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Coupling of photodegradation of RhB with photoreduction of CO_2 over rGO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ catalyst: A strategy for one-pot conversion of organic pollutants to methanol and ethanol

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ABSTRACT

For the first time, a novel strategy is developed to couple photocatalytic oxidation with photocatalytic reduction to achieve one-pot conversion of rhodamine (RhB) to methanol and ethanol by using rGO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ photocatalyst. In the approach, RhB was photocatalytically degraded to CO_2 and water, and then the as-obtained CO_2 was converted into CH_3OH and C_2H_5OH by means of photocatalytic reduction under simulated sunlight irradiation. Photocatalytic experimental results show the 1%rGO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ has the best photocatalytic activity among the as-prepared catalysts and the corresponding product rate of CH_3OH and C_2H_5OH is 10.76 and 6.14 μmol g^{-1} h^{-1}, respectively, with a 1.53% apparent quantum efficiency. Furthermore, a photocatalytic mechanism was proposed to explain the detailed process of one-pot conversion of RhB into hydrocarbons. The present work gives a good example to combine the photodegradation of RhB with photoreduction of CO_2 and proposes a new method to simultaneously tackle the problems of environmental pollution and energy crisis.

1. Introduction

The large amount of discharged wastewater and increasing emissions of greenhouse gases have led to severe threats on human beings. Till now, interest has been increasingly focused on developing new technology for simultaneous treatment of wastewater and better use of CO_2. Photocatalytic technology has developed rapidly since Fujishima and Honda first discovered the photocatalytic splitting of water on TiO_2 electrodes under ultraviolet irradiation in 1972 [1]. In recent decades, there have been a very large number of reports on photocatalytic degradation of organic pollutants from wastewater and photocatalytic reduction of carbon dioxide [2–4]. Photocatalytic degradation of organic pollutant is a process of photocatalytic oxidation but CO_2 reduction is that of photocatalytic reduction. If we can combine photocatalytic oxidation with photocatalytic reduction, the quantum efficiency and the separation efficiency of photo-generated holes and electrons will be markedly improved, which results in excellent degradation of organic pollutants and high output of useful hydrocarbons. However, to the best of our knowledge, there are few reports on one-pot conversion of organic pollutants into useful organic compounds (such as methanol and ethanol). Thus, it is urgent to prepare a kind of feasible, effective and stable photocatalyst to achieve this one-pot conversion of organic pollutants into useful hydrocarbons by coupling photocatalytic degradation of organic pollutants with photocatalytic reduction of CO_2.

Wide band gap semiconductor of $SrTiO_3$ is a good photocatalyst because its minimum of conduction band (CB) is more negative than the CO_2 reduction potential and the maximum of valence band (VB) is more positive than the oxidation potentials of many organic pollutants, so in theory, $SrTiO_3$ can achieve the above one-pot conversion [5–8]. However, the band gap of $SrTiO_3$ is 3.2 eV, which seriously restricts its efficiency of visible light absorption. In order to effectively extend the visible light response of $SrTiO_3$, transition metals doping (such as Fe, V and Mn) and formation of heterostructure with narrow band gap semiconductors have been extensively investigated [9–11]. Graphene is widely

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used to combine with semiconductors due to its large specific surface areas, extraordinary electronic mobility and good visible light absorption and stability [12,13]. In addition, previous studies have demonstrated the enhanced degradation of organic contaminants and good photocatalytic activity of hydrogen evolution from water splitting by using graphene-based semiconductors [14–17].

Therefore, in order to effectively fulfil the one-pot conversion of organic pollutants to useful hydrocarbons, we tried to prepare photocatalysts of rGO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ via combining Fe-doping and graphene loadings. The as-obtained 1%rGO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ catalyst exhibits good photocatalytic performance of one-pot conversion of RhB to useful hydrocarbons with a product rate of CH_3OH and C_2H_5OH of 10.76 and 6.14 $\mu mol\ g^{-1}\ h^{-1}$ (with quantum efficiency of 1.53%), respectively. This work provides an ideal scenario that couples the photodegradation of organic pollutants with photoreduction of CO_2 and opens a new avenue to realize the degradation and recycling of organic pollutants.

2. Experimental section

2.1. Materials and chemicals

Strontium nitrate ($Sr(NO_3)_2$) were bought from Aladdin Chemistry Co. Ltd. (Shanghai, China). Iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), Citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) and Ethylene glycol were obtained from Shantou Xilong Chemical Co., Ltd. (Shantou, China). Tetra-*n*-butyl titanate was attained from Shanghai KEFENG Chemical Reagent Co., Lnc. Rhodamine B (RhB) was provided by Shanghai Chemical Technology Co., Ltd. (Shanghai, China).All the reagents were of analytical grade and used without further purification. Deionized water was further purified using a Milli-Q water system (Bedford, USA).

2.2. Syntheses

2.2.1. Syntheses of $SrTi_{1-x}Fe_xO_{3-\delta}$

All of the reagents used in the experiments are analytic grade and used without further purification. The $SrTi_{1-x}Fe_xO_{3-\delta}$ powders (x = 0.02, 0.05, 0.1 and 0.15) were synthesized by a modified sol-gel method similar to that reported by Subramanian et al. [18]. In a typical procedure, $Sr(NO_3)_2$ (0.01 mol) and stoichiometric amounts of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in citric acid (CA) solution under magnetic stirring to obtain a transparent aqueous solution. Then a mixture of tetrabutyltitanate and ethylene glycol (EG) (3.35 mL) was added to the above solution. The iron and titanium precursors were stoichiometrically added to keep the molar ratio of Sr to (Fe + Ti) at 1:1. The mixture was stirred until the solution turned transparent and clear. Then the solution was kept at 80 °C under stirring until the wet gel was formed. The wet gel was dried at 110 °C for 10 h. Finally, the dry gels were calcined at 350 °C for 5 h and then at 900 °C for 10 h in air. Pure $SrTiO_3$ was also prepared with the same process except for the addition of $Fe(NO_3)_3 \cdot 9H_2O$.

2.2.2. Syntheses of rGO/$SrTi_{0.95}Fe_{0.05}O_3$

rGO/$SrTi_{1-x}Fe_xO_3$ composites were prepared by a simple hydrothermal method similar to that reported in the literature. [19]. In a typical procedure, 0.8 mL GO (3.7 mg/mL) was dissolved in 16 mL deionized water by ultrasonic treatment for 30 min (Biosafer 900-92), then 0.296 g $SrTi_{0.95}Fe_{0.05}O_3$ was added to the obtained GO solution and stirred for 30 min to get a homogeneous suspension. Finally, the suspension was placed in a 50 mL Teflon-lined autoclave and maintained at 180 °C for 12 h to obtain the1% reduced GO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ (1%rGO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$) composite. The solids were obtained via centrifugation and washed with deionized water for several times, and then grounded into fine powder prior to characterization and photocatalytic experiments. The samples of 0.75%rGO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ and 2.5%rGO/$SrTi_{0.95}Fe_{0.05}O_{3-\delta}$ were prepared by the same process by using the GO amount of 0.6 mL and 2.0 mL, respectively.

2.3. Characterizations

The crystal phase was determined with a Bruker D8 Advance X-ray diffractometer (Cu Kα radiation, λ = 1.5406 Å in a 2θ range from 10° to 70° at room temperature with a scanning speed of 2°/min). The morphology and structure were studied with a field-emission scanning electron microscope (SEM, Sirion 200, FEI, Holland) and transmission electron microscope (TEM, Tecnai F20, FEI, USA) and high resolution transmission electron microscopy (HRTEM). Optical properties were analyzed using UV–vis diffuse reflectance spectra (DRS, Varian Cary 300) and photoluminescence spectra (F-7000, Hitachi, Japan) at room temperature. Raman spectra were recorded on a microscopic confocal Raman spectrometer (JY LabRam HR800) with a laser source of 785 nm for excitation. Composition analyses on several randomly selected samples of the as-prepared catalysts were performed on a field-emission scanning electron microscope equipped with an energy dispersive X-ray instrument (EDX). X-ray photoelectron spectroscopy (XPS) measurements were operated with a VG Escalab 250 spectrometer equipped with an Al anode (Al Kα = 1486.7 eV). The photocurrent measurement were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode cell with a working electrode, a graphite electrode as counter electrode, and a standard calomel electrode in saturated KCl as reference electrode. Na_2SO_4 (0.5 M) was used as the electrolyte solution. The working electrodes were prepared by dip-coating: 20 mg of photocatalyst was suspended in 5 mL ethanol to produce a slurry that was then dip-coated onto a 1 cm × 1 cm fluorine-tin oxide (FTO) glass electrode with a sheet resistance of 15 Ω and drying under ambient condition. Electrochemical Impedance Spectroscopy (EIS) was carried out in a $Na_2SO_4/K_3(Fe(CN)_6)/K_4(Fe(CN)_6)$ (Na_2SO_4 0.5 M, $K_3(Fe(CN)_6)$ 0.25 mM, $K_4(Fe(CN)_6)$ 0.25 mM) solution over the frequency range from 0.01 Hz to 100 kHz at 0.24 V, and the amplitude of the applied sine wave potential in each case was 5 mV. The amount of the CO_3^{2-} after degradation was determined with ion vhromatography (DIONEX ICS 1100 USA).

2.4. Photocatalytic activity

The direct conversion of RhB into useful hydrocarbons through the coupling of photocatalytic degradation of RhB and photocatalytic reduction of CO_2 was carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas system (Prefect Light, Beijing, Labsolar-III (AG), as shown in Fig. S1). A 300 W Xe lamp (Wavelength range: 320 nm $\leq \lambda \leq$ 780 nm, light intensity: 160 mW/cm^2) was used as the simulated sunlight source. The as-prepared catalyst (50 mg) was dispersed by using a magnetic stirrer in 50 mL mixed solution containing RhB (10^{-5} M) and NaOH (0.02 M). The reaction setup was vacuum-treated several times, and then high purity Ar gas was flowed into the reaction system until reaching ambient pressure. Before illumination, the solution was stirred for 1 h in the dark in order to reach the adsorption-desorption equilibrium between the photocatalyst and RhB solution. The temperature of the reaction solution was maintained at 6 °C by an external flow of cold water (constant temperature device XODC-0506, Nanjing Shunliu, China) during the reaction in order to make the catalysts absorb the light well. During the irradiation, a certain amount of solution was taken from the reaction cell at given time intervals for subsequent CH_3OH or C_2H_5OH concentration analyses by using a gas chromatograph (GC-7890,