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Photocatalytic, Fenton and photo-Fenton degradation of RhB over Z-scheme g-C_3N_4/$LaFeO_3$ heterojunction photocatalysts

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ABSTRACT

Z-scheme g-C_3N_4/$LaFeO_3$ heterojunction photocatalysts were prepared by calcining the uniformly mixed g-C_3N_4 nanosheets and $LaFeO_3$ nanoparticles at 300 °C for 1 h. The as-prepared g-C_3N_4/$LaFeO_3$ composites were systematically characterized by XRD, SEM, TEM, XPS, UV–vis DRS, PL spectroscopy, EIS and photocurrent response. It is demonstrated that $LaFeO_3$ nanoparticles (average size: ca. 35 nm) are uniformly assembled onto the surface of g-C_3N_4 nanosheets through chemical bonding, leading to the formation of g-C_3N_4/$LaFeO_3$ heterojunctions. The photocatalytic, Fenton and photo-Fenton performances of the samples were investigated by degrading RhB using simulated sunlight as the light source. Compared to bare $LaFeO_3$ and g-C_3N_4, the g-C_3N_4/$LaFeO_3$ composites exhibit significantly enhanced photocatalytic and photo-Fenton degradation of the dye, and the maximum activity is observed for the 15%g-C_3N_4/$LaFeO_3$ composite. Moreover, the photo-Fenton performance of the composites is much higher than the photocatalytic or Fenton performances. The much improved photo-fenton activity is ascribed to the efficient separation of photogenerated electron-hole pairs due to the Z-scheme electron transfer and the synergistic effect between $LaFeO_3$ and g-C_3N_4. •OH radicals were examined by PL spectroscopy using TPA as a probe molecule, clearly revealing the •OH generation, and moreover, the •OH yield and the dye degradation rate show a similar variation between different cases of the catalysis process. This suggested that •OH is the dominant reactive species causing the dye degradation. The underlying photo-Fenton mechanism of the composites is discussed.

1. Introduction

In recent decades, perovskite-type oxides have been received great attention due to their potential application to deal with the two urgent problems of energy shortage and environmental pollution [1–6]. Perovskite-type oxides have the general formula ABO_3 (where A is a rare-earth or alkaline-earth metal element and B is a transition metal element). Due to their unique crystal structures and strong electron-electron interactions, perovskite-type oxides take on a rich variety of physicochemical properties such as catalytic, electrical, magnetic and optical properties. In particular, perovskite-type oxides generally have a relatively narrow bandgap and can efficiently absorb visible light, and moreover they are advantaged by good chemical stability and flexible synthesis. These make perovskite-type oxides attractive as efficiently visible-light-responsive photocatalysts for the degradation of organic pollutants and hydrogen evolution from water splitting. However, the shortcoming of most of the perovskite-type oxides is the high recombination rate of photogenerated electron-hole (e^--h^+) pairs. Therefore, it is indispensable to reduce the unfavorable electron-hole recombination process for enhancing the photocatalytic activity. Numerous strategies have been developed to improve the photocatalytic activity of perovskite-type oxides, such as doping with impurity elements [7,8], construction of heterojunction composites [9,10], decoration with noble metals [11,12] and creation of lattice defects [13,14].

It is well known that, among various wastewater treatment technologies, advanced oxidation processes (AOPs) (such as ozone-based oxidation, electrochemical oxidation, sonochemical oxidation, photocatalytic oxidation and Fenton/photo-Fenton oxidation) have been considered as a high-efficiency and low-cost technology to eliminate organic pollutants [15–20]. As one of the AOPs, Fenton or Fenton-like oxidation technology is particularly attractive, which is mainly based on the generation and utilization of hydroxyl (•OH) radical as the oxidizing agent. The •OH radical is a very powerful oxidizing agent, capable of indiscriminately oxidizing and degrading organic pollutants into harmless inorganic substances. However, the traditional homogeneous Fenton process has some drawbacks including narrow working pH range (pH 2–4), generation of iron sludge, catalyst loss in the effluent

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and treatment of secondary pollution from acid or metal ions [21]. Heterogeneous Fenton oxidation has been developed to overcome these problems existing in the homogeneous Fenton process. Moreover, when the heterogeneous Fenton system is irradiated with ultraviolet (UV) or visible light, it brings about a synergistic effect between Fenton oxidation and photocatalysis, and as a result, the photo-Fenton process is much more effective for the oxidative degradation of organic pollutants than Fenton oxidation or photocatalysis. Recently, it was continuously reported that iron-based oxides exhibited great photo-Fenton performance, such as $BaFe_{12}O_{19}$/g-C_3N_4 [22], Fe_3O_4/C/Cu_2O [23], and yolk-shell structured Fe_3O_4/void/TiO_2 [24]. More importantly, the formation of heterojunctions in these composites can facilitate the separation of photogenerated electron-hole pairs and induce the synergistic effect between iron-based oxide and another semiconductor. This offers a promising strategy for the further improvement of photo-Fenton performance. Among various perovskite-type oxides, $LaFeO_3$ has been increasingly studied not only due to its photocatalytic activity but also due to its Fenton or photo-Fenton performance [25–29]. Wang et al. [30] immobilized $LaFeO_3$ nanoparticles on carbon spheres to achieve an excellent photo-Fenton performance, much higher than the photocatalytic performance. In our previous study, we found that the photocatalytic performance of $LaFeO_3$ nanoparticles can be significantly enhanced by the decoration of Ag nanoparticles [31].

Graphite-like carbon nitride (g-C_3N_4), being a metal-free polymeric semiconductor with relatively small bandgap energy of ca. 2.8 eV, has been shown to be a very promising visible-light-responsive photocatalyst [32]. g-C_3N_4 has a sufficiently negative conduction band (CB) edge potential of ca. -1.2 V *vs* normal hydrogen electrode (NHE), endowing it with a strong photocatalytic reduction capability. Moreover, g-C_3N_4 exhibits a good thermal and chemical stability, and can be simply and cheaply prepared by heating carbon- and nitrogen-containing organic precursors such as urea, melamine, cyanamide, dicyandiamide and thiourea. Due to these outstanding properties, g-C_3N_4 has been extensively studied for the photocatalytic hydrogen generation from water splitting, reduction of carbon dioxide into useful fuels and removal of environmental pollutants [33–35]. Further, two-dimensional (2D) g-C_3N_4 nanosheets have large specific surface area and abundant surface groups, which makes g-C_3N_4 nanosheets especially suitable to incorporate with other semiconductors to form heterojunction composite photocatalysts with much enhanced photocatalytic performances [36–42]. Very recently, several research groups reported the construction of g-C_3N_4/$LaFeO_3$ heterojunction composites and found that they showed enhanced photocatalytic degradation of dyes and photocatalytic water splitting into hydrogen [43–47]. However, there is no work concerned with the Fenton or photo-Fenton performances of g-C_3N_4/$LaFeO_3$ heterojunction composites. In this work, we attempted to prepare Z-scheme g-C_3N_4 nanosheets/$LaFeO_3$ nanoparticles heterojunction composites via a simple mixing–calcining method, and systematically and comparatively investigate their photocatalytic, Fenton and photo-Fenton performances toward the degradation of rhodamine B (RhB). The underlying photo-Fenton synergistic reaction mechanism was discussed.

2. Experimental

2.1. Preparation of g-C_3N_4/$LaFeO_3$ heterojunction composites

The preparation of g-C_3N_4/$LaFeO_3$ composites was accomplished in three steps. The first step was to prepare $LaFeO_3$ nanoparticles via a polyacrylamide gel route. Stoichiometric amount of $La(NO_3)_3$ (0.0075 mol), $Fe(NO_3)_3$ (0.0075 mol), citric acid (0.0225 mol), glucose (20 g) and acrylamide (0.135 mol) were successively dissolved in 20 mL of dilute nitric acid solution (5 mL HNO_3 + 15 mL deionized water) under continuous stirring using a magnetic bar. The mixture solution was added with deionized water to make a total volume of 100 mL and heated at 80 °C for 4 h, during which time a gel was formed. The gel was dried in a thermostat drier at 120 °C for 24 h, and then calcinated in a tubular furnace at 500 °C for 3 h, yielding final $LaFeO_3$ nanoparticles. The second step was to prepare g-C_3N_4 nanosheets by directly heating melamine in a semiclosed system. 5 g of melamine was loaded in a corundum boat with a cover, and submitted to calcination in a tube furnace at 520 °C for 4 h. The obtained product was ground and collected as g-C_3N_4 nanosheets. The third step was to prepare g-C_3N_4/$LaFeO_3$ heterojunction composites. Stoichiometric amount of g-C_3N_4 and $LaFeO_3$ were ground together in an agate mortar for 1 h, and then submitted to heat treatment in a tubular furnace at 300 °C for 1 h. The product was collected as final g-C_3N_4/$LaFeO_3$ heterojunction composite. By varying the mass fraction of g-C_3N_4 in the composite from 10% to 20%, several composite samples of 10%g-C_3N_4/$LaFeO_3$, 15%g-C_3N_4/$LaFeO_3$ and 20%g-C_3N_4/$LaFeO_3$ were prepared.

2.2. Sample characterization

The crystal phase of the as-prepared samples was determined by x-ray powder diffraction (XRD) using Cu Kα radiation with wavelength of $\lambda = 0.15406$ nm on a D8 Advance x-ray diffractometer. A JSM-6701F field-emission scanning electron microscope (SEM) and a Tecnai G2 20 field-emission transmission electron microscope (TEM) were used to characterize the morphology, microstructure and chemical composition of the samples. The chemical states and composition of the samples were measured by x-ray photoelectron spectroscopy (XPS) on a Thermo Scientific Escalab 250Xi x-ray photoelectron spectrometer. The optical absorption and bandgap energy of the samples was investigated by ultraviolet-visible diffuse reflectance spectroscopy (UV–vis DRS) using $BaSO_4$ as the reference on a TU-1901 double-beam ultraviolet-visible spectrophotometer with an integrating sphere attachment. The photoluminescence (PL) spectra of the samples were measured on a LS-55 fluorescence spectrophotometer with the excitation wavelength of 315 nm.

2.3. Photoelectrochemical measurement

The separation and transfer behavior of photogenerated electrons and holes in the samples was investigated by photocurrent response and electrochemical impedance spectroscopy (EIS) on a CorrTest CST 350 electrochemical workstation. The photoelectrochemical measurements were carried out using a three-electrode cell configuration consisting of a working electrode, a platinum foil counter electrode and a standard calomel electrode (SCE) reference electrode. The working electrode was prepared by mixing together 15 mg of the photocatalyst ($LaFeO_3$ or 15%g-C_3N_4/$LaFeO_3$), 0.75 mg of carbon black and 0.75 mg of polyvinylidene fluoride (PVDF) using 1-methyl-2-pyrrolidione (NMP) as solvent to form uniform slurry. The slurry was uniformly coated onto fluorine-doped tin oxide (FTO) glass substrate with an effective area of 1×1 cm^2, followed by drying at 60 °C for 5 h in a thermostat drying oven. 0.1 mol L^{-1} Na_2SO_4 aqueous solution was used as the electrolyte. A 200 W xenon lamp was used as the simulated sunlight source. The transient photocurrent response was measured at a bias potential of 0.2 V. The EIS measurement was carried out by the use of the sinusoidal voltage pulse with amplitude of 5 mV over a frequency range of 10^{-2}–10^5 Hz.

2.4. Photocatalytic test

RhB in aqueous solution was chosen as the target organic pollutant to evaluate its photocatalytic degradation, Fenton degradation and photo-Fenton degradation behaviors over $LaFeO_3$ and g-C_3N_4/$LaFeO_3$ samples. A 200 W xenon lamp was used as the simulated sunlight source to evaluate the photocatalytic activity of the samples. In a typical photocatalytic experiment, 50 mg of the photocatalyst and 100 mL of RhB solution with concentration of 10 mg L^{-1} were loaded into the photoreactor. The mixture was magnetically stirred for 30 min in the