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Fabrication of Ag nanowires–CdS–Au photocatalyst and its excellent visible light photocatalytic activity: The role of synergetic electron transfer

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ABSTRACT

A novel Ag nanowires–CdS–Au (Ag NWs–CdS–Au) photocatalyst was synthesized by a two-step solvothermal method. As a metal core, thioglycolic acid (TGA) functionalized Ag NWs provided abundant active sites, facilitating the attachment of CdS; and the excessive S^{2-} on the surface of CdS favored the loading of Au, leading to the well-developed combined interface of Ag NWs–CdS and CdS–Au. The combination and interaction between Ag NWs–CdS and CdS–Au was beneficial to the electron transfer in the photocatalysis. Multiple electron transfer processes happened in the Ag NWs–CdS–Au photocatalyst, enhancing charge carrier separation efficiency. Therefore, Ag NWs–CdS–Au possessed much higher photocatalytic degradation efficiency (89%) of MB than that of Ag NWs–CdS (45%) under visible light irradiation. Additionally, the Ag NWs–CdS–Au photocatalyst could absorb more visible light, favoring the generation of leuco-methylene blue (LMB) molecules, and further promoting the formation of ·OH. The finding provides a novel method to obtain bimetallic photocatalyst with separated bimetals to achieve high visible light photocatalytic activity and stability.

1. Introduction

Visible light photocatalytic treatment of environmental pollutants is greatly limited by photocatalytic efficiency and stability, mainly due to the low charge separation rate of photocatalysts [1,2]. Inspired by the Schottky junction formed by semiconductor and metal, many creative methods have been applied to form particular heterojunction photocatalysts to reduce charge recombination [3]. Among various semiconductor photocatalysts, cadmium sulfide (CdS) was recognized as one of the most potential visible light photocatalysts due to its narrow energy band gap (2.4 eV), high absorption coefficient and suitable conduction bands [4]. However, the limited catalytic efficiency and the light-corrosion restricted the practical application of CdS [5].

Recently, a variety of strategies have been employed to form CdS-based specific stack architectures, including semiconductor–semiconductor (S–S) heterojunctions (TiO_2/CdS [6], Bi_2S_3/CdS [7]), semiconductor-metal (S-M) heterojunctions (CdS/Pt [8], SiO_2/Au [9], CdS/Pd [10], CdS/Ag [11], graphene/Ag [12], graphene/Au [13]), semiconductor-carbon (S-C) heterojunctions (g-C_3N_4/CdS [14], graphene/CdS [15], graphene/WO_3 [16]) and multicomponent heterojunctions (CdS–Au–TiO_2 [17]). The improvement of charge separation in these heterojunctions played a key role on the enhancement the photocatalytic activity. In S-M heterojunctions, metals, such as Ag and Au [18,19], were used as doping metals for the effect of surface plasmon resonance (SPR). It has been suggested that the photocatalytic activity of the photocatalyst could be promoted by mono metal doping, which could absorb more visible light and enhance the surface electron excitation and interfacial electron transfer [20].

To further improve the photocatalytic activity, bimetallic photocatalysts have been developed, such as PtNi [21], AuPt [22], PtSn [23] and AuCu [24]. It revealed that photocatalysts with bimetallic alloys exhibited much higher activity than monometallic photocatalyst, due to the unique microstructures and particular functions of different components in the catalysts [25–27]. However, previous reports focused on the role of bimetals which were loaded on the surface of photocatalyst as alloys, and few literatures reported the effect of separated bimetal. Based on this, it is speculated that the photocatalytic activity and photostability could be further

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promoted by designing metal supported semiconductor@metal core ternary photocatalysts, in which dual electron transfer may occur to increase the separation of charge carriers.

In addition, the photocatalytic performance of S-M heterojunctions photocatalysts strongly depends on size and morphology of the semiconductor [28]. A convincing fact to reveal this issue is that the photocatalytic activity of Ag NW@TiO_2 with necklace-like structure was lower than that of Ag NW@TiO_2 with core-shell structure because the TiO_2 nanoparticles in core-shell structure could coat densely on the Ag NW surface and the interface of Ag and TiO_2 were well-combined [29].

In order to promote the light-harvesting ability and separation of charge carriers, Ag NWs–CdS–Au ternary photocatalysts were investigated in this study for the first time. As a metal core, Ag NWs can provide many active sites to facilitate the attachment of CdS, which was beneficial to the interface electron transfer [30]. In the ternary photocatalyst, Au nanocrystals played a crucial role in absorbing visible light, providing more active sites and speeding up the photo-electron transfer [19]. Compared with the traditional S-M composite photocatalyst, Ag NWs–CdS–Au exhibited a faster electron transfer from CdS to both Ag NWs and Au nanocrystals, thus enhancing photocatalytic activity [31]. Additional, Ag NWs–CdS–Au ternary photocatalysts could absorb more visible light, favoring the generation of leuco-methylene blue (LMB) molecules, and further promoting the formation of ·OH.

2. Experiment

2.1. Materials

Polyvinylpyrrolidone (PVP), L-cysteine, ethylene glycol (EG), thioglycolic acid (TGA), $AgNO_3$, NaOH, Na_2S, and $NaBH_4$ were purchased from Sinopharm chemical reagent Co. Ltd. $Cd(NO_3)_2{\cdot}4H_2O$, ethanol and Methylene blue (MB) were received from Aladdin industrial Inc. All of the used chemicals were analytical grade without further purification.

2.2. Preparation of Ag nanowires

The Ag nanowires were prepared by a hydrothermal approach. Firstly, 1.67 g PVP (0.3 M) and 0.0061 g L-cysteine (1 mM) were added into 50 ml EG and the mixture was stirred for 30 min. Then the mixture was added into 0.1 M $AgNO_3$ solution in EG (50 ml) slowly. Next, the as-prepared solution was transferred into distillation apparatus, heated to 160 °C and maintained for 2 h under a nitrogen gas flow. Finally, the gray and wispy silver nanowires (Ag NWs) photocatalyst was washed with acetone and ethanol and dispersed in distilled water.

2.3. Preparation of Ag NWs–CdS photocatalyst

Firstly, the as-prepared Ag NWs was added dropwise to 40 mM TGA solution, mixed well and stirred for 30 min. Secondly, 80 mM $Cd(NO_3)_2{\cdot}4H_2O$ solution (the molar ratio of Ag:CdS = 1:30) was added to the mixture and stirred for another 30 min. Then Na_2S was added into the resultant mixture slowly after the pH of the solution was adjusted to 10.5 by 1 M NaOH solution. Followed by adding Na_2S, the mixture was stirred for 30 min and aged for 90 min at 65 °C statically. Finally, the Ag NWs–CdS sample was collected by centrifugating and washing with distilled water and ethanol for several times. The obtained powder was dried in vacuum oven at 60 °C overnight.

2.4. Preparation of Ag NWs–CdS–Au hybrids

The Ag NWs–CdS–Au ternary plasmonic photocatalysts with different Au loading amounts were prepared by the homogeneous precipitation method. Specifically, the as-prepared Ag NWs–CdS powder (0.6 g) was dispersed in 50 ml distilled water and reduced by $NaBH_4$. The molar ratio of $HAuCl_4$:$NaBH_4$ was 1:20. Then different amounts of $HAuCl_4$ solution were added into the mixture under continuous stirring for 90 min and then aged for 60 min. Finally, the sample was centrifugated, washed with distilled water and dried in vacuum oven at 60 °C overnight.

2.5. Characterization

The phase composition and crystal structures of the photocatalysts were obtained by the powder X-ray diffraction (XRD, Bruker D8-Advanced, Germany), which operating with a Cu Kα radiation and the scanning angle ranging from 20° to 80°. The morphology and energy-dispersive X-ray spectroscopy (EDS) profiles were obtained by using a field emission scanning electron microscope (SEM, QUANTA 250 FEG, FEI, America). The transmission electron microscopy (TEM) analyses were conducted using a JEM-2100 electron microscope at an acceleration voltage of 200 kV. The ionic characteristic patterns of the hybrids before and after photocatalysis were obtained by X-ray photoelectron spectra (XPS) on an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with a monochromatic X-ray source (Mg Kα) radiation (with the photon energy of 1253.6 eV). The peak positions of the elements were compared to the C1s peak (284.6 eV). The Au content in the Ag NWs–CdS–Au hybrids was determined by using inductively coupled plasma (ICP, Optima 5300DV, PE, America). Raman spectra were measured by using a high-resolution Raman spectrometer (LabRAM HR Evolution, HORIBA JOBIN YVON SAS).

2.6. Photoelectrochemical measurements

Photoluminescence spectra were measured by jobinYvon SPEX Fluorolog-3-P spectroscope. UV–vis diffuse reflectance spectroscopy was taken on the Hitachi U-3010 UV–vis spectrometer. The photocurrent was obtained by the CHI 660B electrochemical workstation in a standard three-electrode system, using the synthesized samples coated on F-doped SnO_2-coated galss (FTO glass) as the working electrodes, a Pt wire as the counter electrode, and Ag/AgCl (saturated NaCl) as a reference electrode.

2.7. Photocatalytic MB degradation tests

The photocatalytic activities of the photocatalysts were tested by degradation of MB under visible light irradiation using a 500 W xenon lamp. Briefly, 0.02 g of photocatalyst was added into 50 ml MB solution (20 mg/l). The mixture solution was stirring for 0.5 h in the dark to reach the adsorption–desorption equilibrium before turning on the xenon lamp. 1 ml suspension was withdrawn at every 30 min intervals and then filtered to remove all photocatalyst particles. After reaction for 3 h, the concentration of MB was detected by the UV–vis spectrophotometer at the wavelength of 664 nm [32]. To test the stability of photocatalysts, the used photocatalysts were washed with distilled water, dried at 60 °C and then recycled.

3. Results and discussion

3.1. Characterization of the photocatalyst

The formation procedure of the Ag NWs–CdS–Au photocatalyst is illustrated in Scheme 1. The Ag NWs with uniform diameter were prepared and then used as the template for depositing CdS particles. Before addition of $Cd(NO_3)_2{\cdot}4H_2O$, the surface of the Ag NWs was modified by thioglycolic acid (TGA); the mercapto group in TGA were combined with Ag, and the carboxyl group

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