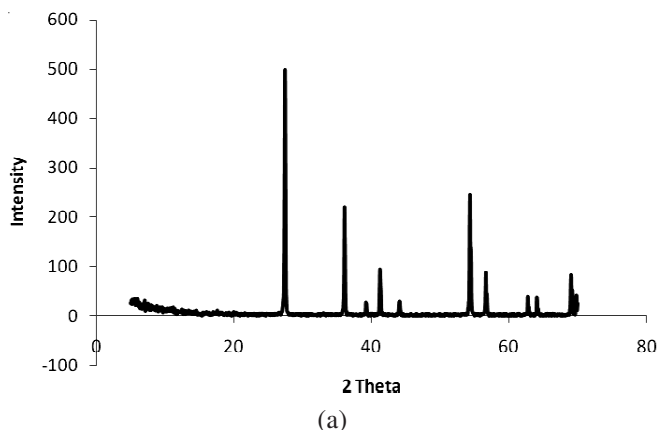


Fig. 4. X-ray diffraction pattern of (a) pure TiO₂ and (b) pure polypyrrole

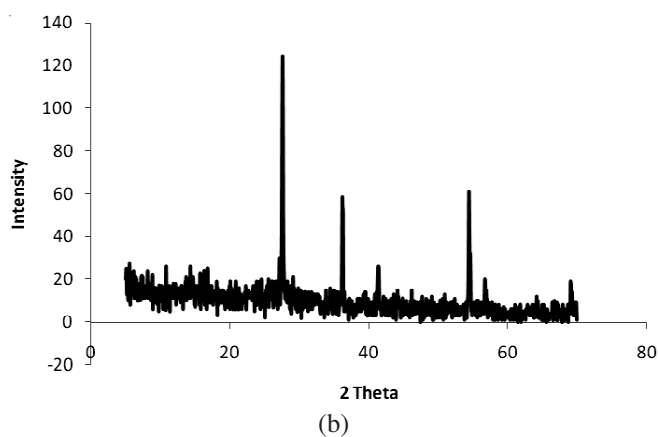
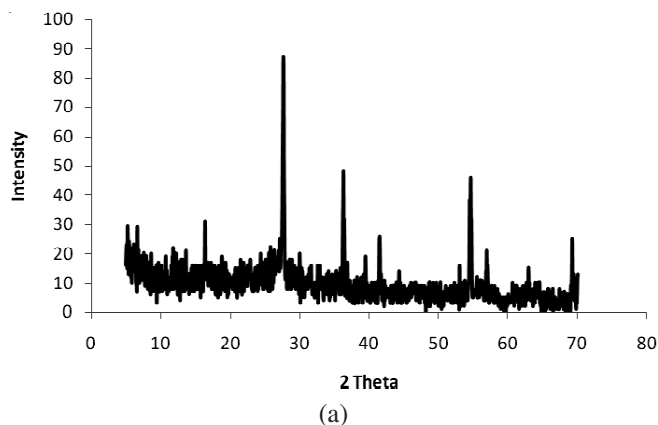


Fig. 5. X-ray diffraction pattern of the (a) TiO₂/polypyrrole composite and (b) TiO₂/polypyrrole composite with poly(vinyl alcohol) as a surfactant

Conclusion

Nanocomposite materials composed of oxides and conducting polymers have brought out more fields of applications^{24,25} such as toners in photocopying, conductive paints, drug delivery, rechargeable batteries, *etc.* In this study polypyrrole/TiO₂ nanocomposite was prepared by dispersing TiO₂ particles in a polypyrrole. The SEM micrographs indicate that, the morphology and particle size of products are dependent on the type and concentration of Titanium oxide and on the presence of surfactant. It was found that the type of surfactant has a considerable effect on the particle size and morphology of the resulting product.

The FT-IR spectral peaks of polypyrrole/TiO₂ composite show presence of oxide in the polymer though TiO₂ in the composites does not effectively involve chemically with polypyrrole. But weak interaction with oxide and polypyrrole may contribute to the conductivity and dielectric behaviour. It is clearly seen from the XRD patterns that TiO₂ was effectively coated on all of polypyrrole composites.

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