

Synthesis of polypyrrole@ZrO₂/Ag nanocomposite and its photocatalytic activity in environmental remediation

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ZrO₂/Ag modified by polypyrrole was synthesized by chemical oxidative polymerization method. ZrO₂ was prepared by hydrolysis of zirconyl chloride by maintaining pH 10. ZrO₂/Ag was prepared by impregnation method. The sample were confirmed using various characterization techniques such as X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FT-IR), Diffuse Reflectance Ultraviolet-Visible Spectroscopy (DRS-UV-Vis), HR-SEM and UV-Visible spectroscopy. It is found that composite shows enhanced photocatalytic activity towards photodegradation of methylene blue (MB) dye under visible light.

Keywords: Photocatalyst, polypyrrole, zirconia, silver, nanocomposite.

Introduction

Water being a valuable resource need treatment especially before consumption as it is polluted by textile and photographic industries which use synthetic dyes and discharge the wastewater into streams without proper treatment. These synthetic dyes are chemically stable and non-biodegradable. Conducting polymers like polypyrrole (PPY) possess excellent chemical and environmental stabilities, easy synthesis, cost efficiency and high mobility¹. Zirconia (ZrO₂) is an n-type semiconductor material possessing optical and electrical properties, strong mechanical strength, thermal stability as well as acid-base and redox capabilities². The noble metal silver have been already reported for the enhancement of photocatalytic activity³.

Materials and methods:

Pyrrole, ammonium persulphate, sulphosalicylic acid, methylene blue (MB) were purchased from Qualigens. Zirconium oxychloride, silver nitrate from Merck were used as received. Pyrrole was distilled under reduced pressure before use. Double distilled water was used throughout the experiment.

Synthesis of polypyrrole@ZrO₂/Ag nanocomposite:

Zirconia was prepared by dropwise addition of aqueous ammonia to 0.5 M zirconyl chloride and adjusting to a final

pH of 10. The precipitate was filtered, washed with deionised water, dried, and calcined at 700°C for 3 h. To the as-synthesized zirconia, 20% amount of silver nitrate was added in double distilled water and stirred for 6 h, the precipitate formed was filtered, washed with deionised water, dried and calcined at 450°C for 2 h. PPY/ZrO₂-Ag composite was prepared by taking the mixture of pyrrole (0.2 mL), desired amount ZrO₂/Ag and sulphosalicylic acid (0.4 g) in 100 mL of double distilled water and stirred for 30 min. 50 mL of aqueous ammonium persulphate solution (APS) was added dropwise to the reaction mixture and kept at 0–5°C for 24 h under constant stirring. The precipitate obtained was centrifuged, washed with distilled water and dried in vacuum for 24 h. The obtained nanocomposite was assigned as PZA.

The X-ray diffraction patterns were recorded using Rich Siefert 3000 diffractometer with Cu K α ₁ radiation ($\lambda = 1.5406 \text{ \AA}$) to determine the phase purity and structure of the as-synthesized samples. DRS UV-Vis absorption spectrum was recorded in the range of 200–800 nm using a Perkin-Elmer Lambda 650 spectrophotometer. FT-IR and UV-Visible spectroscopy was measured using Perkin-Elmer instrument.

Results and discussion

Fig. 1. shows XRD pattern of PZA nanocomposite, which shows peak at 2θ value 17.6°, 28.3°, 31.4°, 34.16°, 35.6°,

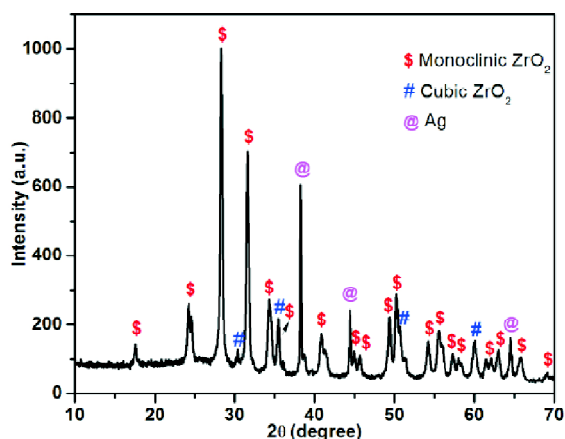


Fig. 1. XRD pattern of PPY@ZrO₂/Ag.

40.9°, 49.3°, 50.2°, 55.6°, 65.8° are ascribed to (001), (-111), (111), (200), (002), (-112), (220), (022), (-311), (-132) crystal planes of monoclinic zirconia with the JCPDS file No. 37-1484. Peaks at 2θ 30.3°, 35.4°, 50.6°, 60.1° are attributed to (111), (200), (220), (311) crystal planes of cubic zirconia phase (JCPDS file No. 65-0461). Silver peaks are observed at 38.2°, 44.4°, 64.6° corresponds to (111), (200), (220) crystal planes of cubic silver with the JCPDS file No. 87-0720. PPY shows broad characteristic peak at 25° confirming amorphous nature of PPY⁴.

Fig. 2 shows FT-IR spectra, the characteristic peaks due to PPY are observed at 1036 cm⁻¹ (C-H in-plane deformation vibration), 1454 cm⁻¹ (C-C asymmetric stretching vibration), and 1542 cm⁻¹ (ring stretching mode of pyrrole), 3426 cm⁻¹ (NH stretching), 1656 cm⁻¹ (C=C ring stretching, quinoid) and 2920 cm⁻¹ (C-H stretching)⁴.

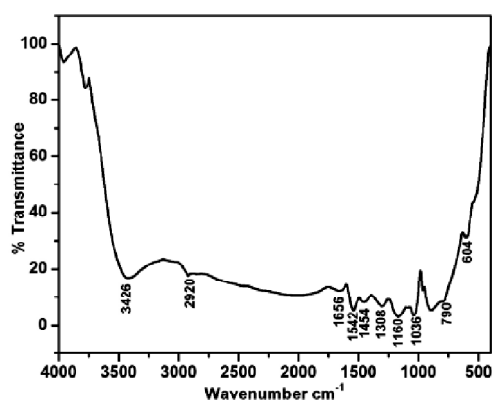


Fig. 2. FT-IR spectra of PPY@ZrO₂/Ag.

The peak at 1308 cm⁻¹ assigned to C-H deformation. The peaks around 725–1110 cm⁻¹ attributes to the C-H in-plane and C-H out-of-plane deformation in PPY units⁵. The peak at 1168 and 794 cm⁻¹ is assigned to N-C stretching band and due to presence of polymerized pyrrole respectively. The peak at 604 cm⁻¹ attributes to silver vibration.

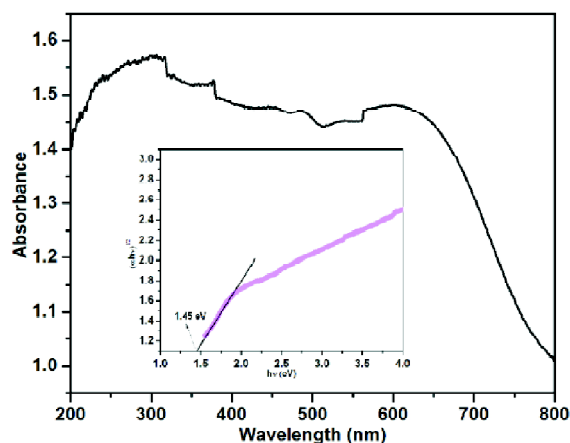


Fig. 3. DRS UV-Visible absorption spectra of PPY@ZrO₂/Ag. Inset: Tauc's plot of the composite.

Fig. 3 shows the DRS UV spectra of PZA composite which shows two absorption peaks at 318 nm and 600 nm. The optical absorption properties above 400 nm in the visible region are attributed to the $\pi \rightarrow \pi^*$ (HOMO-LUMO) transition due to C=C structure of PPY. The band gap (E_g) calculated by using Tauc's relationship:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where α is the absorption coefficient, A is proportional constant, h is Planck's constant, ν is the frequency of vibration, E_g is the band gap, $n = 1/2$ (for indirect band gap). The obtained reduced band gap (E_g) value of the PZA is found to be 1.45 eV which will enhance the photocatalytic activity.

The photocatalytic activity of the PZA nanocomposite was performed using methylene blue dye (MB). The 100 mL of 1×10^{-5} M aqueous MB dye solution were mixed with 40 mg of the photocatalyst and stirred in the dark for 30 min to attain adsorption-desorption equilibrium then exposed to visible light under constant stirring. The photocatalytic activity of the PZA nanocomposite was performed using methylene blue dye (MB). The 100 mL of 1×10^{-5} M aqueous MB dye solution were mixed with 40 mg of the photocatalyst and

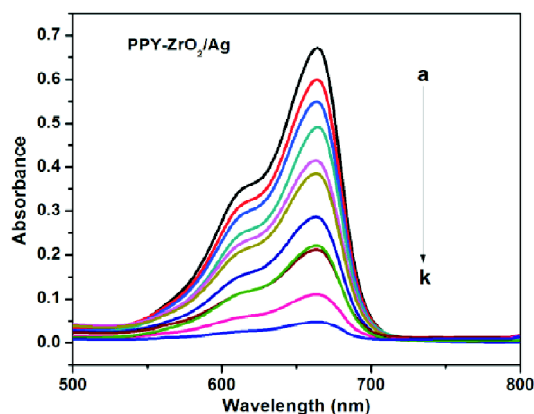


Fig. 4. UV-Vis spectra of aqueous MB at (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 75 min, (g) 90 min, (h) 105 min, (i) 120 min, (j) 135 min, (k) 150 min photodegradation using PPY@ZrO₂/Ag photocatalyst.

stirred in the dark for 30 min to attain adsorption-desorption equilibrium then exposed to visible light under constant stirring.

The absorbance spectra recorded for every 15 min withdrawn dye solution shows regular decrease in absorption maximum at λ_{max} ($\lambda = 663 \text{ nm}$) without any shift in the peak

which implies the degradation is only due to the composite. For PZA the maximum absorbance value is 0.67 before the visible light irradiation and after 150 min the value decreased to 0.05, then continuous exposure to another 20 min did not show any further decrease in absorbance.

Conclusions

PZA nanocomposite were synthesized by chemical oxidative polymerization method. The good visible light harvesting ability due to reduced band gap is responsible for its photocatalytic activity.

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