

Full length article

Efficient interface-induced effect of novel reduced graphene oxide-CoS heteronanostructures in enhancing photocatalytic activities

H.-Y. He

College of Material Science and Engineering, Shaanxi University of Science and Technology, 710021, China



ARTICLE INFO

Article history:

Received 11 August 2016

Received in revised form 18 October 2016

Accepted 20 October 2016

Available online 21 October 2016

Keywords:

Hybrids

Heterostructure

Interface-driven effect

Photocatalysis

ABSTRACT

The interface-induced effects of heteronanostructures are attracting many attentions due to their potentials in photocatalysis applications. In this work, reduced graphene oxide-CoS (rGO-CoS) heteronanostructures were synthesized with a chemical method. The characterization of these nanomaterials was performed by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Raman spectra, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, UV-vis spectroscopy, and photocatalytic activities to understand the physical and chemical behavior of these materials. The effects of rGO/CoS ratio, initial solution pH, and H_2O_2 on the photodegradation of malachite green in a water were studied. The hybrids showed excellent sunlight-excited photocatalytic and Fenton-like photocatalytic activities to the dye, better than that of the CoS nanoparticles and enhanced as increasing rGO/CoS ratio and decreasing initial pH. The photodegradation rate constant, k_{obs} , was determined under pseudo-first order conditions. The enhanced photocatalytic activities with rGO/CoS were ascribed to the enhanced charge transfer at the interface. The interface effect was confirmed by the calculations of band energy level and optical conductivity.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The rGO has a low Fermi energy level and so can accept the electrons from the conduction band of many semiconductors. Such charge transfer can prevent the recombination of photo-generated electron and holes. Therefore, the reduced graphene oxide (rGO) has been attracting many attentions as constructing with other semiconductors because formed heterojunction nanostructures display outstanding photocatalytic performances [1–6]. Recently, Xu [7] has reviewed the effect of graphene in photocatalysis materials, key factors improving photocatalytic properties of graphene-based nanocomposites, and applications of graphene-based photocatalysts. The carriers kinetics of graphene-based materials, comparison of graphene-based photocatalysts with other carbon-based materials and some key issues including development tendency and strategy of graphene-based hybrid photocatalysts are also reviewed and discussed. Han and coworkers [8] also review the structural diversity, tunable properties, and synthetic strategies of these graphene-based materials and highlight their multi-functionality in heterogeneous photocatalysis.

Cobalt sulfide, a significant binary compound semiconductor, has received great attention due to its unique characteristics including narrow direct and indirect bandgap, high absorption coefficient ($\geq 10^4 \text{ cm}^{-1}$) in sunlight, nontoxic and abundant in nature, and low cost. Thus, this material is becoming a candidate for future multifunctional devices and applications. The CoS should also be reasonable for structuring the semiconductor-rGO hybrids for excellent photocatalytic activity.

Malachite green as an alkaline green dye usually exists in the wastewater produced from printing and dyeing industry. This type dye in the environment leads to the generation of carcinogenic, mutagenic, allergenic and toxic hazards for various organisms. Most synthetic dyes are very resistant to biological degradation, heat, and light, chemical and other oxidation compounds [9]. Thus, it must be removed from the wastewater for environmental purification. Heterogeneous photocatalysis combining H_2O_2 /UV technique may be efficient degradation process of this dye.

This work focuses on (i) the facile synthesis of CoS nanoparticles and rGO-CoS hybrids; (ii) the effects of the rGO/CoS ratio on the microstructural and optical properties of the synthesized hybrids; and (iii) the photocatalytic and the Fenton-like photocatalytic degradation of malachite green dye in the water on the CoS nanoparticles and hybrids.

E-mail addresses: hehy@sust.edu.cn, 917894940@qq.com

2. Experimental

The starting materials used were all analytic grade chemicals without any further treatment. The synthesis of CoS nanoparticles was referred to the method present in previous literature [10]. Graphene oxide (GO, Jining LeaderNano Tech L.L.C., China) was first ultrasonically dispersed in deionized water to form dispersion solution with a ratio of 1 mg/ml. The 0.01 mol cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 50 ml solution composed of the GO dispersion solution and deionized water according to mass ratio of GO/CoS = 0, 0.025, and 0.050. Into the solution, small amount of hydrochloric acid (33%, ~0.5 ml) was added to reduce the GO. Magnetic stirring of 30 min was carried out to make a full absorption of Co^{2+} cation onto the GO and/or rGO surface. At same time, 0.01 mol thioacetamide (CH_3CSNH_2) was dissolved in 50 ml deionized water. The two types of solutions were dropwisely mixed together with constant stirring. By further magnetic stirring of 30 min, the all mixed solutions were then heated at 100°C for 1 h in water bath. The products were transferred from dark brown to dark black, indicating crystallization of the CoS and reduction of the GO. The products were finally washed repeatedly with distilled water until washing solution near neutral, and then dried at 60°C for 24 h.

The crystalline structure and phase of the synthesized nanoparticles and hybrids was identified with an X-ray diffractometer (XRD, $\text{CuK}\alpha_1$, $\lambda = 0.15406$ nm, Model No: D/Max-2200PC, Rigaku, Japan) at room temperature. The morphology of the samples was observed using field emission scanning electron microscope (FE-SEM, Model No: S-4800, Hitachi, Japan) and a high-resolution transmission electron microscopy (HR-TEM, Model No: JEM-3010, Japan). Raman spectra of the sample were collected using a spectrophotometer (Model no: Renishaw-invia, U.K.) at a laser excitation wavelength of 532 nm. Fourier transform Infrared spectrum (FTIR) spectra were determined by infrared spectroscopy (Model no: Vector-22, Bruker, Germany). X-ray photoelectron spectra (XPS) was measured with an X-ray photoelectron spectroscopy (XPS, Model no: Axis Ultradld, Kratos, English). The CoS nanoparticles and hybrids were adhered on the glass slides with thin transparent adhesive agent for the measurement of the transmittance and reflectance spectra on an ultraviolet-visible spectrophotometer (Model no: Cary100 UV-vis, Agilent, USA).

The photocatalytic activity of the synthesized photocatalysts was evaluated by photodegrading the malachite green ($\text{C}_{23}\text{H}_{25}\text{ClN}_2$, Tianjing Basifu chemical L.L.C., China) aqueous solution with a concentration of 5×10^{-6} M under sunlight with an average intensities of ~ 450 W/m². One group of the dye solutions were additionally adjusted to initial pH = 5 with diluted HCl. Into two other groups of 50 ml dye solutions with pH = 5 and 7, 1.0 ml hydrogen peroxide (H_2O_2 , 30%) were added, respectively. In each experiment, 50 ml dye aqueous solution and 50 mg photocatalyst were added into a glass beaker. The solutions were placed in dark for 30 min to realize an adsorption balance. Before and after placed in dark, and succedent different irradiation times, ~ 3 ml solutions were taken out and subsequently measured for their light absorbances on a spectrophotometer (Model No: 722N, Hengping, China).

The oxidation reduction potentials (ORP) of the samples in deionized water were measured with an oxidation reduction potential tester (Model no: ORP-286, China). The ORP of the sample surfaces were evaluated by the differences of the measured values after and before the sunlight irradiation.

The quasi-kinetic rate constant (k_1) was calculated with the kinetic relation between the concentration (C) and initial concentration (C_0) of the dye aqueous solution and the photocatalytic reaction time (t) given in previous literature [11,12]:

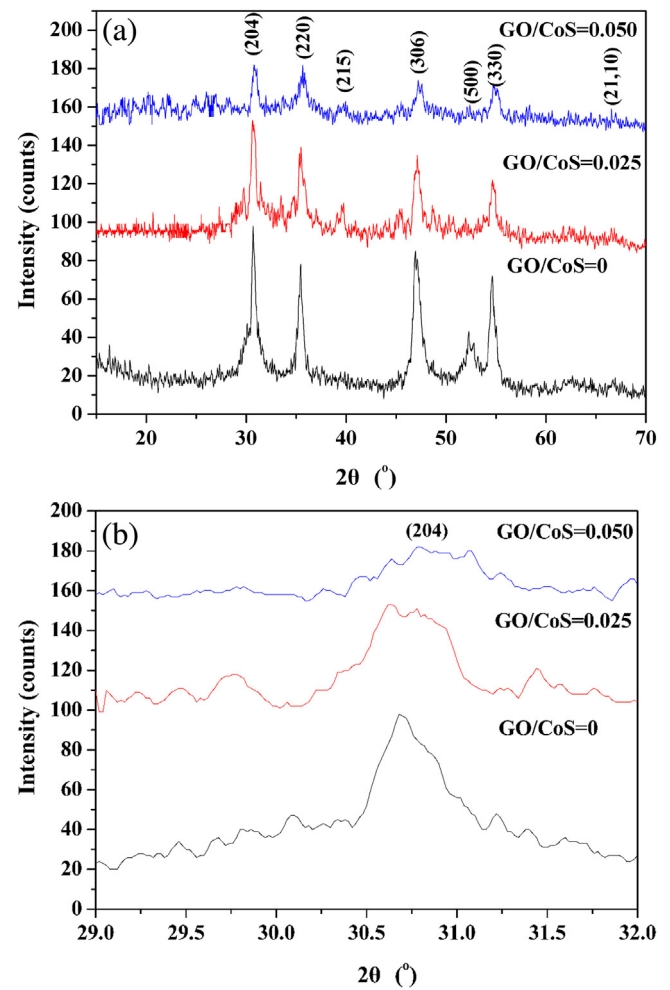


Fig. 1. (a) XRD patterns and (b) strongest (311) XRD peak patterns of the CoS particles and hybrids.

$$\ln \frac{C_0}{C} = k_1 t \quad (1)$$

3. Results and discussion

3.1. Characterizations of the CoS nanoparticles and hybrids

The XRD patterns of the all samples (Fig. 1a) exhibit diffraction peaks at $2\theta \sim 30.7^\circ$, $\sim 35.6^\circ$, $\sim 47.0^\circ$, $\sim 52.4^\circ$, and $\sim 54.6^\circ$. These values are matched with hexagonal $\text{CoS}_{1.097}$ (JCPDS: 19-0366. $a = 10.1 \text{ \AA}$, $c = 15.48 \text{ \AA}$) and same with the values reported in previous literature [10]. The XRD peak intensities decrease as increasing rGO/CoS ratio, indicating a decrease in crystallinity. Crystallites size (D) was estimated from full width at half maximum in radian (β) of the diffraction peak at $2\theta \sim 30.9^\circ$ according to the Scherrer's equation [13]:

$$D = 0.9 \frac{\lambda}{\beta \cos \theta} \quad (2)$$

where λ is the X-ray wavelength. Estimated sizes are ~ 20.33 nm, ~ 16.34 nm, and ~ 15.79 nm for the CoS nanoparticles and hybrids with the rGO/CoS mass ratio of 0.025, and 0.05, respectively. The decrease of the average particle size due to the rGO and with increasing rGO/CoS could be ascribed to the decrease of Co^{2+} concentration in the precursor solution originated from the absorption of Co^{2+} cation onto the graphene oxide. The strongest peak centered at $2\theta \sim 30.7^\circ$ shifts from 30.68° to 30.79° as introducing the rGO

Download English Version:

<https://daneshyari.com/en/article/5347870>

Download Persian Version:

<https://daneshyari.com/article/5347870>

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