Applied Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Interfacial effect of the nanostructured Ag_2S/Co_3O_4 and its catalytic mechanism for the dye photodegradation under visible light

X.P. Qiu [a], J.S. Yu [b], H.M. Xu [a], W.X. Chen [a], W. Hu [a], H.Y. Bai [c], G.L. Chen [a,*]

[a] *Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, 310018, PR China*
[b] *Department of Chemistry and Chemical Engineering, University of New Haven, 300 Boston Post Road, West Haven, CT, 06516, USA*
[c] *The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu, 214122, PR China*

ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form
11 November 2015
Accepted 16 November 2015
Available online xxx

Keywords:
Nanocomposite
Hybrid catalyst
Photocatalysis
Degradation mechanism
Ozone

ABSTRACT

In this study, the synthesis of a highly hybrid, heterogeneously structured nanocomposite catalyst consisting of Ag_2S nanoparticles dotted on a Co_3O_4 microrod array is reported. The average diameter and length of the Co_3O_4 microrods was optimized to be approximately 300 nm and 20 μm, respectively, and the average size of the Ag_2S nanoparticles was approximately 10 nm. When the Ag_2S nanoparticles were deposited on the Co_3O_4 microrods, the characteristic optical band gap energy of Co_3O_4 decreased from 1.26 eV to 1.23 eV, and the intensity of the absorbance peak at 650 nm increased significantly. The catalytic activity of nanosized Ag_2S/Co_3O_4 for the photodegradation of organic contaminants with potassium hydrogen persulfate (PMS) or ozone (O_3) was evaluated using basic green 1 dye (BG1) as a model pollutant. In the presence of the hybrid Ag_2S/Co_3O_4 catalyst developed in this study, the complete photodegradation of the BG1 solution was achieved in 20 min and 6 min when PMS and O_3 were used, respectively. In addition, the experimental results suggest that the catalytic photodegradation of BG1 using the Ag_2S/Co_3O_4/PMS and $Ag_2S/Co_3O_4/O_3$ processes was dominated by the $^{\bullet}OH$ and $^{\bullet}O_2^-$ radicals, respectively.

1. Introduction

Transition metal oxides have attracted increasing attention over the past several decades because they are significantly cheaper than noble metals and possess excellent electric, optical, and catalytic properties [1,2]. An area of particular interest is their applications to the photodegradation of organic pollutants in wastewater. Several metal oxides including TiO_2, ZnO, and Cu_2O act as photocatalysts for decomposing organic compounds [3–5]. Among the many transition metal oxides, tricobalt tetraoxide (Co_3O_4) is increasingly studied as a non-noble catalyst or a support for noble metal catalysts [6–8]. Intrinsically, Co_3O_4 is a p-type semiconductor with two characteristic optical band gaps at 1.27 eV and 2.11 eV [9] and a spinel crystal structure consisting of AB_2O_4 (B-Co^{3+}, A-Co^{2+}), in which the Co^{3+} ions occupy 1/2 octahedral B sites and the Co^{2+} ions occupy 1/8 tetrahedral A sites [10]. Due to these structural characteristics, Co_3O_4 has been extensively studied for its various catalytic applications. For example, Xie et al. [11] fabricated Co_3O_4 nanorods with high reaction rates for CO oxidation at low temperatures, and Ma et al. [12] prepared reversible oxygen evolution electrodes based on hybrid Co_3O_4-carbon porous nanowire arrays. However, a major drawback that limits the catalytic application of Co_3O_4 is related to the facile combination of the electrons and the electron holes in Co_3O_4 during catalytic reactions, which reduces the catalytic efficiency. This drawback is more significant when its absorption abilities in the visible wavelengths are concerned [13].

In addition, Ag_2S, which is a narrow band-gap semiconductor, is also becoming increasingly popular in photocatalysis [14] and bioimaging [15] applications. Ag_2S is an indirect gap semiconductor with a bulk band gap of ~1 eV at room temperature, a high absorption coefficient, and excellent optical limiting properties [16]. Based on these properties, the Ag_2S nanoparticles have been tested for catalytic applications. For examples, Zhu and Xu [17] fabricated heterogeneously structured semiconductor mediated by Ag_2S nanoparticles for the catalytic degradation of organic species, and Jia et al. [18] prepared CdS and Ag_2S micro-nano structures for the photocatalytic degradation of rhodamine B.

---

* Corresponding author. Tel.: +86 571 86843763; fax: +86 571 86843255.
E-mail address: glchen@zstu.edu.cn (G.L. Chen).

http://dx.doi.org/10.1016/j.apsusc.2015.11.161
0169-4332/© 2015 Published by Elsevier B.V.

Because the heterogeneity of the structure has been reported to lower band gap energy and increase oxidative activity of Co_3O_4 [19,20], the combination of Co_3O_4 microrods and Ag_2S nanoparticles to form a hybrid, heterogeneous structure would lead to improved catalytic properties that are better than those of either catalyst functioning alone. However, to the best of our knowledge, this information is scarce. Therefore, a two-step hydrothermal method was developed to synthesize the nanosized Ag_2S/Co_3O_4 catalyst on a Ti foil substrate. The photocatalytic property of the synthesized Ag_2S/Co_3O_4 and the degradation mechanisms for organic species using PMS and ozone were explored using BG1 as a model compound.

2. Experimental

2.1. Materials

Ethyl alcohol, acetone, cobalt nitrate hexahydrate ($Co(NO_3)\cdot 6H_2O$), ammonium nitrate (NH_4NO_3), ammonium hydroxide (NH_4OH 30 wt%), silver nitrate ($AgNO_3$), sodium sulfide nonahydrate ($Na_2S\cdot 9H_2O$), and potassium hydrogen persulfate ($KHSO_5$) were purchased from the Mike Chemical Company in China. Basic Green 1 (BG1) was purchased from the Aladdin Reagent Company in China. All of the chemicals were of analytical grade and used without any further purification.

2.2. Co_3O_4 microrod array preparation

The Co_3O_4 microrod arrays grown on Ti foil were prepared via a template-free growth method. First, a precursor solution consisting of Co_3O_4 was prepared by dissolving 5 mmol of ammonium nitrate and 10 mmol of cobalt nitrate hexahydrate in 35 ml of deionized water, and the solution was magnetically stirred while 15 ml of ammonium hydroxide (30 wt%) was injected. The solution mixture was stirred for approximately 20 min at room temperature until the solution color changed from red to black. Then, this mixture was heated to 90 °C and maintained at this temperature for 2 h. Meanwhile, the Ti foil was soaked in a solution containing H_2O, HNO_3 (1 M) and HF (AR, 40 wt%) at a volumetric ratio of 5:4:1 for 5 min to remove the surface oxide layer, followed by thorough washing with deionized water. Then, the Ti foil was dried at room temperature, and the upper side was treated with a dielectric barrier discharge (DBD) plasma for 2 min to form micro-holes; these micro-holes are beneficial for growing Co_3O_4 microrods. The treated Ti foil was immersed in the reaction solution and maintained at 90 °C for various time periods. After the reaction, the obtain microrods were washed with deionized water three times and calcined at 300 °C for 2 h in air.

2.3. Nanosized Ag_2S/Co_3O_4 heterogeneous structure preparation

The Ag_2S nanoparticles were prepared via a hydrothermal precipitation process. Briefly, precursor solution A was prepared by dissolving 0.51 g of $AgNO_3$ in 50 ml of deionized water, and precursor solution B was prepared by dissolving 0.003 mol of $Na_2S\cdot 9H_2O$ in 50 ml of deionized water. Next, 50 ml of A was added to a beaker, and the Ti foil with the Co_3O_4 microrod arrays was immersed in solution A. Then, 50 ml of solution B was added dropwise to the breaker at the rate of six drops per minute under continuous stirring. After solution B was added, the reaction solution was maintained at 70 °C for 7 h. The final product was sequentially washed with ethyl alcohol and deionized water three times and calcined at 300 °C for 1 h in air.

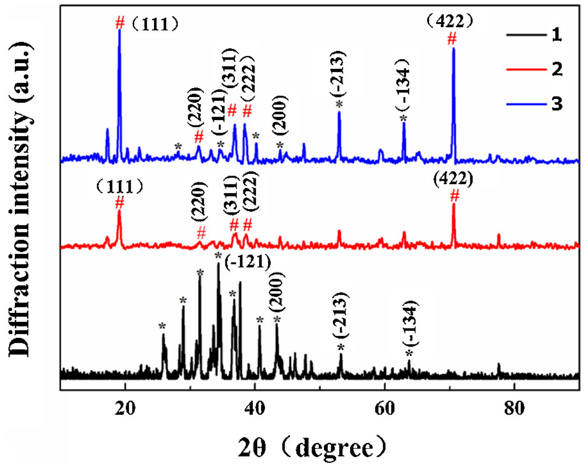

Fig. 1. XRD patterns of the catalysts. Line 1: Ag_2S nanoparticles, Line 2: Co_3O_4 microrods, and Line 3: Ag_2S/Co_3O_4.

2.4. Characterization

The morphologies of the Ag_2S/Co_3O_4 nanocomposite catalysts fabricated under various conditions were characterized using field emission scanning electron microscopy (FESEM, JEOL, Japan) and transmission electron microscopy (TEM, JEOL, Japan). X-ray diffraction (XRD, Thermo Fisher Scientific, USA) was used to examine the crystalline phases of Ag_2S/Co_3O_4 with a Cu Kα radiation source at 35 kV. The diffraction angle (2θ) was set to 10–90° at a scan rate of 2.0° per minute with a step width of 0.02°. X-ray photoelectron spectroscopy (XPS, K-Alpha, USA) was used to investigate the surface chemical composition of Ag_2S/Co_3O_4 with the X-ray source operating at 300 W. Solid-state photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (F-4600, HITACHI, Japan) with λ_{ex} at 490 nm, and UV–vis diffuse reflectance spectra were recorded on a U3900 (Shimadzu) spectrophotometer with $BaSO_4$ as the background. The catalytic activity and degradation mechanism of Ag_2S/Co_3O_4 were investigated with the UV–vis spectrum (Hitachi, U-2900, Japan) and a Waters UPLC Synapt G2-S HDMS, and the detail process was illustrated in the support information (see S1.1 and S1.2).

3. Results and discussion

3.1. Structure of the Ag_2S/Co_3O_4 nanocomposite

Fig. 1 shows the crystalline phases of the synthesized Ag_2S/Co_3O_4 nanocomposite based on the powder XRD characterization. The bottom line 1 (black) shows the diffraction intensity of the Ag_2S nanoparticles, and all of the diffraction peaks were in good agreement with the Ag_2S phase (JCPDS card no. 14-0072) [21]. The peaks assigned for the Ag_2S nanoparticles were primarily in the range of $2\theta = 25–50°$, and the main sharp peaks were assigned to the (1 1 1), (1 1 2), (1 2 1), (1 0 3), (0 3 1), (2 0 0), (2 1 3), and (1 3 4) crystal planes [22]. According to the Scherrer's Equation ($D = K\gamma/B\cos\theta$, where K is the Scherrer's constant and B is the half width of the diffraction peak) [23], the calculated particle diameter was approximately 15 nm. The crystalline structure of the Co_3O_4 microrod is shown as the middle line 2 (red), and all of the diffraction peaks were in good agreement with the cubic Co_3O_4 phase (JCPDS card no. 42-1467) [24]. Four characteristic diffraction peaks were identified at $2\theta = 19.0°$ ($d = 0.4667$ nm), 36.8° ($d = 0.2437$ nm), 38.5° ($d = 0.2333$ nm), and 69.7° ($d = 0.1347$ nm) and assigned to the (1 1 1), (3 1 1), (2 2 2), and (4 2 2) planes, respectively [25]. The top line 3 (blue) depicts the crystal structure of the Ag_2S/Co_3O_4

Please cite this article in press as: X.P. Qiu, et al., Interfacial effect of the nanostructured Ag_2S/Co_3O_4 and its catalytic mechanism for the dye photodegradation under visible light, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.11.161