



The interplay of sulfur doping and surface hydroxyl in band gap engineering: Mesoporous sulfur-doped TiO₂ coupled with magnetite as a recyclable, efficient, visible light active photocatalyst for water purification



Xiaoqing Yan^a, Kun Yuan^a, Nan Lu^a, Hanjiao Xu^a, Siyu Zhang^a, Nobuyuki Takeuchi^b, Hisayoshi Kobayashi^b, Renhong Li^{c,*}

^a Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, China

^b Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

^c Department of Materials Engineering, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou, 310018, China

ARTICLE INFO

Article history:

Received 24 March 2017

Received in revised form 26 May 2017

Accepted 8 June 2017

Available online 9 June 2017

Keywords:

TiO₂

Visible light

Sulfur doping

Surface hydroxyl

Magnetite

ABSTRACT

Photocatalysis based on TiO₂ offers a sustainable pathway to drive chemical reactions, such as water splitting and contaminants decomposition, while band gap engineering of TiO₂ is necessary to achieve a visible light response. Herein, we prepare sulfur doped TiO₂ (TiO₂-S) photocatalyst by using titanium sulfate as a dual precursor for both of TiO₂ and S in a one-pot synthetic strategy. Meanwhile, pre-synthesized Fe₃O₄ nanoparticles are coupled onto TiO₂-S via a hydrothermal method. The resulting Fe₃O₄/TiO₂-S composites with plenty of surface hydroxyl groups act as an efficient photocatalyst for decomposition of Rhodamine B and formaldehyde solution under visible light and solar light irradiation. On the basis of density functional theory (DFT) calculations and experimental observations, we suggest that the electronic interaction induced synergetic effect of doped sulfur and surface hydroxides can not only significantly narrow the band gap (individual surface hydroxyls or S-doping has no such a great effect), but also enhances the surface hydrophilicity of TiO₂, ultimately making itself a robust visible light photocatalyst for organic pollutants decomposition. Thus, this dual nonmetal modification strategy is proved to exert an enormous function on band gap engineering of semiconductor photocatalyst. In addition, Fe₃O₄/TiO₂-S photocatalyst is superparamagnetic and possesses excellent magnetic responsivity and redispersibility, which is advantageous to their photocatalytic applications.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Water pollution is a major global problem, which is considered to be the leading worldwide cause of deaths and diseases [1,2]. To remove organic contaminants in wastewater, one of the “green” and sustainable technologies is heterogeneous photocatalysis driven by solar energy [3–11]. The merits of using environmentally friendly oxidant O₂, ambient reaction conditions, and complete oxidation of the organics compounds to CO₂ and H₂O make photocatalysis outperforming other treatment alternatives. To date, TiO₂ has been undoubtedly demonstrated to be an excellent photocatalyst for the oxidative decomposition of many organic

compounds under UV irradiation, while unfortunately its wide band gap (3.2 eV for anatase phase and 3.0 eV for rutile phase) limits its further application in the visible region ($\lambda > 400$ nm) [12–19]. As the largest proportion of the solar spectrum and artificial light sources, visible light should be effectively utilized, thus the development of a photocatalyst with high visible light activity is of great importance. Typically, cationic doping with transition metal ions is commonly used to tailor the bandgap energies of photocatalysts [20–24]. In this case, the response to visible light is mainly due to high levels of impurities in the forbidden energy band of the photocatalysts, which could serve as recombination centers for photoinduced charges and thus reduce the photocatalytic activity. Previous studies have also shown that modification of TiO₂ by doping with nonmetals, such as nitrogen [3,25–27], carbon [28–31], phosphor [32–34], and boron [35,36] could extend its light absorption edge from UV to visible light region and consequently

* Corresponding author.

E-mail address: lirenhong@zstu.edu.cn (R. Li).

introduce substantial visible light photocatalytic activity. Among these dopants, sulfur (S) doping is one of the most effective strategies, due to its high thermal stability and significant enhancement in visible light driven photocatalytic activity [37–49]. To successfully incorporate S atoms into the TiO₂ crystals, TiS₂, CS₂, thiourea, etc., are usually employed as the S sources, while they are either toxic or expensive. To our knowledge, so far there are limited reports on the fabrication of visible light responsive mesoporous S-doped TiO₂ (denoted as TiO₂-S hereafter) photocatalyst by using titanium sulfate (TiOSO₄·xH₂SO₄·8H₂O) as a dual precursor for both of TiO₂ and S in a one-pot synthetic strategy.

In addition, a photocatalyst slurry reactor is one of the most commonly applied systems to deal with pollutants in water due to its higher efficiency as compared with the immobilized counterparts. However, as nanoparticulate powders, TiO₂ slurry will result in the secondary pollution of water unless they can be recycled after photocatalysis. Therefore, magnetically separable TiO₂-based photocatalyst by coupling with magnetite is indispensable to avoid this problem [19,50]. Herein, we individually prepare TiO₂-S photocatalyst and superparamagnetic Fe₃O₄ magnetite nanoparticles, and subsequently combine them by hydrothermal treatment to ultimately fabricate recyclable mesoporous Fe₃O₄/TiO₂-S heterostructures. More importantly, the hydrothermal treatment introduces a mass of hydroxyl groups on the photocatalyst surface, which pushes forward an immense influence on the photocatalytic activity of Fe₃O₄/TiO₂-S. Based on DFT calculations and experimental observations, an electronic interaction induced synergetic effect between S-doping and surface hydroxyls is determined, which decreases the band gap of TiO₂ on a large scale. Meanwhile, the reduced band gap and the newly formed impurity energy levels enable the production of hydroxyl radicals as the primary oxidant during visible light photocatalytic reaction. Consequently, the interplay of S-doping and surface hydroxyl groups finally makes mesoporous Fe₃O₄/TiO₂-S an efficient visible light active photocatalysts for decomposition of organic pollutants. Therefore, for the first time, the synchronous modification of surface and bulk state by a dual nonmetal modification strategy is demonstrated to be a new route to the successful band gap engineering of a semiconductor.

2. Experimental

2.1. Photocatalysts synthesis

2.1.1. S-doped mesoporous TiO₂ (TiO₂-S)

In a typical synthesis, 0.0625 mol of TiOSO₄·0.13H₂SO₄·1.5H₂O was dissolved in 100 mL deionized water, and was continuously stirred at 60 °C for 30 min (denoted as solution A). Certain amount of surfactants CTAB and template P123 were dissolved in the composite solution of ethanol and water (V_{ethanol}:V_{H₂O} = 1:3) under vigorous stirring for 1 h (Solution B). Solution A was added into solution B dropwise under stirring, and the pH value of the reaction system was controlled at about 1.0 by adding ammonia (1:1, Vol.%). The molar ratio of Ti/CTAB/P123 was 1:0.1:0.01, and the total molar ratio of H₂O/Ti was 140:1. After another 2 h stirring and 3 h static at ambient temperature, the solution with milk-white colloid deposit occurred. Then the solution was transferred into a 500 mL beaker, sealing and aging for 12 h. The resulting gel was filtered, washed repeatedly with distilled water and dried in an oven at 60 °C overnight. Finally, the as-synthesized samples were calcined in air using a heating rate of 2 °C/min, and maintained at 550 °C for 3 h to remove the template.

2.1.2. Fe₃O₄ nanoparticles

Water-dispersible magnetite nanoparticles were synthesized using one-step reverse precipitation method in the presence of

sodium citrate [51]. The magnetite nanoparticle formation is based on aging Fe(OH)₂ gels at 90 °C for 5 h in the presence of KNO₃ as an oxidizing agent. Typically, 0.83 mL 0.50 M KNO₃ was firstly added to 100 mL 0.10 M KOH solution, the obtained transparent solution was degassed with nitrogen for 30 min; then 200 mL of 25 mM FeSO₄·7H₂O and a pre-determinate amount of sodium citrate solution was added to this solution under stirring of 600 rpm. After being stirred for 1 h, the resultant black solution was heated to 90 °C and maintained at this temperature for 5 h. The reaction was protected under nitrogen to void the uncontrollable oxidizing effect of air. After being cooled down to room temperature, the as-prepared magnetite nanoparticles were precipitated by acetone to move the excessive sodium citrate, and then the as-prepared magnetite nanoparticles were collected with a permanent magnet and vacuum dried at 30 °C over night.

2.1.3. Fe₃O₄/TiO₂-S

15 or 30 mg Fe₃O₄ as-synthesized nanoparticles and 60 mL acetone were added into a single neck flask, and then sonicated for 30 min 300 mg TiO₂ powders were added and stirred for 2 h. After the upper solution becoming transparent, the precipitate was collected by a magnet, which was then transferred into a 100 mL hydrothermal reactor with a certain amount of glycol. The hydrothermal reaction was maintained at 180 °C for 24 h before it is cooled to room temperature. The precipitate was collected by magnet and washed by ethanol for 3 times, and finally dried at 60 °C in vacuum over night. The final powder was Fe₃O₄/TiO₂-S photocatalyst and kept under Ar protection before use.

2.2. Characterizations

High-resolution X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers. All binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. Wide-angle XRD patterns were recorded on a Bruker D8 diffractometer using CuK_α radiation. Nitrogen adsorption-desorption analysis was carried out at 77 K on a Micromeritics ASAP 2020 adsorption analyzer. Before the adsorption analysis, calcined samples were outgassed under a vacuum at 200 °C in the port of the adsorption analyzer. Transmission electron microscopy (TEM) images were taken using a JEOL 2010 electron microscope operating at 80 keV. X-band EPR signals were recorded at ambient temperature on a Bruker EPR A-300 spectrometer. The settings for the EPR spectrometer were as follows: center field, 3511.39 G; sweep width, 100 G; microwave frequency, 9.86 G; modulation frequency, 100 kHz; power, 101 mW; conversion time, 10 mS. The spin trapping experiments were performed as follows: The solid catalyst (~5.0 mg) was mixed with calculated amount of ice-cooled DMPO solution (0.08 M) in the presence of aqueous methanol solution (0.1 M). The mixture was quickly transferred into a glass capillary tube and tested by EPR spectroscopy at room temperature with visible light irradiation. A 100 W Hg lamp (LOT Oriol) with an optical filter was used to provide visible light with λ > 420 nm.

DFT calculations with the periodic boundary conditions were carried out using a plane wave (PW) based program, Castep [52,53]. The Perdew-Burke-Ernzerh of (PBE) functional [54,55] was used together with the ultrasoft-core potentials [56]. The basis set cutoff energy was set to 300 eV. The electron configurations of the atoms were H: 1s¹, O: 2s²2p⁴, S: 3s²3p⁴, and Ti: 3s²3p⁶3d²4s². The lattice parameters were a = 7.552 Å, b = 10.210 Å, α = 88.99°, β = γ = 90°. The surface normal was taken in the direction c, and c = 30 Å including the vacuum region. The catalyst was modeled by a (TiO₂)₁₆ slab representing the (101) face of anatase structure. A single S atom as an impurity replaced Ti atom. For the hydrated surface, four water

Download English Version:

<https://daneshyari.com/en/article/6453691>

Download Persian Version:

<https://daneshyari.com/article/6453691>

[Daneshyari.com](https://daneshyari.com)