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Optical and photoconductivity properties of pure Polypyrrole and titanium dioxide-doped Polypyrrole nanocomposites

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ABSTRACT

Polypyrrole (PPy) and PPy/Titanium oxide (TiO_2) nanocomposites have been synthesized by a chemical oxidative polymerization method at room temperature with various compositions (10, 15 and 20 wt%) of TiO_2 in PPy. The structural characterization is accomplished by X-ray diffraction and optical characterizations are made using Fourier transform spectroscopy, ultra-violet visible spectrophotometry, and photoluminescence spectroscopy. The morphology of these nanocomposites is studied with scanning electron micrograph. The photoconductivity properties of pure PPy and PPy/TiO_2 nanocomposites such as growth and decay of photocurrent have been studied in detail

1. Introduction

In recent years, electro-active polymers, particularly aromatic conducting polymers, have received much research attention for use as advance materials due to their remarkable physical attributes [1–3]. Conducting polymers (CP), however, arouse an immense interest among researchers because of their curious electronic, magnetic and optical properties. Conducting polymers can be prepared by chemical or electrochemical polymerization. In the chemical polymerization process, monomers are oxidized by oxidizing agents or catalysts to produce conducting polymers. The advantage of chemical synthesis is that it offers mass production at reasonable cost. On the other hand, the electrochemical method involves the direct formation of conducting polymers with better control of polymer film thickness and morphology, which makes them suitable for use in electronic devices [4,5]. Therefore, the physical and chemical properties of conducting polymers are considerably dependent upon the dopant and polymerization conditions. In terms of CP, Polypyrrole (PPy) is one of the most studied polymers due to its environmental stability, relative ease of synthesis and good electrical conductivity. Long term stability of PPy is a key factor for application of the new polymeric material in future applications and seems to be a good candidate [6]. PPy is most frequently used in commercial application such as batteries, supercapacitors, sensors and corrosion protection. Polymer–inorganic nano-particle hybrids have attracted much attention, since they have interesting physical properties and potential applications [23]. These particles not only combine the advantageous properties of metals and polymers but also exhibit many new characters that single phase materials do not have [7]. The incorporation of the conducting polymer as the shell in the core–shell structure can increase the surface area of the conducting polymers over that of the bulk polymer. This structure can be obtained from in-situ chemical oxidative polymerization in the presence of nanoparticles [8]. The inorganic core can be a metal or a metal oxide, and the organic shell can be a conducting polymer. Incorporation of inorganic fillers into conducting polymer matrices has also been studied, utilizing both chemical and electrochemical polymerization processes. For example, Titanium oxide (TiO_2), Zirconium dioxide and Silicon dioxide particles have been incorporated in Polyaniline and Polypyrrole matrices [9].

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Moreover, recent investigations on PPy/TiO_2 nanocomposites (NCs) for use as pigments indicate that a TiO_2 nanoparticle (NP) core can increase the charge resistance of the coatings [10,11].

This present work describes an efficient method for synthesization and characterization of pure PPy and PPy/TiO_2 nanocomposites by one-step in-situ polymerization of pyrrole. TiO_2 nanoparticles were used as a dopant of PPy because of their excellent physical and chemical properties as well as their extensive usage in many areas like coatings, solar cell, etc. [12]. The characteristics of the molecular structure, crystalline, optical properties, photoconductivity properties, and morphology of the pure PPy and PPy/TiO_2 nanocomposites are also discussed.

2. Experimental

2.1. Sample preparation

Pyrrole was distilled before use. All other reagents and solvents obtained from SDL were of reagent grade and were used as received. All solutions were prepared using distilled water; all reactions were performed at a temperature of 5 °C. The solution of the oxidizing agent, Ammonium persulphate (APS), was prepared using distilled water and was used in the ratio of 1:2.4 (monomer: oxidant). Dopants were mixed with Pyrrole solution (10% w/w) and stirred for 30 min for proper mixing and then the oxidant solution was added slowly. The Polypyrrole was prepared by a chemical polymerization method; 0.1 M Pyrrole solution was prepared using distilled water and then mixed with an oxidizing agent in the ratio mentioned above, slowly under constant stirring for 30 min. Then the polymerization was performed for 4 h under constant stirring. This preparation was kept unagitated for 24 h so that the PPy powder settled down. The PPy powder was filtered out under vacuum and washed with distilled water several times to remove any impurity present. The Polypyrrole was dried for 2 days at room temperature [13]. The pure and TiO_2 mixed PPy composites were grinded in the form of a fine powder. Pellets were prepared by compressing the powder under a pressure of 10 tons with the help of a hydraulic press machine. All the pellets were annealed at 100 °C for 1 h. The thickness of the pellets sample was found to be 3 mm. The diameter of the pellets was found to be 13 mm.

2.2. Characterizations

The X-ray diffraction (XRD) spectra of all the samples recorded by a PANalytical, X'pert PRO diffractometer using CuKα radiation ($\lambda = 1.54056$ Å) were presented for structural analysis of the samples. The scanning electron micrograph (SEM) images of all the sample pellets were taken by a scanning electron microscope (Model-430, LEO Cambridge, England). Fourier transform spectroscopy (FTIR) of all the samples in the form of powder was recorded on a Bruker Alpha spectrometer to determine the formation of Polyaniline. To record absorbance spectra, 0.02 g of each sample was dissolved in 5 mL of m-cresol, and then the absorption spectra of the solutions thus formed were recorded with a ultra-violet visible (UV–vis) spectrophotometer (Model no.V-670 Jasco).

2.3. Measurement of UV photocurrent

The photo- and dark conductivities of pure PPy and PPy/TiO_2 nanocomposites have been measured using a thick film of powder without any binder. Photoconductivity measurement was carried out at room temperature using an inter-digitated cell type device [14]. The cell was formed by putting a thick layer of powdered samples on Cu electrodes having a spacing of 1 mm and the area of illumination was 0.25 cm^2. The powdered layer was pressed with a transparent glass plate. In this cell type device, the direction of illumination is normal to the field across the electrodes. The cell was mounted in a dark chamber with a slit where from the light is allowed to fall over the cell. The photo-response was measured using a 300 W mercury lamp as the photo-excitation source. Photo-response was performed by a regulated dc power supply (APLAB: 23202) (0–32 V); a stabilized dc field (from 0 V/cm to 32 V/cm) was applied across the cell. The rise and decay of photocurrent were recorded using a RISH Multi-18S with adapter RISH Multi SI-232. Before measuring photoconductivity of the sample, the cell is first kept in dark till it attains equilibrium.

3. Result and discussion

3.1. XRD analysis

The XRD pattern study of nanocomposites of pure PPy and the synthesized PPy/TiO_2 nanocomposites is presented in Fig. 1. The XRD pattern of pure PPy as shown in Fig. 1(a) in the absence of TiO_2 nanoparticles is amorphous. It can be seen from curves Fig. 1(b)–(d) for the PPy/TiO_2 nanocomposites that as the TiO_2 percentage was increased, the amorphous nature disappeared and the PPy/TiO_2 nanocomposites samples became more strongly oriented along the (101) direction, which shows that all PPy/TiO_2 nanocomposites samples are polycrystalline in nature with a tetragonal structure and their most intense peaks are located at 25.5°. The angle obtained from the 2θ value which corresponds to

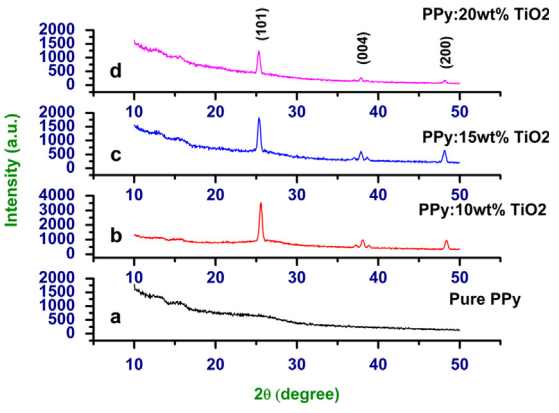

Fig. 1. XRD spectra for samples a–d. Curves a, b, c and d correspond to 0, 10, 15 and 20 wt% TiO_2 doped PPy nanocomposites, respectively.