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Synthesis and characterization of hybrid nanocomposites of polypyrrole filled with iron oxide nanoparticles

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ABSTRACT

Hybrid polypyrrole (PPy)/α-Fe_2O_3 nanocomposite films were fabricated by spin coating on a glass substrate. X-Ray diffraction analysis revealed the crystalline structure of α-Fe_2O_3 nanostructures and the nanocomposites. The broad PPy peak weakened in intensity as the α-Fe_2O_3 content increased in PPy/α-Fe_2O_3 nanocomposites. Characteristic Fourier-transform IR peaks for pure PPy shifted to higher wavenumbers on addition of α-Fe_2O_3 to PPy/α-Fe_2O_3 nanocomposites. This can be attributed to better conjugation and interactions between PPy and α-Fe_2O_3 nanoparticles. Field-emission scanning electron microscopy, transmission electron microscopy, and atomic force microscopy images of the nanocomposites reveal a uniform distribution of α-Fe_2O_3 nanoparticles in the PPy matrix. UV-vis absorption spectroscopy revealed a blue shift from λ_{max}= 441 nm for PPy to λ_{max}= 392 nm for PPy/α-Fe_2O_3, reflecting strong interactions between PPy and α-Fe_2O_3 nanoparticles. The room-temperature dc electrical conductivity increased from 4.33×10^{-9} to 1.81×10^{-8} S/cm as the α-Fe_2O_3 nanoparticle content increased from 10 to 50 wt.% in PPy/α-Fe_2O_3 nanocomposites.

1. Introduction

Research in the field of conducting polymers is focused on suitable modifications of existing polymers so that their applicability can be improved. Among the different techniques available, one of the most widely studied and applied is the formation of composites from different origins. Conducting polymer composites have a suitable composition of a conducting polymer with one or more insulating materials to yield desirable properties. There is increasing interest in nanocomposites. These materials are especially important owing to their bridging role between conducting polymers and nanoparticles. There are many examples of nanocomposite hybrid materials in which organic materials such as polystyrene [1,2] and poly(vinyl chloride) [3] are combined with inorganic oxides or salts such as CuO [4], SiO_2 [5], ZrO_2 [6], SnO_2 [7], and $BaSO_4$ [8]. In almost all cases, some specific nature of the association between the two components has been observed. Insulating materials, rather than being simply blended or mixed, are encapsulated or entrapped in the conducting polymer core, resulting in significant improvements in different physical properties of the conducting polymer [9].

Intrinsic conducting polymers with conjugated double bonds have attracted much attention as advanced materials. Among these, polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis, and higher conductivity than many other conducting polymers. PPy can be easily prepared by either oxidative chemical or electrochemical polymerization of pyrrole. PPy has been used in biosensors [10,11], gas sensors [12,13], wires [14], microactuators [15], and anti-electrostatic coatings [16].

Iron oxide (Fe_2O_3), the most common oxide of iron, has important magnetic properties and is a convenient compound for the general study of polymorphism and the magnetic and structural phase transitions of nanoparticles. The existence of amorphous Fe_2O_3 and four polymorphs (α, β, γ, and ε) is well established [17,18]. The most abundant polymorphs are α-Fe_2O_3 (hematite), which has a rhombohedral–hexagonal corundum-type structure, and γ-Fe_2O_3 (maghemite), which has a cubic spinal structure.

Here we report on the synthesis of an organic–inorganic nanocomposite comprising PPy as the organic and iron oxide as the inorganic component. To achieve this goal, nano-sized iron oxide particles were synthesized using a sol–gel method and embedded in a PPy matrix via solid-state synthesis. Films of PPy/α-Fe_2O_3 nanocomposites were fabricated by spin coating on a glass substrate and the effects of α-Fe_2O_3 content on the structure, morphology, optical properties, and electrical conductivity were investigated.

2. Experimental

2.1. Materials

PPy, ammonium persulfate, iron chloride hexahydrate, and methanol were all obtained as AR grade reagents commercially.

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2.2. PPy synthesis

PPy was synthesized by oxidative polymerization using pyrrole as the monomer and ammonium persulfate as the oxidizing agent. Polymerization was carried out in a beaker by mixing 0.1 M aqueous pyrrole and 0.1 M ammonium persulfate in a 1:1 volume ratio. Polymerization was allowed to proceed for 3 h and the resulting precipitate was then filtered. The product was washed successively with methanol and distilled water [19].

2.3. Nanoparticle synthesis

α-Fe_2O_3 nanoparticles were synthesized using a sol–gel method with iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) as the Fe source. In a typical experiment, 1.693 g of $FeCl_3 \cdot 6H_2O$ was added to 50 mL of methanol and stirred vigorously at 60 °C for 1 h to form a gel. The heating was then stopped and the solution was stirred continuously until a brownish colored powder formed. The powder was filtered and washed repeatedly with methanol and dried. The dried powder was sintered in a furnace at 700 °C for 1 h in air to obtain a nanocrystalline α-Fe_2O_3 powder [20].

2.4. Synthesis of PPy/α-Fe_2O_3 nanocomposites

Nanocrystalline α-Fe_2O_3 powder was added to PPy powder in different weight percentages (10–50 wt.%). The powders were ground in a smooth agate mortar with a pestle for 1 h to obtain PPy/α-Fe_2O_3 hybrid nanocomposites. The nanocomposite powder was placed in *m*-cresol and stirred for 11 h to obtain a casting solution. Thin films were prepared on glass substrates (10×10 mm^2) by spin coating at 3000 rpm for 40 s and dried on a hot plate for 10 min. Fig. 1 shows a flow diagram for the synthesis and deposition of PPy/α-Fe_2O_3 nanocomposites.

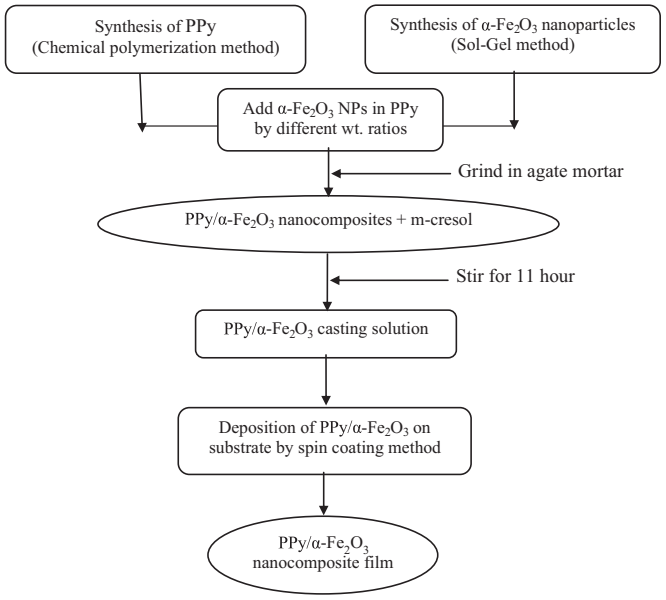
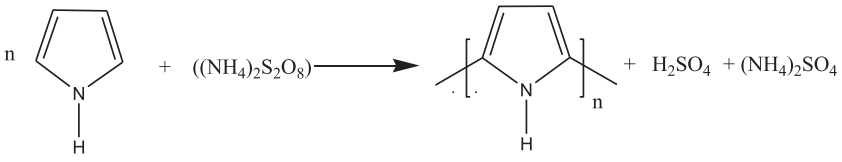


Fig. 1. Flow diagram for the synthesis and deposition of PPy/α-Fe_2O_3 nanocomposites.

2.5. Reaction mechanisms

The reaction mechanism for PPy formation is [21]

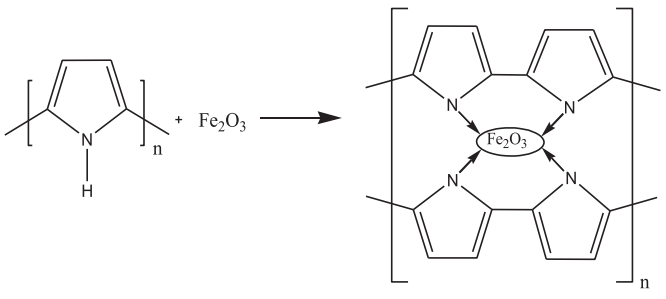


Pyrrole monomer APS (as oxidant) PPy

The reaction for α-Fe_2O_3 formation via the sol–gel method is [20]

$$FeCl_3 \cdot 6H_2O + 2CH_3 - OH \underset{\text{Condensation}}{\overset{\text{Hydrolysis}}{\Longrightarrow}} Fe_2O_3 + 2H_2O\uparrow$$

The possible reaction mechanism for PPy/Fe_2O_3 nanocomposite formation is



PPy PPy/Fe_2O_3 hybrid nanocomposite.

2.6. Characterization

X-Ray diffraction (XRD) patterns were recorded on a Philips PW-3710 diffractometer using Cu K_α radiation ($\lambda = 1.5406$ Å) in the 2θ range 10°–80° to determine the crystal structure and estimate the average crystallite size. Fourier-transform IR (FTIR) spectra (Perkin Elmer 100, 400–4000 cm^{-1}) were recorded for solid powder samples dispersed in potassium bromide and compressed into pellets for chemical structural analysis [22]. The surface morphology of samples was observed by scanning electron microscopy (SEM; Jeol 6360) at 20 kV. Atomic force microscopy (AFM) images were obtained using a scanning probe microscope (NT-MDT SPM-Solver P47) in contact mode. High-resolution transmission electron microscopy (HRTEM) images were recorded using a Hitachi H-800 instrument. UV-vis spectra of PPy, α-Fe_2O_3, and PPy/α-Fe_2O_3 nanocomposites were recorded on a Shimadzu-100 spectrophotometer. The two-probe technique was used to measure the electrical dc conductivity of PPy, α-Fe_2O_3, and PPy/α-Fe_2O_3 nanocomposites. An Ambios XP-1 surface profilometer was used to measure the film thickness.

3. Results and discussions

3.1. XRD analysis

Fig. 2 shows XRD patterns for PPy, nano α-Fe_2O_3, and PPy/α-Fe_2O_3 nanocomposites. The pattern for PPy has a broad peak at $2\theta = 24.15°$, confirming the amorphous nature of the polymer [23]. The broad peak results from scattering of X-rays by the PPy chain. The XRD pattern for nano α-Fe_2O_3 has peaks at $2\theta = 24.16°$, 33.11°,