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Synthesis, characterization and visible light photocatalytic activity of PANI modified TiO_2/Cu nanocomposite

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TiO_2 was synthesized by hydrolysis of tetra ethyl ortho titanate at room temperature in presence of ammonia. TiO_2/Cu was prepared by conventional impregnation method. PANI modified TiO_2/Cu was prepared by chemical oxidative polymerization method. The synthesized composite was characterized by X-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FT-IR), Diffuse Reflectance Ultraviolet-Visible Spectroscopy (DRS-UV-Vis) and UV-Visible spectroscopy. It is found that composite exhibits excellent photocatalytic activity towards photodegradation of organic dye under visible light.

Keywords: Polyaniline, titania, photocatalyst, nanocomposite, organic dye.

Introduction

PANI is most extensively used conducting polymer possessing π-conjugated long chain and shows visible light absorption property, redox properties, high mobility of charge carriers, stability, non toxicity, corrosion protection and low cost synthesis. During light irradiation PANI acts as electron donor as well as electron acceptor these characteristics makes PANI to improve charge separation efficiency in the photocatalysis field[1]. Titania is a semiconductor metal oxide possessing potential applications as photocatalyst, sensors due to its electronic and optical properties, also easily available, low cost, non toxic and biocompatible[2]. However the application of titania is limited with charge-recombination phenomenon and wide band gap of 3.2 eV[3]. In this work, we added copper to titania to significantly improve the visible light photocatalytic activity.

Materials and methods:

Aniline, ammonium persulphate, sulphosalicylic acid, methylene blue (MB) were purchased from Qualigens. Tetraethyl ortho titanate, copper acetate from Merck were used as received. Aniline was distilled under reduced pressure before use. Double distilled water was used thoroughout the experiment.

Synthesis of PANI-TiO_2/Cu nanocomposite:

Titania was prepared by dropwise addition of ammonia to tetraethyl ortho titanate with vigorous stirring at room temperature, filtered, dried, and calcined at 400°C for 3 h. To the as-synthesized titania, 20% amount of copper acetate was added in double distilled water and stirred for 6 h, the precipitate formed was filtered, dried and calcined at 450°C for 2 h. PANI/TiO_2-Cu composite was prepared by taking the mixture of aniline (0.2 mL), desired amount TiO_2/Cu and sulphosalicylic acid (0.4 g) in 100 mL of double distilled water and stirred uniformly 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. The precipitate obtained was centrifuged, washed with distilled water and dried in vaccum for 24 h. The obtained nanocomposite was assigned as PTC.

The X-ray diffraction patterns were recorded using Rich Siefert 3000 diffractometer with Cu $K\alpha_1$, radiation (λ = 1.5406 Å) 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 the XRD of PTC composite, where TiO_2 exhibits peaks (2θ) at 25.3°, 37.8°, 48°, 54°, 55°, 62.7°, 68.8° corresponding to (101), (004), (200), (105), (211), (204), (116)

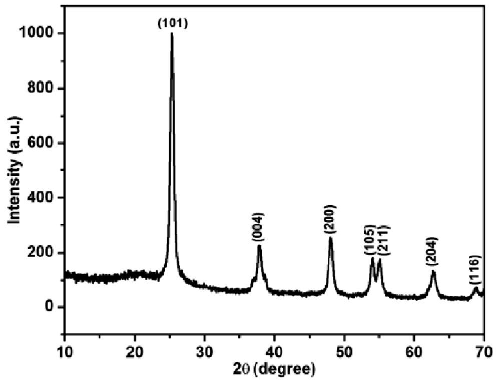

Fig. 1. XRD pattern of PANI modified TiO_2/Cu.

planes of tetragonal TiO_2 with (JCPDS file No. 21-1272) respectively. XRD of PANI shows broad amorphous peak at (2θ) 19.5° corresponds to periodicity parallel to polymer chain[7].

Fig. 2 shows the FT-IR spectrum of PTC, the main characteristic peaks of PANI are 1586 cm^{-1} (C=N for quinone ring), 1498 cm^{-1} (C=C for benzene ring), 1300 cm^{-1} (C-N stretching mode for benzene ring), 1143 cm^{-1} (quinonoid unit doped PANI) respectively[1]. Typically anatase TiO_2 shows the strong absorption band at 550–800 cm^{-1} corresponds to Ti-O-Ti stretching vibrations. The strong IR absorption peak at 3440 cm^{-1} attributes to hydrogen bonding interaction exist between PANI and titania[4]. The peak at 589 cm^{-1} indicates the formation of CuO[5,6].

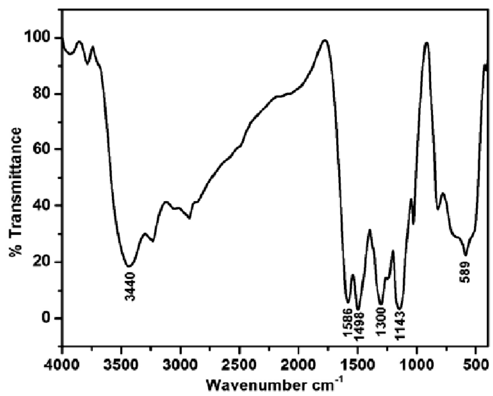

Fig. 2. FT-IR spectra of PANI modified TiO_2/Cu.

Fig. 3 shows the DRS UV-Vis diffuse absorbance spectra of the composite reveals two absorption peaks at 315 and 600 nm, which attributes $\pi \rightarrow \pi$ transition of the benzenoid rings and charge transfer from the benzenoid to the quinoid, respectively[7]. The band gap (E_g) was 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 band gap (E_g) value of the PTC is found to be 1.39 eV.

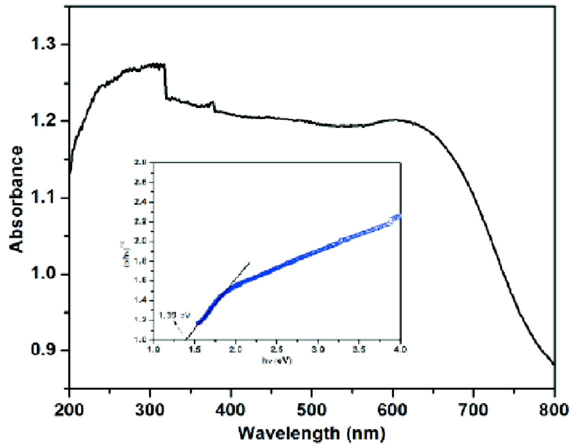

Fig. 3. DRS UV-Visible absorption spectra of PANI modified TiO_2/Cu. Inset: Tauc's plot of the composite.

The photocatalytic activity of the PTC 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 absorbance spectra of every 15 min withdrawn dye shows regular decrease in ab-

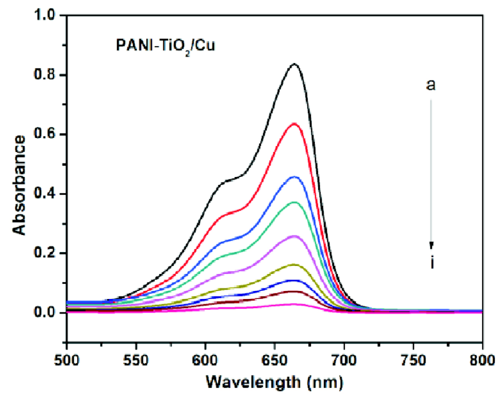

Fig. 4. UV-Vis spectra of aqueous MB at (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 75 min, (g) 90 min, (h) 105 min, (i) 120 min photodegradation using PTC photocatalyst.

sorption maximum at λ_{max} (λ = 663 nm) without any shift in the peak which implies the degradation is only due to the composite. For PTC the maximum absorbance value is 0.83 before the visible light irradiation and after 120 min the value decreased to 0.03, then continuous exposure to another 20 min did not show any futher decrease in absorbance.

Conclusions

PTC nanocomposite were synthesized by chemical oxidative polymerization method. Phase of CuO is absent in XRD, which was revealed through vibrational modes occurring in FTIR spectroscopy. The wide absorption band of PANI in the visible region easily allows charge transfer from HOMO to LUMO and then electrons are excited to conduction band of TiO_2. These electrons are trapped by oxygen/water molecules adsorbed on Cu/TiO_2 to yield superoxide and hydroxide radicals responsible for visible light photodegradation process.

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