



Phosphotungstic acid supported on magnetic core–shell nanoparticles with high photocatalytic activity



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ABSTRACT

$\text{Fe}_3\text{O}_4@SiO_2@HPW$ (12-tungstophosphoric acid) nanoparticles have been successfully obtained by a simple solvothermal and impregnation process. The as-obtained products were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), fourier transform infrared spectrum (FT-IR), inductively coupled plasma (ICP) and MPM5-XL-5 superconducting quantum interference device (SQUID). The results revealed that the heteropolyacids were successfully grown on the $\text{Fe}_3\text{O}_4@SiO_2$ nanoparticles. The photocatalytic studies suggested that the $\text{Fe}_3\text{O}_4@SiO_2@HPW$ nanoparticles show excellent photocatalytic efficiency for the degradation of Rhodamine B (RB) under UV light irradiation. More importantly, the obtained nanoparticles ($\text{Fe}_3\text{O}_4@SiO_2@HPW$) could be effectively separated for reuse by simply applying an external magnetic field. Furthermore, the synthesized nanoparticles could keep their efficiency till four cycles.

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1. Introduction

Nowadays, organic pollutants constitute an important family of pollutants of waste water produced by chemical, petrochemical, food-processing or textile industries. So photocatalysis becomes a hot topic of research for the elimination of toxic chemicals in the environment through its efficiency and broad applicability [1–12]. Due to very strong acidity, lower corrosivity and higher catalytic activity, heteropolyacids have already attracted extensive research as green catalysts [13–18]. 12-tungstophosphoric acid (HPW) is the strongest acid in the heteropolyacid series, thus it is particularly recommended. Because limited specific area (less than $10\text{ m}^2/\text{g}$) and lacking accessibility of surface active site, heteropolyacids are usually supported on solid supports such as silica, carbon, molecular sieve, clay, alumina, titania and

resin [18,19]. Among those, silica is the most frequently used support because of the relative inertness towards heteropolyacids [19]. Although the activity of heteropolyacids was enhanced after being supported on silica, the approach share the disadvantage that heteropolyacid was immobilized on powdery substrate. Hence, the approach still could not avoid the separation difficulty of photocatalyst. Nano-magnetic photocatalyst appears to be a promising material as it permits easy recovery by external magnetic field and keeps the advantage of high degradation efficiency.

Here, we report an attempt for supporting heteropolyacids by constructing the $\text{Fe}_3\text{O}_4@SiO_2@HPW$ nanoparticles. The photocatalytic activity of the $\text{Fe}_3\text{O}_4@SiO_2@HPW$ photocatalysts in the UV light region is investigated by measuring the degradation of RB. In this study, RB has been chosen as a model representative dye owing to its wide application in various industries. The experimental results showed that the as-obtained $\text{Fe}_3\text{O}_4@SiO_2@HPW$ photocatalysts exhibited excellent UV light photocatalytic activity.

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2. Materials and methods

2.1. Synthesis

2.1.1. Materials

All of the chemical reagents and solvents were analytical grade without any further purification. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate anhydrous, sodium citrate, tungstophosphoric acid (HPW), ethylene glycol, ethanol, nitric acid and ammonia solution (28 wt%) were supplied by Beijing Chemical Plant, China. Tetraethyl orthosilicate (TEOS) was purchased from Aladdin.

2.1.2. Synthesis of Fe_3O_4 particles

The magnetic particles were synthesized according to the method reported previously with some modification [20]. The magnetic Fe_3O_4 nanoparticles were prepared by a solvothermal method. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.08 g, 4.0 mmol), sodium acetate anhydrous (1.8 g, 21.9 mmol), and sodium citrate (0.25 g, 0.85 mmol) were dissolved in ethylene glycol (20 ml) with stirring. The mixture was stirred vigorously for 30 min and then transferred into a Teflon-lined stainless-steel autoclave. The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water three times and then dried in vacuum for 12 h at 60 °C.

2.1.3. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles

The core-shell structured $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres were prepared via a modified sol-gel process [21]. The obtained Fe_3O_4 particles (0.10 g) were well dispersed in the mixture solution of ethanol (40 ml), deionized water (10 ml) and concentrated ammonia aqueous solution (28 wt%, 1.2 ml) by ultrasonication for 1 h. Then, 0.35 ml of tetraethoxysilane (TEOS) was added dropwise to the solution. After stirred at room temperature for 2 h, the particles were separated by magnetic force and rinsed with ethanol and deionized water three times, dried at 60 °C for 12 h.

2.1.4. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HPW}$ particles

2.1.4.1. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HPW}$ particles by the impregnation method.

The $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HPW}$ 0.1 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HPW}$ 0.4 particles were prepared through a versatile impregnation method as follows. The $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles (0.2 g) and the aqueous of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.1 or 0.4 g, 20 ml) were prepared and stirred rapidly in a clean and new round-bottom flask for 24 h. Then, the precipitate was separated by magnetic force and washed three times with ethanol and dried at 60 °C for 12 h for further use.

2.1.4.2. Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HPW}$ particles by the sol-gel method for comparison.

The $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HPW}$ (sol-gel) 0.1 particles were prepared through a sol-gel method. In a typical experiment, with the catalysis of diluted nitric acid, TEOS was hydrolyzed in a mixture of 2.0 ml of TEOS, 6.0 ml of ethanol, and 8.0 ml of deionized water for 5 min at 70 °C, and the silica sol was obtained. 0.2 g of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles was redispersed in 50 ml of deionized water, then the resulted silica sol and the aqueous of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.1 g, 10 ml) were introduced to the magnetic suspension under agitation at 70 °C. 6 h

later, the product was separated by permanent magnet and washed with deionized water, thereafter dried at 60 °C for 12 h.

2.2. Photocatalytic test

The photoreactor was designed with an internal light source surrounded by a water-cooling quartz jacket (50 W high-pressure mercury lamp with main emission wavelength of 313 nm), where the suspension includes the nanoparticle catalyst (0.01 g) and the aqueous RB (100 ml, 10 mg L⁻¹) completely surrounding the light source. The solution was stirred in the dark for 30 min to obtain a good dispersion and reach adsorption-desorption equilibrium between the organic molecules and the catalyst surface. Decreases in the concentrations of dyes were analyzed by a UV-visible spectrophotometer (UV-2550) at $\lambda = 554$ nm. At given intervals of illumination, the samples (3 ml) of the reaction solution were taken out and centrifuged. Finally, the filtrates were analyzed.

2.3. Characterization

Transmission electron microscopy (TEM) was performed on JEM-3010 and scanning electron microscopy (SEM) was performed on JEOL JSM-6700F. X-ray diffraction (XRD) measurements were carried out using a D/max 2500 XRD diffractometer (Rigaku) with Cu K α line of 0.1541 nm. Fourier transform infrared (FT-IR) spectra were obtained using a Magna Model 560 FT-IR spectrometer with a resolution of 1 cm⁻¹. UV-2550 spectrophotometer was used to measure the UV-vis absorption spectrum of the solutions to monitor the concentration of RB at different time intervals. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loading in the support materials was determined on Perkin-Elmer Optima 3300DV by inductively coupled plasma emission spectroscopy (ICP). Magnetization measurements were performed on a MPM5-XL-5 superconducting quantum interference device (SQUID) magnetometer at 300 K.

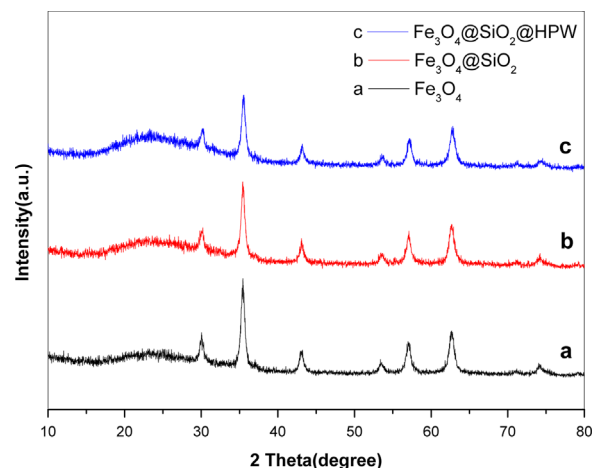


Fig. 1. Wide-angle XRD patterns of pure Fe_3O_4 (a), $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (b), and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{HPW}$ (c).

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