

Enhanced Photocatalytic Activity of Polypyrrole/TiO₂ Nanocomposites for Acid Violet Dye Degradation under UV Irradiation

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Abstract-In-situ chemical polymerization was used to synthesize PPy/ TiO₂ nanocomposite. The nanocomposite was characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) to ensure the crystallite size, functional groups and morphology of the polymer nanocomposite. The band gap of the PPy/TiO₂ nanocomposite was found to be by using Ultra-Violet Diffuse Reflectance Spectra (UV-DRS). Additionally, the photocatalytic activity of the materials was investigated by monitoring the decolorization of Acid Violet dye under UV irradiation. Finally, PPy/TiO₂ nanocomposite was found to possess higher photocatalytic activity than pure TiO₂.

Keywords- Nanocomposites; Polypyrrole; Photocatalysis; Acid Violet; TiO₂

I. INTRODUCTION

Heterogeneous conducting polymer composites (organic/inorganic) have been attracting attention owing to their applications in various fields such as charge storage materials, catalysts, solar cells and electrological ER fluids conducting polymers have also been used as the supporting matrix in different composites for intercalation of catalytically important nanoparticles so that catalytic activity is retained in the composite.[1]. A combination of the conducting polymer and TiO₂ further enhances the degradation rate of the conducting polymer. TiO₂ supported or coated photocatalyst is becoming more popular in water and air purification in the recent days.[2]. TiO₂ has also been studied to prepare its composite with conducting polymers. Although there are so many candidates for polymeric matrix, one particular interest is the integration of inorganic nanoclusters with conducting polymers because the resulting nanocomposites may possess unique electrical and optical properties. Because of the combination of conductivity of polyaniline and UV-sensitivity of anatase TiO₂, such nanomaterials are expected to find applications in electrochromic devices, non-linear optical system and photoelectrochemical devices.[3-4]. Among various conductive polymers, PPy is one of the most promising conductive polymers due to its superior conductivity, electrochemical reversibility, high polarizability and the ease of preparation through chemical or electrochemical routes.[5]. Several studies have been reported that PPy/TiO₂ nanocomposites were prepared by insitu chemical polymerization method. The photocatalytic activity of PPy/TiO₂ nanocomposite showed better performance than TiO₂.

II. EXPERIMENTAL MATERIALS

TiO₂ nanoparticles with particle size of ~21nm was obtained from Sigma-Aldrich Chemicals. Ammonium persulfate (APS) was received from Thomas Baker Chemicals, are used as received. Pyrrole (98+%) obtained from Alfa Aesar and Acid violet dye was purchased from Qualigens Fine Chemicals. All the other chemicals and reagents were analytical grade used without further purification

1. Instrumental analysis

UV-visible spectrum (DRS) was recorded using “SHIMADZU” model: UV 2450, FT-IR spectrum was recorded using “SHIMADZU” (Model: 8400S). The crystallographic structures of the materials were determined by High resolution powder diffractometer model – RICH SIEFRT & CO with Cu as the X-ray source ($\lambda = 1.5406 \times 10^{-10}$

¹⁰m). The surface morphology of the sample was recorded using Scanning Electron Microscopy (SEM) (Model: FEG Quantum 250).

2. Catalyst Preparation

The required amount of Pyrrole was dissolved in 0.1M solution of Sulphuric acid solution. Then various amounts of TiO₂ nanoparticles were dissolved in prepared sulphuric acid containing Pyrrole solution. Then 20ml of prepared APS solution was added drop by drop. The beaker was kept in ice-cooled condition. After few hours green precipitate was obtained. Then it was filtered and washed with DD water.

3. Photocatalytic degradation of Acid Violet

A stock solution of Acid violet dye was prepared with distilled water. Dilutions were made depending on the desired textile dye concentration and the pH was adjusted with sodium hydroxide or sulphuric acid. Proper amount of catalyst was added to the dye solutions at the beginning of the experiment. A series of photocatalytic decolorization experiments were carried out employing UV-light using photochemical reactor. The results are obtained in Table. 2.

III. RESULTS AND DISCUSSION

1. SEM and EDX analysis

The surface morphology of the prepared PPy-TiO₂ nanocomposite was examined by SEM as depicted in Fig.1. The surface morphology of TiO₂ is ball like round shape and the surface morphology of pure polypyrrole is ball like spherical shape. Based on these findings, one can induce that the PPy-TiO₂ nanocomposite has been successfully obtained. It is also observed from the results TiO₂ nano particles deposited on the surface of polypyrrole .[6]. The EDX analysis was also carried out for the prepared catalysts. The results are shown in Table 1. EDX analysis revealed the presence of oxygen, nitrogen, carbon and a relatively high Ti content on all the PPy/ TiO₂ nanocomposites .

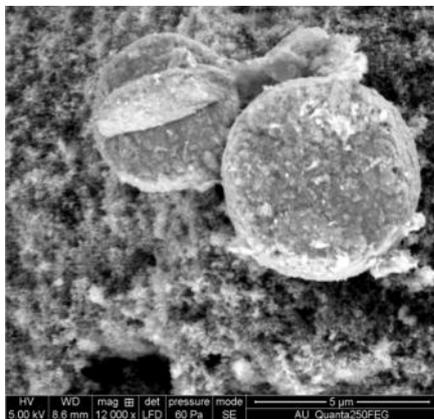


Fig. 1 SEM analysis of PPy-TiO₂ nanocomposite

TABLE. 1 EDX ANALYSIS

Element	Weight (%)	Atomic weight (%)
Carbon	50.70	63.46
Nitrogen	07.77	08.34
Oxygen	23.76	22.33
Ti	16.22	05.09

2. XRD analysis

The crystallographic structure of obtained PPy-TiO₂ nanocomposite was evidenced by XRD measurements. Fig.2 shows the XRD pattern of PPy/TiO₂ nanocomposites.. The XRD peaks denote the formation of PPy-TiO₂ nanocomposite. The respected peaks occur at 25.3°, 26.2°, 36.0°, 38.2°, 48.9°, 54.3°, 56.6°, 63.1° and 69.9°. Moreover, it can be noted that the TiO₂ deposited on the surface structure of Polypyrrole. [7].

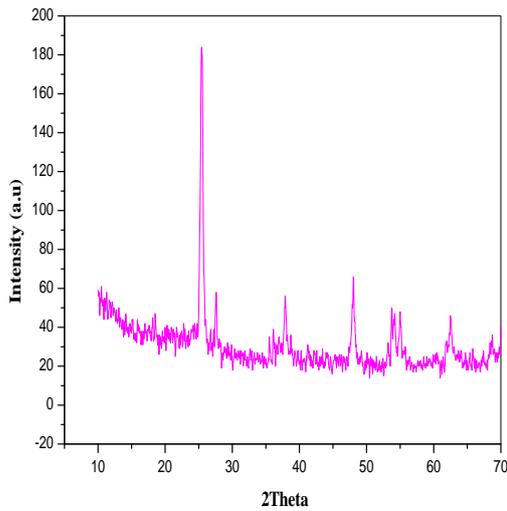


Fig . 2 XRD analysis for PPy-TiO₂ nanocomposite

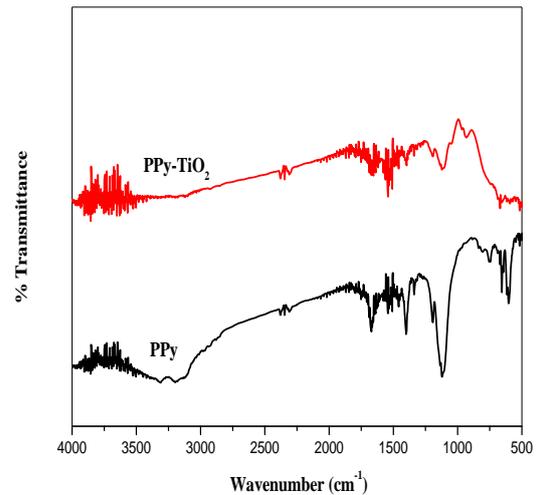


Fig. 3 FT-IR analysis for PPy-TiO₂ nanocomposite

3. FT-IR ANALYSIS

The molecular structures of PPy and PPy-TiO nanocomposites were characterized by FT-IR as shown in Fig.3. The typical FTIR spectra of PPy polymer, the bands at 1552.15 and 1635.13cm⁻¹ are ascribed to the stretching vibrations of C=C and C=N in the phenazine ring, respectively. The peaks at 1400.22 and 1100 cm⁻¹ are ascribed with the C-N stretching in the benzenoid and quinoid imine units. Moreover, the bands at 520.78 cm⁻¹ which are characteristics of C-H out-of plane bending vibrations of benzene nuclei of PPy. The results of FTIR spectra of PPy agree well with previous reports [8-9].

4. UV-vis DRS studies of PPy-TiO₂ nanocomposite

The optical properties of PPy-TiO₂ nanocomposites were investigated by the UV-DRS spectroscopy as shown in Fig. 4

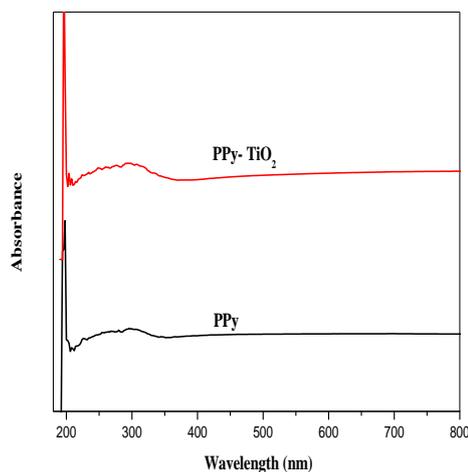


Fig.4 UV-DRS analysis for PPy-TiO₂ nanocomposite

The position of fundamental absorption edge of PPy-TiO₂ is determined using equation

$$(\alpha h\nu)^2 = A(h\nu - E_g)^n$$

Where α , $h\nu$, E_g and A are the absorption coefficients, Planck constant, light frequency, band gap and a constant, respectively. The n value depends on the transition characteristics. The E_g value can be estimated by extrapolating the straight portion of the $(\alpha h\nu)^2 - (h\nu)$ plot.[10]

TABLE. 2 DATA OBTAINED FROM THE EXPERIMENTAL PARAMETERS OF AV DYE UNDER UV LIGHT IRRADIATION.

S.No	Parameters	% Removal of AV dye	
		TiO ₂	PPy-TiO ₂
1	Initial concentration of AV dye ($\times 10^{-5}$ M)	87.0 - 27.5	97.0 - 54.5
2	p H variation	15.0 – 84.5	25.5 – 94.5
3	PPy-TiO ₂ concentration (g/L)	84.5 – 45.0	98.0 – 64.0
4	Irradiation Time (min)	10. 5 – 85.5	30. 5 – 97.5

Conclusion

PPy-TiO₂ nanocomposites were successfully prepared by chemical oxidative polymerization method. The results from SEM analysis consistently indicate that the PPy has been deposited on TiO₂ particles. The FT-IR results show the main functional group present in PPy-TiO₂ nanocomposites. The UV-vis diffuse reflectance spectra confirmed that the modified catalyst absorbed more photons under UV light irradiation. The percentage removal of dye degradation was higher in PPy-TiO₂ nanocomposite than TiO₂.

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REFERENCES

- [1] S. Xu, L. Gu, K.H. Yang, Y. Song, L. Jiang, Y. Dan, "The influence of the oxidation Degree of poly(3-hexylthiophene) on the photocatalytic activity of poly(3-hexylthiophene)/TiO₂ composites", *Sol. Energy Mater. Sol. Cells* 96 2012, pp. 286–291.
- [2] A. K.Subramani, K. Byrappa*, S . Ananda, K.M. Lokanatha rai, C. Ranganathaiah and M.Yoshimura, "Photocatalytic degradation of indigo carmine dye using TiO₂ impregnated activated carbon", *Bull. Mater. Sci.*, Vol. 30, No. 1, February 2007, pp.37–41.
- [3] H. Zhang, R.L. Zong, J.A. Zhao, Y.F. Zhu, "Dramatic visible photocatalytic degradation performances due to synergetic effect of TiO₂ with PANI", *Environ. Sci. Technol.* 42,2008, pp.3803–3807.
- [4] L. Zhang, P. Liu, Z. Su, "Preparation of PANI/TiO₂ nanocomposites and their solidphase photocatalytic degradation", *Polym. Degrad. Stab.* 91, 2006, pp. 2213–2219.
- [5] F. Denga, Y. Li, X. Luob, Y. Lixia, X. Tu, "Preparation of conductive polypyrrole/TiO₂ nanocomposite via surface molecular imprinting technique and its photocatalytic activity under simulated solar light irradiation", *Colloid Surf A: Physicochem. Eng. Aspects* 395, 2012, pp.183–189.
- [6] Shreyam Chatterjee, Arnab Shit and Arun K. Nandi*, "Nanochannel morphology of polypyrrole–ZnO nanocomposites towards dye sensitized solar cell application", *Journal of Materials Chemistry A*, 1, 2013, pp.1-8.
- [7] Y. Yucheng, W. Junwei, W. Jianhong, R. Xiong, J. Shi, P. Chun-Xu, "Polypyrrole decorated Ag-TiO₂ nanofibers exhibiting enhanced photocatalytic activity under visible light illumination", *ACS Appl. Mater. Interfaces*, 2013, pp.1-27.
- [8] M. A. Chougule • G. D. Khuspe • Shashwati Sen • V. B. Patil, "Polypyrrole–ZnO nanohybrids: effect of CSA doping on structure, morphology and optoelectronic properties", *Appl Nanosc*, 2012, pp. 1-7
- [9] D. Juraj , K. Martin , B. Gabriela, K. Martin, M. Iva, "Electrochemical Fabrication and Characterization of Porous Silicon/Polypyrrole Composites and Chemical Sensing of Organic Vapors", *Int. J. Electrochem. Sci.*, 8, 2013, pp.1559 – 1572
- [10] B. Rohit, S. Madhulika and D. Bahadur, "Visible light- driven nanocomposites (BiVO₄/CuCr₂O₄) for efficient degradation of organic dye+", *Dalton Transactions*, 2013, pp. 1-9.