



The structure and properties of polypyrrole/ titanium dioxide nanospheres of various dopant percentages by chemical oxidation method

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ABSTRACT

Polypyrrole-TiO₂ nano composite samples with various dopant percentages of TiO₂ were synthesized by chemical oxidative method at room temperature. The samples were characterized by Fourier transforms infrared (FTIR), SEM with EDAX, UV vis Spectrum, X-ray diffraction (XRD), Photoluminescence (PL) and Conductivity measurements. Electrical conductivity measurements indicate that the conductivity of nano composites increases with TiO₂ content. The doped H₂SO₄ may interact with PPy by donating either hydrogen sulfate (HSO₄) or sulfate (SO₄²⁻) ions as dopants. SEM images confirm that introduction of higher content of TiO₂ leads to the formation of nano spheres.

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Introduction

Conducting polymers (CP), however, arouse an immense interest among researchers because of their curious electronic, magnetic and optical properties. 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 new polymeric material in future applications and seems to be a good candidate [1]. PPy is most frequently used in commercial application such as batteries, super capacitors, sensors and corrosion protection. Polymer – inorganic nano particle hybrids have attracted great attention, since they have interesting physical properties and potential applications. 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 [2]. On the other hand, the nano scale metal particles such as gold, silver and titanium provide a very exciting research field due to their interesting properties. Among them, TiO₂ nano particles are appealing because of their excellent physical and chemical properties as well as extensive uses in many areas like coatings, solar cell [3].

Experimental

0.1 M of Pyrrole monomer and 1M solution of sulphuric acid were stirred with double distilled water and necessary quantity of TiO₂ nano powder (20%) was added to it .The oxidant Ammonium Persulphate was added drop wise to the Pyrrole-acid- TiO₂ mixture with constant stirring. The reaction was conducted at room temperature. After the addition, the stirring was continued for 5 hours for ensuring complete polymerization. The gradual change of color from light black to deep black indicated the formation of PPy/ TiO₂ nano composite. The total black mass was centrifuged, and then washed thoroughly with distilled water and methanol. Finally, the black mass was dried at 60°C for 12 hours. The process was repeated by adding different weights of TiO₂ (40%, 60% and 80 %) nano powder to the monomer. Before polymerization, the monomer

was distilled and guarded against exposure to light to prevent residual polymerization.

Results and discussion

Polypyrrole/TiO₂ nano composites with different dopant percentages of TiO₂ (20%, 40%, 60 %and 80%) were synthesized using sulphuric acid (H₂SO₄) by chemical oxidation method. The polymer samples obtained were powdery. They were characterized by Fourier transform infrared spectroscopy (FTIR), UV-Visible spectroscopy, X-ray diffraction (XRD), Scanning Electron Microscope (SEM), EDAX, Photoluminescence spectrum and Conductivity studies. The results are discussed.

FT-IR spectra of PPy/ TiO₂ with various dopant percentages of TiO₂

The FT-IR transmittance spectra of PPy/TiO₂ using KBr pellet was recorded in the range of 400 cm⁻¹–3500 cm⁻¹. Fig.1 (a), (b), (c), (d) shows the FTIR spectrum of PPy/TiO₂ nano composite. Metal oxygen stretching of 569 cm⁻¹ (Ti - O stretching mode) of pure TiO₂ nano particles are shifted to 615 cm⁻¹ in the PPy/TiO₂ composite, which indicates the weak interactions between TiO₂ and PPy [4]. The band at 1580, 1400, 1109 and 936 cm⁻¹ in the spectrum of PPy is related to the C-C stretching vibrations of the pyrrole rings [5].

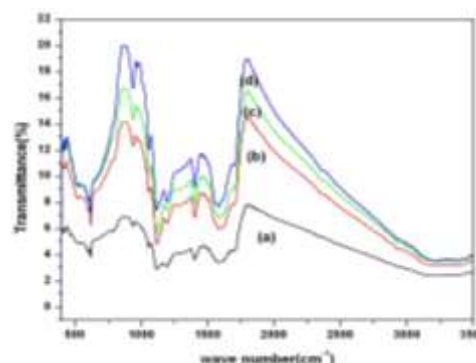


Fig.1 FT-IR spectra of PPy/ TiO₂ with various dopant percentages of TiO₂ (a) 20%, (b) 40%, (c) 60%, and (d) 80%

The absorption band at 1583cm^{-1} is caused by the bending vibration of coordinated H_2O as well as from the $\text{Ti} - \text{OH}$. It has been reported that H_2SO_4 may interact with PPy by donating either hydrogen sulfate HSO_4^- or sulfate SO_4^{2-} ions as dopants. The band at 1109cm^{-1} is attributed to SO_4^- anions. The relatively strong IR absorption peak related to the hydrogen bonding of oxygen atom in the composite indicates the presence of the functional groups in the spectrum [6].

3.2 SEM images of Polypyrrole/ TiO_2 nanospheres with various dopant percentage of TiO_2

AJEOL JSM -5610 Scanning electron microscope was used to study the surface morphology of the Polypyrrole with Titaniumdioxide by chemical oxidation method. Fig 2(a), (b), (c), (d) shows the sphere shape of nano particles. When ammonium persulphate (APS) is used, the polypyrrole forms nano aggregates. SEM images confirm that the polypyrrole / TiO_2 nanospheres are due to the introduction of the relatively higher content of TiO_2 .

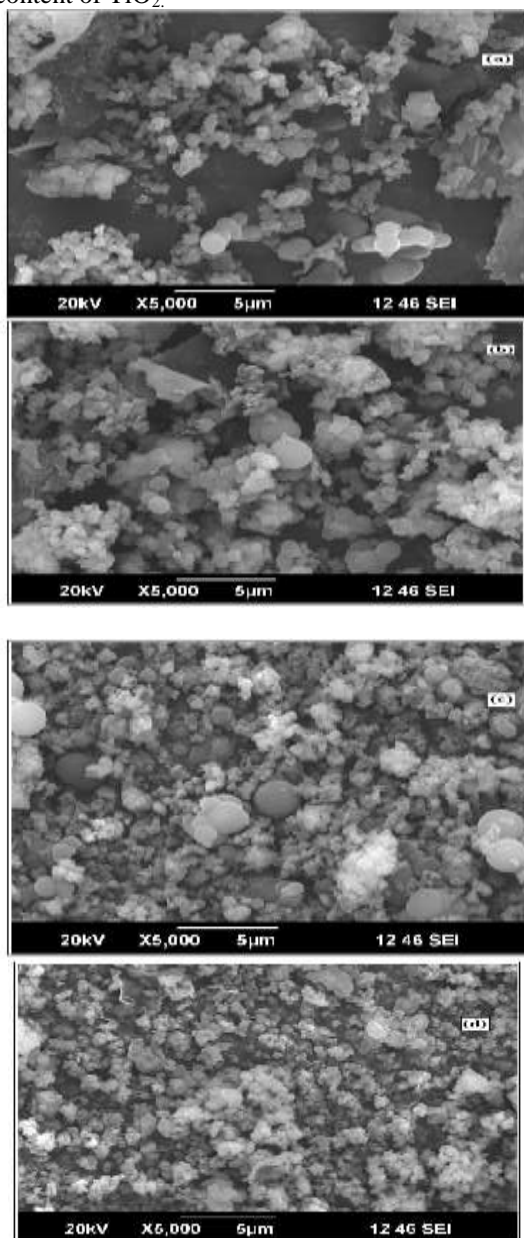


Fig. 2 SEM images of polypyrrole / TiO_2 nanospheres synthesized with various dopant percentage (a) 20%, (b) 40%, (c) 60%, and (d) 80%

In contrast, the size of the polypyrrole nanospheres increases from 250 to 450 nm. When the larger doping weight percentage is used (Figure 2a, b), the conductivity of these polypyrrole nanospheres is comparable to that of polypyrrole nanofibers already reported. That is to say, the initiator molecules act as a stabilizer for the as-formed nano micelles. These nano micelles likely act as templates to encapsulate pyrrole and oxidant leading to the formation of nano spheres during polymerization. When smaller size acids are employed, smaller diameter micelles are obtained leading to smaller sized polypyrrole nanospheres [7].

EDAX images of Polypyrrole / TiO_2 nanospheres various dopant percentages

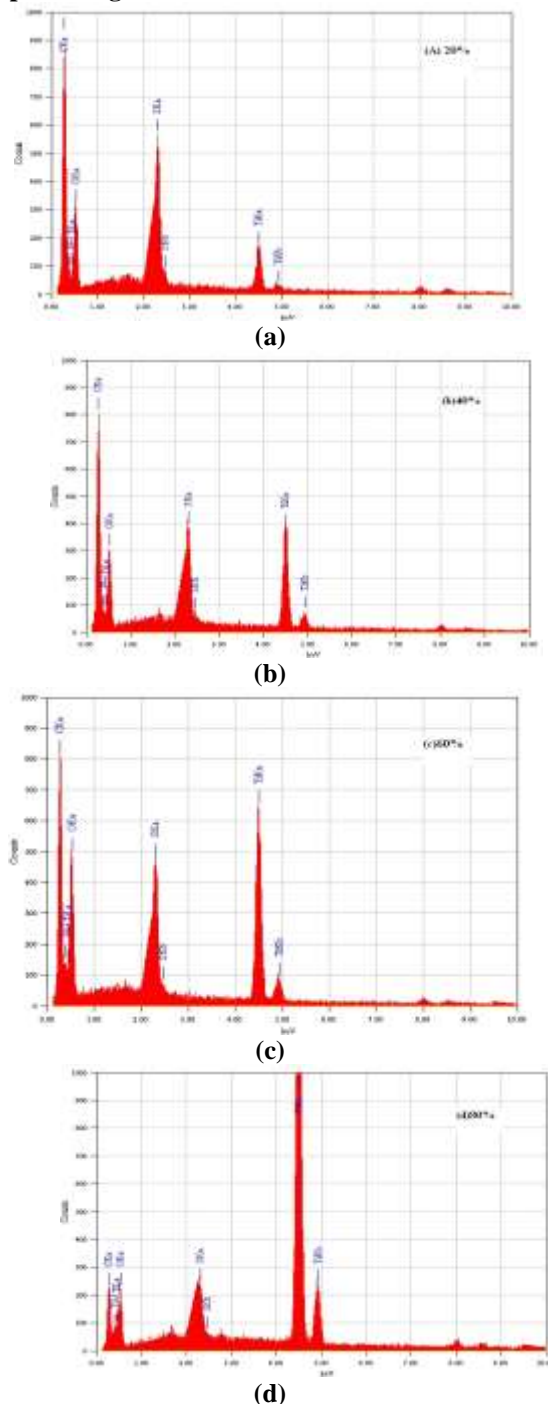


Fig 3. EDAX images of Polypyrrole / TiO_2 nanospheres of various dopant percentages (a) 20%, (b) 40%, (c) 60%, and (d) 80%

The EDAX spectra of the prepared PPy / TiO₂ composite nanospheres were recorded in the binding energy range 0-10 KeV as shown in (Fig.3a, 3b 3c and 3d).The purity and composition of the prepared samples were determined by EDX analysis. The quantitative analysis result indicates that the atomic ratio of Ti is 54.24% and O is 9.47% in the obtained nano spheres. Also, the EDX spectrum of the chemically synthesized composite material shows a remaining balance percentage which may be due to the of carbon (C) and Silicon (S) present in the samples which represents the existence of PPy with TiO₂ composite nanospheres.

Weight %	20%	40%	60%	80%
Element	Ti	O	Ti	O
Mass%	10.57	8.6	24.98	8.0
Atom%	3.29	7	8.48	5

XRD patterns of the PPy/TiO₂ composite with various dopant percentages

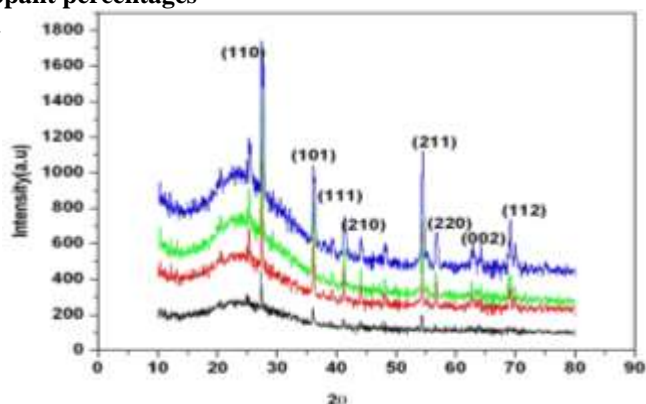


Fig.4 XRD patterns of the PPy/TiO₂ composite with various dopant percentages (a) 20%, (b) 40%, (c) 60%, and (d) 80%.

Fig.4 shows the X-ray diffraction patterns of PPy/TiO₂ composite materials recorded using an X-ray diffractometer with CuK α radiation ($\lambda=1.54\text{\AA}$). The phase and the purity of the prepared TiO₂ nanoparticles were determined by X-ray powder Diffraction (XRD) pattern.

The appearance of peaks at 25.31°, 27.43°, 36.0°, 41.24°, 44.06°, 48.06°, 54.31°, 56.63°, 62.75°, 64.06° and 69.79° match well with JCPDS 21-1276 and confirm the existence of PPy/TiO₂. However, it can be noted that due to the PPy deposition on the surface structure of TiO₂ nanoparticles, the diffraction peaks of TiO₂ gets slightly shifted from their positions at 25.31°, 48.06°, and 54.31°.

The Debye Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where, 'D' is the Grain Size, 'k' is proportionality constant approximately equal to unity, ' β ' the FWHM of the peak in radians (theoretically corrected from the Instrumental broadening), ' θ ' is the Bragg's angle, ' λ ' is the wavelength of X-rays (1.5406 Å for CuK α),

The dislocation density (δ) can be evaluated from Williamson and Smallman's formula, $\delta = \frac{1}{D^2}$ lines/m²

The (1 1 0) peak indicates the tetragonal specimen lines of TiO₂ [8]. The average crystalline size was found to be about 49.33 nm for the sample prepared by chemical oxidation method. The values of the distance (d) between adjacent planes in the (h k l) are calculated from the Bragg equation $n\lambda = 2d \sin \theta$

the lattice constants a, b, c, the interplanar angle, the angle ϕ between the plane (h1 k1 l1), of spacing d1, and the plane (h2 k2 l2), of spacing d2, and the cell volumes are calculated from the Lattice Geometry equation [9]. The (1 1 0), (2 1 1) and (0 0 2) peaks were used to calculate the structure parameters (Table 1).

Table. 1

Sample	2 θ	hkl	Structure	Daverage(nm)	Dislocation density	Strain
	27.4	110				
	34	0		54	3.429	6.41
TiO ₂	54.3	211	Tetragonal	41.6	5.778	8.31
	62.7	002		52.4	3.642	6.615
				49.33nm		

UV-Vis Spectrum of the PPy/TiO₂ composite with various dopant percentages

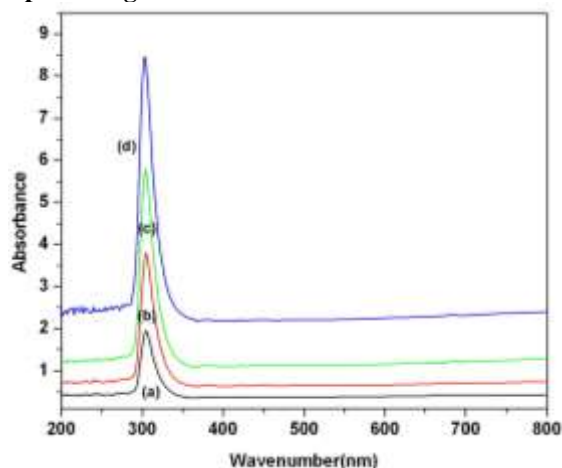


Fig.5 UV-Vis Spectrum of PPy/TiO₂ composites of various dopant percentages (a) 20%, (b) 40%, (c) 60%, and (d) 80%.

UV-vis spectroscopies of PPy/TiO₂ composites were examined employing Jasco V-530 dual beam spectrometer. The peak observed at 305 nm was assigned to the $\pi \rightarrow \pi^*$ transition or the excitation transition. As seen in the Figure 4a, 4b, 4c and 4d as the dopant percentage of TiO₂ increases, the polaron band appears to be sharp peak. This indicates that an increase in the dopant percentage leads to the formation of a chain which forms the best sharp peaks. The differences between the two spectra are due to the presence of an electron-withdrawing sulfonic group in the complex and therefore the transition band is observed at a lower wavelength. The absorption of the polaron band is strongly dependent on the molecular weight of the polymer [10].

Applied voltage Vs Current of the PPy/TiO₂ composite with various dopant percentages

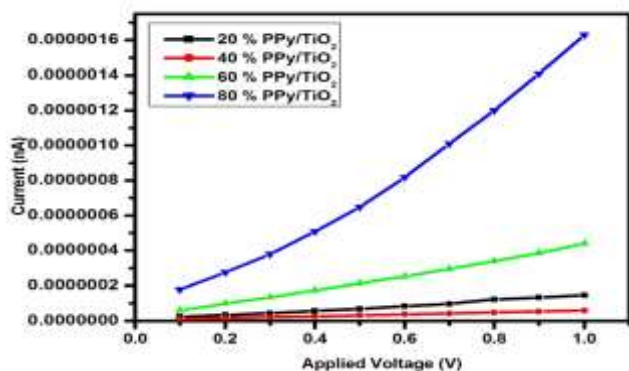


Fig.6 Applied voltage Vs Current of the PPy/TiO₂ composites with various dopant percentages (a) 20%, (b) 40%, (c) 60%, and (d) 80%.

Fig.6 shows Electrical conductivity measurement data measured according to the standard four - point probe technique at room temperature. Electrical conductivity was calculated from the relation:

$$\sigma_{dc} = 1/\rho_{dc} \text{ or } 1/R(L/A)$$

where R is the resistance, L is the thickness of the sample, A is the cross-sectional area of the sample and σ_{dc} is the resistivity of the sample under rest. They are parallel process namely band conducting and hopping conducting. The excitations of the charge carry into non-localized and localized states. Thus the total conductivity is given as

$$\sigma = \sigma_i + \sigma_h$$

where, σ_i is the intrinsic conductivity and σ_h is the hopping conductivity.

Fig.6 shows the conductivity of TiO₂ doped PPy composite increased remarkably. This may be attributed to the doping effect associated with TiO₂ nanoparticles that were believed to induce the formation of more efficient charge transport. However due to the increasing contents of TiO₂ the relative contents of the conducting polymer PPy gets decreased, which caused a decrease in the conductivity of composites which may be accredited to the diode properties.

Photoluminescence spectrum of PPy/TiO₂ with various dopant percentages

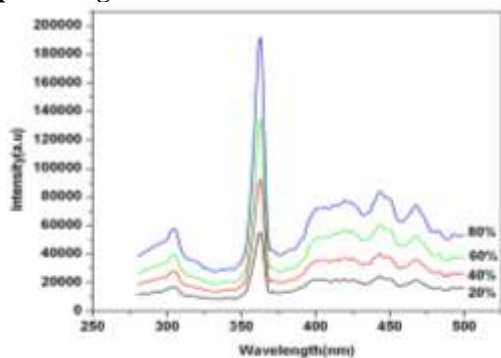


Fig.7 Photoluminescence spectrum of PPy/TiO₂ composites of various dopant percentages (a) 20%, (b) 40%, (c) 60%, and (d) 80%.

The Photoluminescence properties of the polypyrrole/TiO₂ nanospheres were studied using FP-6500 Spectrofluoro meter- 67 at room temperature. Fig.7 shows the main emission band of the

nano composites are located at 362 nm with three shoulders at 304 nm, 443 nm and 468 nm. We also note that an increase in intensity of the 362 nm, which becomes the dominant emission band as the TiO₂ concentration increases.

The direct band gap was calculated by using this formula,

$$(E_g = hc/\lambda)$$

where,

'h' is a constant,

'c' is velocity of light,

' λ ' is emission wavelength in Photoluminescence spectrum.

The direct band gap energies of the PPy / TiO₂ composite of different ratios are found as 4.05 eV and 3.4 eV. The band gap gets decreased due to increased content of TiO₂ nano particles. As the luminescence of these oxide/polymer nanocomposites is proportional to the surface features, it is possible to tailor the wavelength and the intensity of the luminescence by varying the particle size. Therefore, we can conclude that a p-n heterojunction at nanosphere TiO₂/ polypyrrole interface has been created [11].

Conclusion

It has been reported that H₂SO₄ may interact with PPy by donating either hydrogen sulfate HSO₄ and sulfate, SO₄²⁻ anions as dopant anions by FTIR. SEM images confirm that introduction of higher content of TiO₂ leads to the formation of nano spheres. The quantitative analysis result indicates that the atomic ratio of Ti is 54.24% and O is 9.47%. The (1 1 0) peak indicates the tetragonal specimen line of TiO₂ nano particles. The absorption of the polaron band is strongly dependent on the molecular weight of the polymer. The peak observed at 305 nm is assigned to the $\pi \rightarrow \pi^*$ transition or the excitation transition represented in UV vis Spectrum. Conductivity studies result in the formation of a more efficient charge transport and may be applied in diode properties. Therefore, we can conclude that a p-n heterojunction at nanosphere TiO₂/ polypyrrole interface has been created.

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