Journal of Alloys and Compounds 684 (2016) 445–452

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Au/Cu_2O Schottky contact heterostructures with enhanced photocatalytic activity in dye decomposition and photoelectrochemical water splitting under visible light irradiation

Weiwei Zhang [a], Baoshun Wang [b], Chenchun Hao [a], Yujie Liang [a], Honglong Shi [a], Ling Ao [a], Wenzhong Wang [a], *

[a] School of Science, Minzu University of China, Beijing 10081, PR China
[b] College of Nuclear Science and Technology, Beijing Normal University, Beijing 100875, PR China

ARTICLE INFO

Article history:
Received 3 January 2016
Received in revised form
8 May 2016
Accepted 18 May 2016
Available online 19 May 2016

Keywords:
Cuprous oxide
Schottky contact
Visible light
Dye decomposition
Water-splitting

ABSTRACT

In this work noble metal Au nanoparticles have been successfully deposited on the surface of Cu_2O microcubes to construct close Au/Cu_2O Schottky contact heterostructures, in which both an inner electronic field from Au to Cu_2O and a Schottky barrier are established at the interface of Au and Cu_2O due to the Schottky junction. Benefiting from this unique structure with synergistic effect of inner electronic field and Schokkty barrier, the as-fabricated Au/Cu_2O Schottky contact heterostructures exhibit enhanced photocatalytic activity to pure Cu_2O microcubes in dye decomposition and water splitting under visible light illumination. The photodegradation rate of the as-constructed Au/Cu_2O Schottky contact heterostructures for methyl orange (MO) is 1.2 times higher than that of pure Cu_2O microcubes under visible light irradiation for 90 min. The photocurrent density of the as-prepared Au/Cu_2O heterostructures electrode reaches up to 30 μA cm^{-2}, which is 3 times higher than that (10 μA cm^{-2}) of pure Cu_2O microcube electrode at 1.23 V vs RHE. The enhanced photocatalytic activity of the as-constructed Au/Cu_2O Schottky contact heterostructures is attributed to the synergistic effect of inner electronic field and Schokkty barrier. The transfer process of the photoexcited electrons and holes, and the enhancement mechanism of photocatalytic performance of the as-fabricated Au/Cu_2O heterostructures are discussed in detail. This study opens up new opportunities in designing photoactive materials with highly enhanced performance for solar energy conversion.

1. Introduction

Photocatalysis based on semiconductor technology has attracted increasing attention due to its effective utilization of solar energy for H_2 generation and water purification. The potentially bifunctional applications in clean energy and water purification make photocatalysis to be as a promising way to the worldwide energy shortage and environmental pollution treatment [1–3]. So far many semiconductors such as ZnO, TiO_2, ZnS, and Cu_2O have been used as photocatalysts to split water towards generation of H_2 or to degrade organic pollutants in wastewater [4–13]. As is well known, the photocatalytic performance of semiconductor catalyst is greatly determined by the separation efficiency of photogenerated electrons and holes [14,15]. Many research works have demonstrated that the fast recombination of photoinduced electrons and holes in bare semiconductor is one of the bottlenecks for improving its photocatalytic efficiency, and hence significantly limits the practical applications of semiconductor photocatalyst in water splitting or organic pollutant degradation [16,17]. Therefore, it is key issue to enhance the photocatalytic performance of semiconductor photocatalysts by improving the separation efficiency of photogenerated electron-hole pairs.

Recently, many methods have been employed to improve the separation efficiency of photoinduced electron-hole pairs and therefore to enhance the photocatalytic performance of semiconductor photocatalysts. Especially, coupling noble metals like Ag, Pt and Au onto a semiconductor surface to construct the semiconductor-metal heterostructures has been developed as a new strategy for fabricating enhanced photocatalysts [18–22]. It has been believed that the photoinduced electrons in the

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* Corresponding author.
E-mail address: wzhwangmuc@163.com (W. Wang).

http://dx.doi.org/10.1016/j.jallcom.2016.05.192
0925-8388/

conduction band (CB) of the semiconductor can be effectively transferred to the metal nanoparticles in the semiconductor-metal heterostructures. Here the metal nanoparticles act as electron sinks due to the Schottky barrier built at the semiconductor-metal interface, while the photoinduced holes can be remained on the valence band (VB) of semiconductor [23,24]. Thus the recombination of the electrons and holes can be prevented effectively, and the photocatalytic efficiency of the semiconductor photocatalysts can be significantly improved. Various methods have therefore been developed to construct semiconductor-metal heterostructures by loading Ag or Au nanoparticles onto a semiconductor surface. For instance, it has been reported that the metallic Ag nanoparticles loading on TiO_2 surface can serve as electron traps to separate the photogenerated electron-hole pairs and suppress their recombination [25]. The photocatalytic water-splitting activity of 8 nm TiO_2 nanotubes modified by Au nanoparticles was reported. Under the visible illumination a significant enhancement in photoresponse with a photocurrent density of 11 $\mu A/cm^2$ has been achieved, which is 3.5 times higher than that of the pure TiO_2 nanotubes [26]. These studies greatly encourage research people to fabricate other semiconductor-metal photocatalysts and then to study their photocatalytic performance.

As reported in the previous documents, cuprous oxide (Cu_2O) is a p-type oxide semiconductor with band gap of 2.0–2.2 eV [27], and its CB level is qualified for water reduction to produce hydrogen [28–30]. Hence, Cu_2O is supposed to have photocatalytic activity in a broad visible spectral region due to its band structure features [28], however, the low migration rate of electrons and holes remains a bottleneck to its photocatalytic performance. In order to improve the photocatalytic activity, Au or Ag nanoparticles have been deposited on the Cu_2O surface to construct Au–Cu_2O or Ag–Cu_2O heterogeneous photocatalyst for enhancing photocatalytic performance through surface plasmon resonance (SPR) of Au ro Ag nanoparticles. For example, the photocatalytic activities of Cu_2O octahedra and Ag/Cu_2O composite octahedra for the degradation of MO aqueous solution were reported. The degradation rates are about 90% and 82% over Ag/Cu_2O composite octahedra and Cu_2O octahedra, respectively, after UV light irradiation for 6 h [31], demonstrating that the Ag/Cu_2O composite octahedra exhibit enhanced photocatalytic performance compared to pure Cu_2O octahedra. It has been reported that the photocatalytic activity of Au/Cu_2O nanocomposites with tunable coverage of Au nanoparticles were greatly dependent on the coverage density of Au nanoparticles. The photocatalytic efficiency of Au/Cu_2O nanocomposites initially increased with the increase coverage density of Au nanoparticles. However, the photocatalytic efficiency of the as-fabricated Au/Cu_2O nanocomposites decreased as the surface of Cu_2O was densely covered by Au nanoparticles. Under visible light illumination, the highest degradation of methylene blue (MB) with the optimal Au/Cu_2O nanocomposites is about 44%, which is 2 times higher than that (23%) of pure Cu_2O nanoparticles. The results clearly demonstrated that the photodegradation efficiency of Au/Cu_2O nanocomposites was enhanced obviously due to the presence of Au nanoparticles [32]. Furthermore, recently research work has demonstrated that the optical properties of metal-Cu_2O nanocrystals significantly depend on the morphology of Cu_2O nanocrystals. For example, Cu_2O nanocubes and octahedral with Au crystal cores shows a strong SPR absorption in the near-infrared (NIR) region [33], which may find potential applications for development of wide light harvesting plasmonic metal-Cu_2O photocatalyst. However, to the best of our knowledge, there are a few studies on photoelectrochemical (PEC) water-splitting performance of Cu_2O microcubes decorated with Au nanoparticles.

In this work, Au/Cu_2O Schottky contact heterostructures have been constructed by coupling 10 nm Au nanoparticles with Cu_2O microcubes through a facile chemical route. Because the work functions of Au and Cu_2O are 5.27 and 5.10 eV, respectively, both an inner electronic field from Au to Cu_2O and a Schottky barrier are established at the interface of Au and Cu_2O due to the Schottky junction. The inner electronic field drives transfer of the photoexcited electrons on the CB of Cu_2O to Au nanoparticles, while the Schottky barrier prevents migration of the photogenerated holes on the VB of Cu_2O to Au nanoparticles. Meanwhile, the electrons on Au nanoparticles cannot be transferred to Cu_2O due to Schottky barrier; hence the photogenerated electrons and holes of Cu_2O are separated effectively. Thus the as-fabricated Au/Cu_2O Schottky contact heterostructures are expected to exhibit the enhanced photocatalytic activity.

The bifunctionally photocatalytic performance of Au/Cu_2O Schottky contact catalysts for the photodegradation of MO in water and towards water splitting have been studied systemically. Achieved results demonstrate that the as-fabricated Au/Cu_2O heterostructure exhibits an enhanced photocatalytic performance for the degradation of MO and towards water-splitting activity, compared to pure Cu_2O microcubes under visible light irradiation. Based on the band structure feature in the as-fabricated Au/Cu_2O heterostructures, a rational transfer and separation process of photogenerated electrons and holes has been proposed and discussed in detail.

2. Materials and methods

2.1. Preparation of Cu_2O microcubes

A low-temperature chemical method was employed to prepare the Cu_2O microcubes. A synthetic procedure was briefly described as follows: 1 g of ethylene diamine tetraacetic acid (EDTA) powder was dissolved into 120 mL of a 0.01 M $(CH_3COO)_2Cu$ aqueous solution in a flat bottom flask, which was placed in an oil bath at 60 °C and kept for 10 min under magnetic stirring. Then 20 mL of 1 M NaOH solution was slowly dropped into the flask by using a pipette. 8 min later, 60 mL of 0.11 M glucose aqueous solution was slowly dropped into the flask by using a pipette. The reaction was processed for 15 min at 60 °C under magnetic stirring. The final obtained precipitates were separated by centrifugation, washed with deionized water and ethanol for several times, and finally dried at room temperature.

2.2. Fabrication of Au/Cu_2O heterostructures

The Au/Cu_2O heterostructures were fabricated by a facile chemical route at room temperature. First, 50 mg of the as-prepared Cu_2O microcubes were distributed in 18.2 mL mixed solution with a 1:1 volume ratio of water and alcohol under magnetic stirring, then 1.5 mL of 0.05 M sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) solution was added. Subsequently, the mixed solution was sonicated at 70 Hz for 10 min. Finally, 0.5 mL of 0.015 M chloroauric acid ($HAuCl_4$) solution was injected into the mixed solution under light shielded and kept under magnetic stirring for 20 min. The obtained precipitates were separated by centrifugation, washed with deionized water and ethanol for several times, and finally dried under room temperature.

2.3. Characterizations

X-ray powder diffraction (XRD) patterns of pure Cu_2O microcubes and Au/Cu_2O heterostrctures were recorded on a Rigaku (Japan) Dmax γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu-Kαradiation (λ = 1.54178 Å), employing a scanning rate of 0.02° s^{-1} in the 2θ range from 20° to