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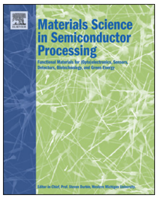

p-n heterojuction in organic (polyaniline)-inorganic (Ag_2CO_3) polymer-based heterojuction photocatalyst

A. Asadollahi, Sh. Sohrabnezhad*, R. Ansari*, M.A. Zanjanchi

Department of chemistry, Faculty of science, University of Guilan, P.O. Box: 41635-1914, Rasht, Iran

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ABSTRACT

Polyaniline (PANI), a conjugated polymer, was used as a support to produce heterojunctions with Ag_2CO_3. The synthesized Ag_2CO_3-PANI composite with simple precipitation method, was characterized by UV–visible diffuse reflectance spectroscopy (UV–Vis DRS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The optimum photocatalytic activity of Ag_2CO_3-PANI at a weight content of 50% PANI for the degradation of methylene blue (MB) was almost 86% that is much higher than the pure Ag_2CO_3 and PANI. The high visible light activity was mainly attributed to synergistic effects including the strong visible light absorption, the strong adsorption of MB upon the surface of PANI, high charge transfer and separation efficiency. to investigate stability, four cycle experiments on composite indicated the high photostability. Finally, a probable photocatalytic mechanism of charge transfer was proposed for the enhanced photocatalytic performance.

1. Introduction

The colored wastewater is the result of using the synthetic dyes as one of the most toxic pollutants generated by the textile industries. Due to the presence of complex aromatic ring(s) in the molecular structure of dyes, the degradation process for reactive dyes is really difficult. Thus, the reactive dyes are stable and non-biodegradable [1,2]. Various methods, such as biological treatment, coagulation/flocculation, ozonation, membrane filtration, electrochemical, photocatalytic degradation and adsorption, have been used for the removal of dyes from wastewaters [1,3]. Among the various techniques of dye removal, adsorption and photocatalytic degradation methods have been considered to be the most effective methods to the environmental problems [4,5]. Adsorption has been reported to be one of the most effective methods to remove classes of pollutants that is not easily degradable. This is an easy and cost-effective technique for purification. However, this method has disadvantages: it is a non-destructive process and it requires chemical modification [6,7]. The advanced oxidation processes like photocatalytic degradation methods have been used for remediation of wastewater. No sludge production, efficiency for recalcitrant dyes, low consumption of chemicals, relatively fast degradation rate and high mineralization efficiency are their advantages, but these processes may be formed by-products, they have technical constraints and cannot be used for all type of dyes [8]. Thus, combining these two methods can be used for the effective remediation of wastewater.

Silver compounds such as Ag_2CO_3, due to the remarkable surface plasmon resonance (SPR) effect of metallic silver nanoparticles, are a visible light photocatalyst [9–11]. However, the photocatalytic activities of silver compounds are reduced by photocorrosion of silver photocatalysts [12,13]. The formation of heterojunctions can change the direction of transportation, separation efficiency and recombination rate of charges [13–15].

Conjugated polymers such as polyaniline, polythiophene and polypyrrole have high absorption coefficients to absorb the visible light. These polymers can be excited upon visible-light and act as electron donors and hole acceptor. The conjugated polymers are also stable photosensitizers and can correct the wide band gap semiconductors. Polyaniline (PANI) is one of the most attractive conducting polymers due to its good stability, fascinating optical and electrical properties, low cost synthesis and nontoxicity, high absorption coefficients for numerous dyes, and high electron mobility (get easily excited under visible-light illumination) [16]. The heterojunctions photocatalyst due to have the appropriate optical and electrical properties, can increase the photocatalytic activity and the stability of the semiconductors. The various heterojunctions of PANI/semiconductor such as ternary titania–cobalt Ferrite–polyaniline [4], PANI nanotube@ TiO_2 composite [17], polyaniline/CdO nanocomposite [18], polyaniline/mesoporous Cu_2O nanocomposites [19] have been reported. These heterojunctions

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* Corresponding authors.
E-mail addresses: sohrabnezhad@guilan.ac.ir (S. Sohrabnezhad), ransari271@guilan.ac.ir (R. Ansari).

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can significantly increase the photocatalytic activity, compared with the single-component photocatalysts. PANI can be used not only as an appropriate adsorbent for the removal of dyes and metal ions in the separation and purification of systems but also as a support the immobilization of photocatalyst. It can increase the adsorption of pollutants on the photocatalyst [4,20]. Up to now, PANI and its composites have been explored for the removal of sulfonated dyes [21], chromium [22], acid green 25 [3], tartarazine [23], and methylene blue (MB) [7,24]. The synthesis of PANI and silver based photocatalysts (AgBr, AgCl and Ag_3PO_4) was reported [5,25,26] but there is no report on their application as a photocatalyst. Herein, Ag_2CO_3 and Ag_2CO_3-PANI were prepared via a simple precipitation method. The polymer based photocatalyst was used for the degradation of MB under visible light. The influences of support amount on the adsorption and photocatalytic activity are also investigated systematically. Finally, the possible photocatalytic mechanism is discussed in details.

2. Materials and methods

2.1. Materials

Ag_2CO_3 was synthesized from silver nitrate ($AgNO_3$) and sodium carbonate (Na_2CO_3) was used as a source of cation and anion sources, respectively. Aniline (An) monomer was purified by distillation and stored below 0–4 °C before polymerization. The used reagents were of analytical grade without any further treatment. The other reagent, including ammonium persulfate ($(NH_4)_2S_2O_8$, APS) was analytical grade regent. Hydrochloric acid and sodium hydroxide were used for the adjustment of the pH solutions. Methyleneblue (C.I. name: Basic Blue 9, $C_{16}H_{18}ClN_3S{:}3H_2O$), HCl and NaOH were analytical grade regents and were used as received.

2.2. Synthesis of Ag_2CO_3, PANI and Ag_2CO_3-PANI

The synthesis of Ag_2CO_3 was based on the literature [27]. PANI was prepared via chemical oxidative polymerization of aniline. To prepare PANI, 100 mL of freshly distilled aniline 0.2 M was taken in HCl 1 M solution and cooled up to 5 °C. Then, $(NH_4)_2S_2O_8$ (0.5 M) as the oxidant solution, was added into the mixture slowly, and the reaction was allowed to continue for 4 h at room temperature under stirring. The reaction mixture was remained for one hour. The blackish green precipitation was filtered, washed with distilled water and dried in an oven at 70 °C for 24 h [28].

The typical procedure for preparing Ag_2CO_3-PANI (50%) was as follows: initially, 0.1 g PANI was dispersed into 25 mL distilled water under ultrasonic condition for 5 min. Then, 0.12 g $AgNO_3$ was added to the suspension and was stirred for 1 h. The Na_2CO_3 solution (containing 0.038 g Na_2CO_3) was added dropwise into the mentioned suspension and stirred for 3 h. The precipitate was collected by centrifugation, thoroughly washed with distilled water and dried at room temperature. Accordingly Ag_2CO_3-PANI (20%, 30%, 40% and 60%) composites were prepared following the same method.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra were measured on a bruker spectrometer using KBr pellets. For each sample, 128 scans in the 4000–400 cm^{-1} spectral range were recorded with a resolution of 2 cm^{-1}. The powder X-ray diffraction patterns were recorded in a XRD Philips PW 1840 instrument, using Cu Kα radiation ($\lambda = 1.54$ Å), running at 40 kV and 30 mA, scanning from 10° to 70° (2θ) with a step size of 0.02 with a scan rate of $0.05^\circ\,s^{-1}$. The UV–Vis spectrophotometer (UV–Vis scinco 4100 spectrometer with an integrating sphere reflectance accessory) was used in the region of 330–950 nm to recording the UV–Vis diffuse reflectance spectra (DRS) of the prepared products. The UV–Vis absorption spectra were recorded using a CECIL CE3041 in the spectral range of 190–900 nm. The morphology and size of the as-synthesized products were characterized using scanning electron microscopy (SEM) on a JEM-100 CX microscope at 10 kV accelerating voltage.

2.4. Evaluation of photocatalytic activity of prepared PANI and Ag_2CO_3-PANI

The application of the as-prepared Ag_2CO_3-PANI (50%) photocatalyst to the degradation of MB was assessed under visible light by using 200 W tungsten filament Philips lamp ($\lambda > 400$ nm). For photodegradation of the MB, 50 mg of Ag_2CO_3-PANI (50%) photocatalyst were added into 50 mL of MB aqueous solution (50 ppm). Before the illumination, the suspensions were magnetically stirred in dark for 60 min to reach absorption-desorption equilibrium between the photocatalysts and MB. After the equilibrium, the analytical samples (volume of each is 3 mL) were taken at an interval of 15 min, centrifuged at 10,000 rpm for 5 min and filtered through a 0.22 μm Millipore filter to remove the remaining particles. As a comparison, the photocatalytic experiments of PANI and Ag_2CO_3 without catalysts were also performed when other conditions were the same. The removal efficiency was calculated with respect to the change in intensity of absorption peak at 664 nm (λ_{max} of MB). The value of percentage removal (%Removal) was calculated using the following equation [29]:

$$\%\text{Removal} = (c_0 - c_e)/c_0 \times 100 \tag{1}$$

3. Results and discussion

3.1. Characterization of structure of support, photocatalyst and composite

Fig. 1 represents the FT-IR spectra of the PANI doped with HCl and Ag_2CO_3-PANI (50%) composite. In Fig. 1 the absorption band at 1560 and 1472 cm^{-1} is assigned to C=N stretching vibration of a quinonoid ring and the C=C stretching vibration of a benzenoid ring, respectively [30,31]. The presence of the band in 1296 cm^{-1} and 1242 cm^{-1} are assigned to aromatic C–N stretching indicating secondary aromatic amine group and bipolar on structure related to the C-N stretching vibration, respectively. The absorption band at 1102 cm^{-1} is due to the C–H in plane bending vibration. The presence of the band appearing at 796 and 612 cm^{-1} is a characteristic of the C–H out of plane bending vibrations [31]. It was observed that after the formation of composite between Ag_2CO_3 and PANI, the absorption bands assigned to all vibrations have shifted to the higher wavenumbers: 1579, 1488, 1306, 827 and 624 cm^{-1}. These results indicated the hybridization of the Ag_2CO_3 and PANI. In addition, the absorption band in 1385 cm^{-1} was assigned to the presence of CO_3^{2-}.

The XRD patterns of PANI, Ag_2CO_3 and Ag_2CO_3-PANI composite are represented in Fig. 2. In the XRD pattern of the prepared PANI (Fig. 2A),

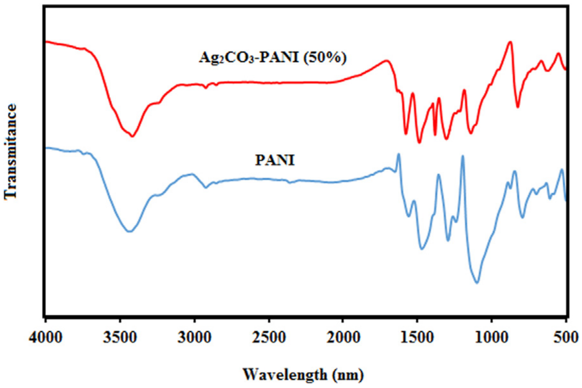

Fig. 1. FT-IR spectra of PANI and Ag_2CO_3-PANI (50%) composite.