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Highly efficient visible-light photocatalyst of nitrogen-doped TiO_2 nanoparticles sensitized by hematoporphyrin

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ABSTRACT

A novel hybrid nanocomposite based on N-doped TiO_2 nanoparticles was prepared and sensitized with hematoporphyrin for visible light utilization. The product was characterized by thermogravimetric analysis (TGA), different thermal analysis (DTA), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), BET surface area analysis, UV–vis spectroscopy and field emission scanning electron microscopy (FE-SEM). The results showed that the N-doped TiO_2 has smaller crystalline size and larger specific surface area than bare TiO_2 particles. Surface oxygen defects, produced by nitrogen doping, would improve the advantage of hematoporphyrin placement and then facile electron exciting and transferring to the conduction band of N-doped TiO_2. The crystal structure of N-doped TiO_2 was not affected by the sensitizing; however, the surface area was significantly increased. Application of the hybrid nanocomposite exhibited higher visible-light absorption leading to an enhancement of about 1.7 and 4.2 times in photocatalytic degradation of methyl orange compared with N-doped TiO_2 and just bare TiO_2 utilization, respectively. The photocatalytic degradation of methyl orange with the products was demonstrated to follow first order kinetic model. The produced nanocomposite can be reused at least four times recycling without significant loss of activity.

1. Introduction

Today, the presence of injurious organic pollutants in wastewaters has caused serious environmental problems and thereupon purification of contaminated water is one fascinating challenge [1]. Accordingly, use of renewable energy has become an interesting research area because of its sustainability and positive effect on environment and the limited utilization of fossil fuels [2,3]. Solar energy, because of its great availability, its cleanliness as well as easy operation and use, has become the first choice in the field of renewable energy sources [4,5].

Another matter of interest is utilizing efficient and selective metal oxide semiconductors in the process of the photocatalytic degradation of organic pollutants [6,7]. A well-known semiconductor is TiO_2 with excellent photocatalytic properties that make it highly valuable for the oxidation of organic pollutants. It is a superior photocatalyst for both purification of water and air due to its nontoxicity, long-term stability, inexpensiveness and chemical stability over a wide pH range and also in a large number of solvents [8,9].

One problem with pure TiO_2 nanoparticle is its large band gap energy that can be activated under UV light irradiation. However, this situation limits its application under direct solar light, as UV light accounts for only a small fraction (<5%) of the solar spectra compared to visible region (45%) [10]. In order to eliminate this drawback and enhance the visible region absorption of TiO_2, different approaches have been proposed in the literature. Since the discovery of activity of nitrogen-doped TiO_2 under visible light irradiation by Asahi et al. [11], great attention has been given to doping TiO_2 by nitrogen atom [12–15]. Insertion of N atom produces a localized energy state above the valence band of TiO_2, thus when N doped TiO_2 is exposed to visible light, electrons are transferred from these localized states to the conduction band [16]. Compared to the other non-metal dopants (S, P and C), N-doped TiO_2 materials represent a considerable photocatalytic activity and strong absorption under visible light irradiation [17,18]. Evidently, the mechanism of nitrogen doping to increase the visible-light absorption and photocatalytic activity of TiO_2 is different from that of dye sensitization. It is therefore, concluded that coupling of nitrogen doping with dye sensitization is a good way to significantly improve the visible-light absorption and photocatalytic activity of TiO_2.

The sensitization of TiO_2 by dyes such as ruthenium polypyridyl complexes [19], squaraines [20], porphyrins [21] and natural dyes [22] has been widely used for achieving desired electronic and

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optical properties. As a surface modification technology, dye sensitization can solve two major drawbacks of ultrafast recombination of photogenerated electron–hole pairs and a low quantum yield [5]. Highly efficient dye sensitizers should meet the following needs: (i) a wide range of absorption spectrum, intense substrate adsorption capacity efficiency; (ii) high quantum yield and excited states with long lifetime; and (iii) matching band structure to decline energy loss during the process of electron transfer [23–25]. Porphyrin and porphyrin derivatives, because of their strong light absorption in the region of 400–450 nm (Soret band), as well as 500 – 700 nm (Q band), are appropriate candidates for sensitizing different structures of TiO_2 semiconductors. One of porphyrin derivatives, hematoporphyrin (HP), is of natural origin derived from acid extraction of blood. The chemical structure of HP is similar to chlorophyll and the "hem" of hemoglobin, that are well known in nature [26]. HP consists of very large conjugated double bonds of tetrapyrrole, this extended conjugation leads to strong absorption of the visible spectrum with a thermal and photochemical stability. In this case, the sensitizer dye molecules bonded on the surface of TiO_2 can be excited by visible light and then the photoinduced electrons transfer into the conduction band (CB) of TiO_2 is facilitated. While CB injected electron reacts with acceptor molecules, i.e. with dissolved oxygen in solutions around TiO_2 surface and forming $O_2^{\bullet-}$ and $HO^{\bullet}$; the valence band (VB) remains unaffected [27,28]. The use of HP has been reported to meet the requirements relating to cost efficiency, non-toxicity and complete biodegradation.

In the present investigation, we present a novel hybrid nanocomposite, produced from N-doped TiO_2 nanoparticles and hematoporphyrin (HP/N-TiO_2). Nanoparticles of N-doped TiO_2 (N-TiO_2) are used as a matrix to prepare a dye-sensitized and visible-light active photocatalyst. The synthesized N-TiO_2 nanoparticles and the hybrid nanocomposite are then characterized by different techniques and the photocatalytic activity of the products are evaluated by the degradation rate of methyl orange (MO) as a model pollutant. Accordingly, the synergism effect of nitrogen doping and HP sensitizing is discussed.

2. Experimental

2.1. Materials

Sigma–Aldrich HP (≥45%) was used without further purification. The tetraisopropyl-orthotitanate (≥98%), urea (≥99.5%), ethanol (≥99.9%), acetyl acetone (≥99.0%), mannitol (≥99.0%) and methyl orange (C.I. 13025) were purchased from Merck and used as received without any further purification. Fresh deionized water was prepared from a deionizer apparatus (Hastaran Co.) and used in the preparation of solutions.

2.2. N-TiO_2 and HP/N-TiO_2 preparation

The nitrogen-doped titania, N-TiO_2, product were prepared by the sol–gel method. For this aim, tetraisopropyl-orthotitanate (2.5 mL) was slowly added to a mixture of anhydrous ethanol (20 mL) and acetyl acetone (2.5 mL) with stirring at room temperature. Acetyl acetone was used as chelating agent to prevent precipitation of the tetraisopropyl-orthotitanate. After stirring for at least 60 min, the clear and yellow solution was obtained. We then added 3.0 mL dioionized water and stirred the mixture for 30 min. A few drop of concentrated HCl solution was then added to the sol to adjust the pH at about 1.7. At the next step, urea (4.0 g) was dissolved in ethanol and then added to the above solution. The mixture was stirred for 180 min at room temperature. The final solution was left overnight to form a wet gel. The wet gel was dried at 60 °C and the resultant precipitate was ground in agate mortar. Finally the precursor was calcined at 550 °C for 1 h. The bare TiO_2 was also prepared using a similar method unless urea addition.

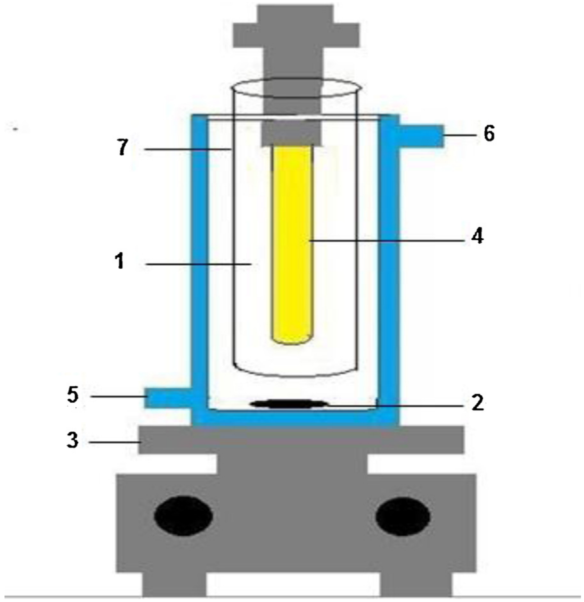

Fig. 1. Scheme of the used photoreactor; (1) dye solution; (2) magnetic stir bar; (3) magnetic stirrer, (4) visible lamp; (5) cooling water in; (6) cooling water out; (7) quartz tube.

The main product, HP/N-TiO_2 nanocomposite, was prepared in the way that the synthesized N-TiO_2 (1.0 g) was added into 3.0×10^{-3} M of HP solution in ethanol and the suspension was sonicated for 30 min. The mixture was stirred for 48 h at room temperature to obtain the absorption/desorption equilibrium. Finally, the solid was separated by centrifugation, washed several times with ethanol in order to remove the unloaded HP molecules and dried at room temperature. For the aim of activity comparison, HP/TiO_2 nanocomposite was also prepared by following the same procedure. The amount of adsorbed HP was estimated by measuring the concentration of the dyes desorbed from the N-TiO_2 surface which was attained by immersing 25 mg of the HP/N-TiO_2 samples into 5 mL of NaOH solution (0.1 M) [29,30]. The absorbance of the resulting solution was measured at HP maximum wavelength of 397 nm using a UV–vis spectrophotometer (Jasco-V630) and compared with reference solutions (HP concentrations of: 0.003, 0.006, 0.009 and 0.012 mM in 0.1 M NaOH solutions).

2.3. Products characterization and photocatalytic activity

The prepared xerogels were thermally analyzed in air by a PerkinElmer Pyris Diamond apparatus at a scanning rate of 5 °C/min. All samples were analyzed by a Structures-APD 2000 X-Ray Diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm) radiation in the 2θ range of 10–80°. The crystalline size of TiO_2 was determined according to the Scherrer equation using the full-width at half maximum (FWHM) of peak broadening. The FT-IR spectra were recorded on a PerkinElmer 65 spectrophotometer. Specific surface area of the sample was measured by BET method on Phschina 1020 at −196.15 °C nitrogen adsorption–desorption mode. The UV–vis spectra of TiO_2 samples in the 200–1100 nm were recorded. The morphology of hybrid nanocomposite was determined using Zeiss-Sigma field emission scanning electron microscopy.

Photodegradation of MO in the presence of photocatalyst products was examined in a Pyrex reactor with a magnetic stirring bar and water circulating jacket (Fig. 1). The visible light source