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PHOTOCATALYTIC PROPERTIES OF POLYANILINE/TiO₂ NANOCOMPOSITE

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Abstract

Polyaniline/TiO₂ (PANI/TiO₂) nanocomposite was synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate (APS) in water, in the presence of colloidal TiO₂ nanoparticles of an average diameter ~5 nm. The resulting PANI/TiO₂ composite powder was used for photocatalytic degradation of methylene blue (MB). Its photocatalytic activity has been compared with activity of neat colloidal TiO₂ nanoparticles.

Introduction

TiO₂ is one of the most investigated semiconductors in the field of photocatalytic degradation of pollutants. Its high chemical stability, adsorption capability, photocatalytic efficacy for decomposition of organic compounds in air and water, relative low-price and nontoxicity are the reasons for such keen researcher's interest. However, the wide band gap of TiO₂ (3.2 eV) only allows it to absorb the photons of ultraviolet light (< 400 nm) that occupies only small fraction (< 5 %) of solar spectrum, which limits its wider use. One of the possible ways to utilize the broader part of the solar spectrum is sensitization of TiO₂ with a suitable sensitizer [1]. High absorption coefficients in the visible part of the spectrum, high mobility of charge carriers (consequence of the presence of extended π -conjugated electron systems) and good environmental stability of conductive polymers make them a good choice for TiO₂ sensitization. Moreover, many conductive polymers in their doped or undoped states are efficient electron donors and good hole transporters upon visible light excitation [2]. The subject of this work was in situ synthesis and characterization of PANI/TiO₂ nanocomposite. Its potential applicability as a photocatalyst was checked using a typical photodegradation reaction of methylene blue (MB) in a suspension. MB is a stable organic dye occasionally used as a model compound for estimation of activity of TiO₂ based photocatalysts, in reactions of photodegradation.

Experimental

Colloidal TiO₂ solution, containing nanoparticles of an average diameter ~5 nm, was prepared according to the procedure described elsewhere [3]. In a typical procedure for preparing PANI in the presence of TiO₂ nanoparticles, the aqueous

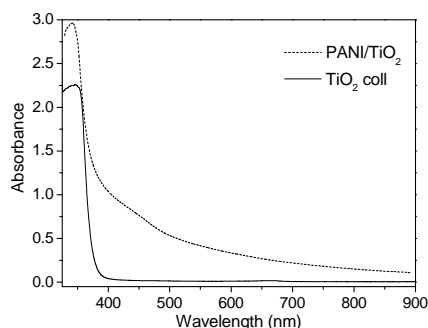


Fig.1. UV/vis absorption spectra of pure TiO_2 and PANI/ TiO_2 nanocomposite.

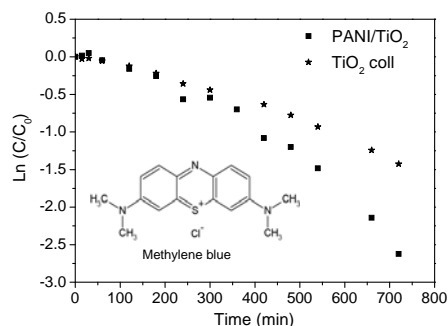


Fig.2. Kinetic plots of degradation of MB using neat TiO_2 and PANI/ TiO_2 nanocomposite as photocatalyst.

solutions of aniline, oxidant (APS), and colloidal TiO_2 were mixed at room temperature [4]. Initial mole ratio of aniline/ TiO_2 was 1:100. The reaction mixture was stirred for 20 days. In order to remove residual monomer, oxidant and low-molecular weight fractions, PANI/ TiO_2 composite was dialyzed in Milli-Q deionized water. Finally, the nanocomposite was dried in vacuum oven at 60°C until a constant mass was reached (~ 3 h). As a reference sample dry colloidal TiO_2 powder was used.

UV/Vis spectra of the samples were obtained using Evolution 600 spectrophotometer (Thermo Scientific).

The photocatalytic activities of the prepared samples were evaluated by the degradation of MB in aqueous solution. MB aqueous solution (50 ml) with concentration of $10 \text{ mg}\cdot\text{L}^{-1}$ was mixed with $1 \text{ g}\cdot\text{L}^{-1}$ catalyst (PANI/ TiO_2 or neat colloidal TiO_2). Suspensions were placed into quartz vessel which was exposed to light of Xenon lamp (300 W). Samples were saturated with air and stirred during the irradiation. Aliquots of 1 ml were taken out from the suspensions every 15 min during the irradiation. The photocatalyst was separated from the solution by centrifugation and absorbance intensity of the MB in the supernatant was measured at $\lambda=664 \text{ nm}$.

Results and Discussion

UV/Vis absorption spectra of the colloidal TiO_2 nanoparticles and PANI/ TiO_2 nanocomposite are shown in Figure 1. It can be seen that both TiO_2 nanoparticles and PANI/ TiO_2 nanocomposite absorb light below 400 nm. Above this wavelength only the nanocomposite absorbs light giving rise to a peak at 440 nm, which corresponds to PANI chains in emeraldine salt form [5]. In addition to the band at about 440 nm, ordinary conducting PANI emeraldine salt usually shows the band at $\sim 780 \text{ nm}$, both bands at ~ 440 and $\sim 780 \text{ nm}$ being connected with creation of polarons (radical cations) [5]. The absence of distinct band at $\sim 780 \text{ nm}$ in the UV-Vis spectrum of PANI/ TiO_2 could be result of partial deprotonation of PANI with water during the dialysis procedure, and reduced extent of delocalization of electrons in PANI.

Kinetic plots of photodegradation of MB, obtained using neat TiO₂ and PANI/TiO₂ nanocomposite as a photocatalyst, are presented in Figure 2. Direct photolysis of MB was also followed and it was less than 10% of the initial MB concentration. At the beginning of the photodegradation process, until about 300 min, both photocatalysts had almost the same efficacy. It can be observed that PANI/TiO₂ nanoparticles significantly enhance photocatalytic activity compared to bare colloidal TiO₂ nanoparticles for longer times of irradiation. This effect could be explained by enhanced absorption and synergistic effect between PANI and TiO₂ nanoparticles [2, 6].

Conclusion

PANI/TiO₂ nanocomposite has been in situ synthesized by the chemical oxidative polymerization of aniline with APS in colloidal TiO₂ solution without added acid. Obtained nanocomposite has enhanced absorption in visible part of spectrum, compared to neat colloidal TiO₂. PANI/TiO₂ nanocomposite was successfully applied for discoloration of methylene blue using whole spectral range of Xenon lamp (simulation of solar spectrum). Nanocomposite catalyst showed higher efficacy toward discoloration of MB compared to bare TiO₂, for longer irradiation times (> 300 min).

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