



Enhanced photocatalytic activity of sulfated silica-titania composites prepared by impregnation using ammonium persulfate solution

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ABSTRACT

Sulfate (SO₄²⁻) modified silica-titania (SiO₂-TiO₂) composite photocatalysts with different loadings of SO₄²⁻ were prepared by a facile pore impregnating method using ammonium persulfate (NH₄)₂S₂O₈ solution. The surface parameters, structure, morphology, the adsorption ability of light, the binding energy of Ti2p and O1s, and the formation rate of •OH radicals produced during the photocatalytic reaction process were characterized by the Brunauer-Emmett-Teller (BET) method, X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS) and terephthalic acid photoluminescence probing technique (TA-PL), respectively. The results reveal that sulfating of SiO₂-TiO₂ induces the shift of Ti2p and O1s, and increases the adsorption of rhodamine B on the sulfated photocatalysts and the formation rate of •OH radicals produced during the photocatalytic reaction process. The photocatalytic activity of SO₄²⁻/SiO₂-TiO₂ for de-colorization of rhodamine B aqueous solution was evaluated. The result shows that when wt% of SO₄²⁻ is 8.6%, SO₄²⁻/SiO₂-TiO₂ exhibits the best photocatalytic activity under ultraviolet light irradiation and the possible reason is discussed.

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1. Introduction

Studies demonstrate that most dyes are acutely toxic and difficult to biodegrade [1]. Dyes contaminants possess strong genotoxicity and can disrupt endocrine systems even at low concentrations, causing a major health concerns [2]. Dyes effluents can threaten the surrounding ecosystems, apart from the environmental pollution. Therefore, it is crucial to control the employment of these dyes and treat the effluents

before being released into the aquatic environment. Tremendous efforts have been devoted to cleaning dye wastewater, and methods such as activated sludge-based biological processes, coagulation/flocculation, adsorption, and ion exchange have been developed and widely used in this field [3]. However, these methods have low cost-effectiveness and may not eliminate the color completely [4]. So, the search of new treatment approaches with high efficiencies and low costs is still a hot topic.

Among these methods for treatment of dyes, photocatalysis has attracted increasing attention in recent years [5–9]. TiO₂, as one of the most investigated semiconductor photocatalysts, has been widely investigated recently as a

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useful material in the treatment of wastewater due to its appropriate band gap, strong oxidizing ability, long-term stability against photo-corrosion and chemical corrosion, low cost and facile preparation [10]. However, the high rate of recombination of photon-induced electron–hole pairs limits the practical application of TiO₂ materials [11]. Therefore, it is promising and indispensable to enhance photocatalytic efficiency of TiO₂. To date, much effort has been devoted to enhancing photocatalytic activity of TiO₂. Among these approaches, an effective and simple strategy is the modification of TiO₂ with sulfate. SO₄^{2−}/TiO₂ catalyst has been studied by many groups. Samantaray et al. prepared SO₄^{2−}/TiO₂ using (NH₄)₂SO₄ and H₂SO₄ as the source of sulfate [12]. The results demonstrate that complete decomposition of 4-nitrophenol (0.05 g/L) takes place using 0.6 g/L sulfated TiO₂ in 3 h. Fu et al. synthesized SO₄^{2−}/TiO₂ solid acids by reacting amorphous TiO₂ with H₂SO₄ at high temperature [13]. The high photocatalytic performance of SO₄^{2−}/TiO₂ is due to the improved surface acidities: the Lewis acidic sites could react with H₂O and were then converted to Brønsted acidic sites, leading to the activation of the water. Li et al. prepared an active SO₄^{2−}/TiO₂ photocatalyst for phenol degradation under supercritical conditions [14]. The results illustrate that SO₄^{2−}-modification through supercritical drying can enhance the quantum yield of the photocatalysis, since the recombination between the photo-induced electrons and holes is effectively inhibited. Yu et al. prepared TiO₂ thin films by sulfuric acid treatment [15].

Sulfuric acid treatment can enhance photocatalytic activity of thin films deposited on both glass and quartz. Swaminathan et al. prepared sulfate modified titania (TiO₂-SO₄^{2−}) by the sol–gel method using tetraisopropyl orthotitanate with sulfuric acid [16]. Sulfated titania is found to be more efficient than TiO₂-P25 in the degradation of reactive orange 4. Moreover, SO₄^{2−}/TiO₂ was used as a catalyst to synthesize organic compounds [17,18].

However, in photocatalysis field, the effects of formation rate of ·OH radicals and the loading of SO₄^{2−} on the photocatalytic performance of SO₄^{2−}/SiO₂-TiO₂ prepared by the pore impregnating method using ammonium persulfate have been seldom addressed. The objective of this work is to enhance the photocatalytic activity of SiO₂-TiO₂ by modification of SiO₂-TiO₂ using ammonium persulfate as the sulfate source. The photocatalytic performance was studied by de-colorization of rhodamine B aqueous solution under ultraviolet light irradiation.

2. Experimental section

2.1. Preparation of photocatalysts

All chemicals (analytical grade reagents) were supplied from Chengdu Kelong Chemical Reagent Factory and used as received. SiO₂-TiO₂ containing 16.6 mol% SiO₂ was fabricated according to the procedure given in Ref. [19]. First, 17.0 mL titanium tetrabutoxide was mixed with 5.1 mL acetylacetone and 10.0 mL anhydrous ethyl alcohol (forming Ti sols). Second, 2.25 mL tetraethyl orthosilicate was mixed with the solution containing 10.8 mL bi-distilled water, 23.9 mL ammonia water, and 20.0 mL

anhydrous ethyl alcohol under stirring (forming Si sols). In the final step, Ti and Si sols were added simultaneously and slowly into a beaker containing 10.0 mL anhydrous ethyl alcohol under stirring. Then the sample was aged for 72 h. Finally, the sample obtained was evaporated, dried, and annealed in air at 823 K for 5 h in a muffle furnace.

SO₄^{2−}/SiO₂-TiO₂ photocatalysts with different SO₄^{2−} loadings were prepared by a pore impregnating method using (NH₄)₂S₂O₈ solution. Briefly, 5 g as-prepared SiO₂-TiO₂ was put in a beaker; water was added to humidify SiO₂-TiO₂ (no water was observed on the surface of SiO₂-TiO₂) assisted by ultrasonication; the volume of water is the water pore volume of 5 g SiO₂-TiO₂. Desired (NH₄)₂S₂O₈ was dissolved in water (the water pore volume of 5 g SiO₂-TiO₂); then 5 g SiO₂-TiO₂ was added into (NH₄)₂S₂O₈ solution as mentioned above and ultrasonic dispersed for 20 min. After that, the mixture was kept in a static condition for 1 h, dried at 353 K for 1 h, and then dried at 373 K overnight. Finally, the powders were heated in air at 573 K for 2 h. In this way, SO₄^{2−} decorated SiO₂-TiO₂ photocatalysts with different wt% of SO₄^{2−} were prepared. The samples with different wt% of SO₄^{2−} (0%, 1.7%, 5.1%, 6.8%, 8.6% and 10.3%) were named 0%, 1.7%, 5.1%, 6.8%, 8.6% and 10.3%, respectively. SiO₂-TiO₂ was dealt with the same procedure as mentioned above also without the presence of (NH₄)₂S₂O₈.

2.2. Characterization of the photocatalysts

The specific surface area and pore size measurements were performed by an SSA-4200 automatic surface analyzer (Builder, China). The solid samples were evacuated at 523 K for 1 h, and then cooled to 77 K using liquid N₂ at which point N₂ adsorption was measured. X-ray diffraction (XRD) patterns were recorded on a DX-2600 X-ray diffractometer using Cu K α ($\lambda=0.15406$ nm) radiation and equipped with a graphite monochromator. The X-ray tube was operated at 40 kV and 25 mA. Samples were scanned from 2 θ equal to 10° up to 90° and the X-ray diffraction line positions were determined with a step size of 0.03°. The UV–vis diffuse reflectance spectroscopy was recorded using a TU-1901 UV–vis spectrophotometer equipped with an integrating sphere, and BaSO₄ was used as the reference. Scanning electron microscope (SEM) images were taken with a JSM-7500F scanning electron microscope (JEOL, Japan), using an accelerating voltage of 5 kV. Before SEM measurement, the sample was dispersed in water assisted by ultrasonication for 10 min and then gold plating was performed. Fourier-transform infrared (FT-IR) characterization was performed using an FT-IR spectrophotometer (NICOLET 6700, America) in KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements were performed by an XSAM 800 using Mg K α at 12 kV and 12 mA. The X-ray photoelectron spectra were referenced to the C1s peak ($BE=284.80$ eV) resulting from adventitious hydrocarbon (i.e. from the XPS instrument itself) present on the sample surface. The level of ·OH was detected by a photoluminescence (PL) technique using terephthalic acid (TA) as a probe molecule. The detailed experimental procedures have been reported in early reports [20]; 50 mg of photocatalyst was suspended in

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