



Synthesis of long-lived photogenerated charge carriers of Si-modified α -Fe₂O₃ and its enhanced visible photocatalytic activity



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ABSTRACT

Si-modified α -Fe₂O₃ with small nanoparticle size has been synthesized by a simple one-pot water-organic separated hydrolysis-solvothermal method. It is demonstrated the modification with an appropriate amount of silicon obviously prolongs the lifetime and promotes the separation of photogenerated charge carriers of resulting α -Fe₂O₃, well responsible for the much high photocatalytic activity for degrading acetaldehyde and phenol under visible illumination compared with the unmodified one. It is suggested that the prolonged lifetime and promoted separation of photogenerated charges are attributed to the decreased nanocrystallite size and to the enhanced O₂ adsorption. Interestingly, the lifetime and separated situation of photogenerated charges of Si-modified Fe₂O₃ are further increased after thermal treatment at a proper high temperature, leading to the further enhancement of its visible photocatalytic activity. This mainly results from the increased crystallinity of Fe₂O₃ favorable to transport charge, and the slightly increased nanocrystallite size because of SiO₂ introduction.

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1. Introduction

Hematite (α -Fe₂O₃), as a kind of promising semiconductor oxide with virtues of peculiar and fascinating physicochemical properties such as low cost, nontoxic and high resistance to corrosion, has been intensively studied in photoelectrochemical (PEC) water splitting for sustainable hydrogen production as a popular solar fuel [1–8]. Simultaneously, Fe₂O₃ is also an attractive candidate for photocatalytic degradation of organic pollutants applied in water purification and air cleaning with favorable band gap of 2.0–2.2 eV for solar harvesting that allows to absorb up to 40% portion of the solar spectrum [9–14]. Unfortunately, the poor conductivity and extremely short hole diffusion length (~4 nm) hamper the charge transport in the semiconductor, increasing the probability of charge recombination [15], so that the photocatalytic activity of hematite frequently suffers from the high recombination rate of the photogenerated electron–hole pairs on the oxide surface so as to significantly restrict its practical applications [9,16,17]. Therefore, much ongoing effort is focused on addressing this problem by compositing Fe₂O₃ with other semiconductors [18–24], loading with noble metals [12,14,17], doping with metallic and non-metallic elements to promote the

separation of photogenerated carriers and then improve the performance of α -Fe₂O₃ [16,25–28].

Silica is considered to be a viable candidate for modification because of its relative ease in preparation, good environmental stability and compatibility with other materials. Up to now, previous studies have revealed that the size of Fe₂O₃ nanoparticles was partially controlled through confinement effects into silica mesopores, leading to the increased surface area [29,30]. Grätzel's group demonstrated that the introduction of a small amount of Si into the α -Fe₂O₃ film dramatically increased the photooxidation current, attributed to the reduced distance which the photogenerated hole had to travel to the electrode/solution interface. And, it was also proposed that a thin silica interfacial layer might be responsible for part of the gain in the film performance [31]. In addition, α -Fe₂O₃ nanoparticles dispersed on silica (Fe₂O₃/SiO₂) have also been prepared in parallel so as to minimize particle growth during the sintering process for photocatalytic degradation of dyes in an aqueous suspension under UV light irradiation, demonstrating that the rate constants of photocatalytic activity measured with Fe₂O₃/SiO₂ were larger than those obtained with Fe₂O₃ under similar conditions [32].

Nevertheless, the performance-enhanced mechanisms on the Si modification are not fully clear, which is generally because of lacking of direct evidences. And also, there are few investigations on the photocatalytic degradation of colorless organic pollutants of Si-modified Fe₂O₃ under visible light irradiation. Considering

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UV-active TiO₂, it is expected that the small nanoparticle size, large surface area and high crystallinity would be favorable for effective photocatalytic reactions. Therefore, it is of great significance to clarify the above-mentioned issues from the scientific or engineering points.

Herein, we try to synthesize Si-modified nanocrystalline α -Fe₂O₃ by a simple one-pot water-organic two-phase separated hydrolysis-solvothermal (HST) method developed previously in our group [33], and the effects of Si modification on the nanoparticle size and thermal stability of α -Fe₂O₃ are investigated in detail, along with their effects on the photocatalytic activity. In particular, the time-resolved surface photovoltage responses and atmosphere-controlled surface photovoltage spectra are employed to explore the photogenerated charge properties, further revealing the mechanism by which the visible photocatalytic activity of α -Fe₂O₃ is enhanced. This work would help us in-depth understand the fundamental physical and photoelectric properties of hematite, and provide us with a feasible way to modify oxide-based semiconductors for practical applications in the photocatalytic degradation of contaminants both in water and air.

2. Experimental

All of the reagents were of analytical grade and used as received without further purification, and deionized water was employed throughout.

2.1. Synthesis of materials

Fe₂O₃ nanoparticles have been synthesized by the hydrolysis-solvothermal (HST) method, using Fe(NO₃)₃·9H₂O and *n*-butanol as Fe resource and organic solvent, respectively [33]. For Si-modified Fe₂O₃, a desired amount of Si is introduced into the organic solvent in advance. A 30 mL of Teflon lined stainless-steel vessel, in which a 10 mL of weight bottle is installed to contain the organic butanol, is used as the reaction device to carry out the HST experiment. In a typical process, 10 mL of water phase containing 0.5 mL ammonia and 8 mL of *n*-butanol phase containing 0.8 g Fe(NO₃)₃·9H₂O and a desired amount of tetraethoxysilane (TEOS) [(C₂H₅O)₄Si] are placed in the device separately. Then, the sealed device is kept at 140 °C for 6 h, followed by naturally cooling to room temperature. The resulting Fe₂O₃ is collected in the *n*-butanol and subsequently washed thoroughly with distilled water and absolute ethanol in turn, and then dried at 80 °C in air. After thermal treatment at a certain temperature for 1 h, un-modified and Si-modified nano-sized Fe₂O₃ are obtained. The resulting un-modified and Si-modified samples are defined as XSF-Y, in which S means Si, F is used to represent Fe₂O₃, X is the molar percentage ratio of Si to Fe, and Y is the thermal treatment temperature.

2.2. Characterization of materials

The samples were characterized by X-ray Powder Diffraction (XRD) with a Rigaku D/MAX-rA powder diffractometer (Japan), using Cu K α radiation ($\lambda = 0.15418$ nm), and an accelerating voltage of 30 kV and emission current of 20 mA were employed; The morphology of the samples was studied with a JEOL JEM-2010 EX transmission electron microscope (TEM) operated at 200 kV accelerating voltage; The UV-vis diffuse reflectance spectra (DRS) was tested by a Model Shimadzu UV-2550 spectrometer; The specific surface areas of the samples were measured with Brunauer-Emmett-Teller (BET) instrument (Micromeritics automatic surface area analyzer Gemini 2360, Shimadzu), with nitrogen adsorption at 77 K. The Fourier transform infrared spectra (FT-IR) of the samples were recorded with a Bruker Equinox 55 Spectrometer, using KBr as diluents; The X-ray photoelectron

spectroscopy (XPS) was performed by a Kratos-AXIS ULTRA DLD apparatus with Al (Mono) X-ray source to gain further insight into the surface composition and elemental chemical state of the samples, and the binding energies were calibrated by using the signal for adventitious carbon (binding energy = 284.6 eV) as reference.

The surface photovoltage spectroscopy (SPS) measurements of samples were carried out with a home-built apparatus that had been described elsewhere in detail [34–36]. The powder sample was sandwiched between two ITO glass electrodes under different atmosphere conditions, such as O₂, N₂ and air, by holding the testing electrodes in a sealed container. The change in the surface potential barrier of the sample between in light and in dark contributes to the SPS signal; The time-resolved surface photovoltage (TPV) measurements were performed with a self-assembled device in air atmosphere at room temperature [33], in which the sample chamber was connected to an ITO glass as the top electrode and to a steel substrate as the bottom electrode, and a 10 μ m thick mica spacer was placed between the ITO glass and the sample to decrease the space charge region at the ITO-sample interface. The samples were excited by a 532 nm-laser radiation with 10 ns pulse width from a second harmonic Nd:YAG laser (Lab-130-10H, Newport, Co.). The laser intensity was modulated with an optical neutral filter and measured by a high energy pyroelectric sensor (PE50BF-DIF-C, Ophir Photonics Group). The TPV signals were registered by a 1 GHz digital phosphor oscilloscope (DPO 4104B, Tektronix) with a preamplifier.

In order to probe the interaction of O₂ with oxide surfaces, temperature programmed desorption (TPD) of oxygen was conducted in a flow apparatus described in our previous report [36]. 50 mg of the sample powder was pretreated at 275 °C for 30 min in a 20 mL/min of ultra-high-purity He flow. Then, the temperature was cooled to 25 °C. After that, the sample continuously adsorbed O₂ for 90 min at 25 °C. Finally, the O₂-TPD profile of the sample was recorded by increasing the temperature from 25 °C to the desired temperature at a heating rate of 10 °C/min under 20 mL/min of He flow. The desorbed O₂ amount was detected by a gas chromatograph (GC-2014, Shimadzu) with a TCD detector.

2.3. Photocatalytic activity evaluation of materials

The activities of the samples were evaluated by photodegradation of gas-phase acetaldehyde and liquid-phase phenol under visible light irradiation, respectively. Photocatalytic degradation of gas-phase acetaldehyde was conducted in 640 mL of cylindrical quartz reactor with 3 mouths for introducing desired amount of photocatalyst powders and planned concentration of acetaldehyde gas. The reactor was placed horizontally and irradiated from the top side by using a 150 W GYZ220 high-pressure Xenon lamp made in China with a cut-off filter ($\lambda > 420$ nm). In a typical photocatalytic process, 0.15 g of photocatalyst was placed in a pre-mixed gas system containing 810 ppm of acetaldehyde, 20% of O₂, and 80% of N₂. To reach adsorption saturation, the mixed gas continuously moved through the reactor for 0.5 h prior to the irradiation. The determination of acetaldehyde concentrations at different time intervals in the photocatalysis were performed with a gas chromatograph (GC-2014, Shimadzu) equipped with a flame ionization detector.

The liquid-phase phenol photocatalytic experiments were carried out in a 100 mL of open photochemical glass reactor equipped with an optical system provided from a side of the reactor by using a 150 W high-pressure Xenon lamp with a cut-off filter ($\lambda > 420$ nm), which was placed at about 10 cm from the reactor. During the evaluation of photocatalytic degradation of phenol, 0.15 g of photocatalyst was dispersed in 60 mL of 10 mg L⁻¹ phenol solution, and then stirring for 2 h under visible

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