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Photocatalytic synthesis of Schiff base compounds in the coupled system of aromatic alcohols and nitrobenzene using $Cd_XZn_{1-X}S$ photocatalysts

Yahui Wu[a,b], Xiangju Ye[b,*], Sujuan Zhang[a], Sugang Meng[a], Xianliang Fu[a], Xuchun Wang[b], Xuemei Zhang[b], Shifu Chen[a,b,*]

[a] *Key Lab of Clean Energy and Green Circulation, Huaibei Normal University, Huaibei 235000, PR China*
[b] *Department of Chemistry, Anhui Science and Technology University, Bengbu 233100, PR China*

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ABSTRACT

Achieving green synthesis and transformation of organics is always an ambition of scientists under mild conditions. In this paper, a series of $Cd_XZn_{1-X}S$ ($0 \le X \le 1$) samples were synthesized by a simple wet-chemical method using cadmium nitrate, zinc nitrate and sodium sulfide as precursors, and were thoroughly characterized by many techniques, including X-ray diffraction, UV–vis absorption spectra, nitrogen adsorption-desorption isotherms, scanning electron microscopy, transmission electron microscopy and (photo)electrochemical measurements. The photocatalytic performance of the as-prepared samples was evaluated by photocatalytic synthesis of Schiff base compounds in the coupled system of benzyl alcohol and nitrobenzene under visible light irradiation. Results reveal that when X is 0.78 ($Cd_{0.78}Zn_{0.22}S$), the sample exhibits the highest photocatalytic performance. The yield of Schiff base is 55.2% under visible light illumination for 4 h, and the theoretical yields of benzaldehyde and aniline could reach 96.6% and 67.9%, respectively. The quantum efficiency (QE) of the sample with $\lambda = 450 \pm 10$ nm is 15.8%. In addition, many other Schiff base compounds were also synthesized from the different coupled systems of aromatic alcohols and nitrobenzene. A possible reaction mechanism involving the oxidation of benzyl alcohol to benzaldehyde by photogenerated holes and the reduction of nitrobenzene to aniline by photoinduced electrons, followed by a condensation reaction between benzaldehyde and aniline to generate Schiff base compound was proposed. It is expected that the current work could offer an avenue to fabricate a high-performance photocatalyst used in the fields of photocatalytic selective organic transformations under mild conditions.

1. Introduction

As is well-known, many traditional organic transformations and synthesis are generally carried out under high temperature and high pressure accompanied by energy consumption and environmental pollution. Therefore, it is imperative to find a clean and efficient organic synthesis method instead of traditional industrial synthesis. Photocatalysis as a promising technique based on the semiconductor has aroused wide interest because of its potential applications in clean energy and environmental remediation [1–4].

Up to now, photocatalytic selective transformations and synthesis of organics have attracted extensive attention due to its green process and feasible application in industry [5–11]. Among them, the photocatalytic selective oxidation of aromatic alcohols to aromatic aldehydes under oxygen condition, and reduction of nitrobenzene to aniline under nitrogen atmosphere have been considerably investigated. It is known that the aromatic aldehydes are widely utilized as versatile building blocks for the synthesis of pharmaceuticals and fine chemicals, and aniline is also an important chemical intermediate used for the synthesis of dyes, resins, pharmaceuticals and thiofide [12–14]. However, traditional oxidation methods for aromatic alcohols to the corresponding aldehydes need stoichiometric oxidants, such as permanganate and dichromate, *etc.* These reaction processes generate a mass of heavy-metal waste by-products. Aniline is synthesized by catalytic hydrogenation of nitrobenzene. The catalysts (such as transition and noble metals) used in the reaction process are expensive, and it also generates an amount of heavy-metal pollutant [15–18]. Therefore, it is urgent and necessary to develop an environmentally friendly method for selective oxidation of aromatic alcohols to aromatic aldehydes and reduction of nitrobenzene to aniline.

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* Corresponding authors at: Key Lab of Clean Energy and Green Circulation, Huaibei Normal University, Huaibei 235000, PR China (S. Chen).
E-mail addresses: yexj@ahstu.edu.cn (X. Ye), chshifu@chnu.edu.cn (S. Chen).

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The use of solar energy to drive organic reactions under mild conditions by semiconductor materials provides a sustainable pathway for green synthesis [19–23]. Unfortunately, their conversion and selectivity are poor. One of the prime reasons may be that the photocatalytic selective oxidation of aromatic alcohols needs oxygen to eliminate the photoexcited electrons, and photocatalytic reduction of nitrobenzene requires organics (such as methanol) to remove the photogenerated holes. Thus, the actual utilization ratio of photoexcited electron-hole pairs is low. The designed photocatalysts used in the reactions have not reached what we expected. Recently, simultaneously photocatalytic selective oxidation of aromatic alcohols into aromatic aldehydes by photogenerated holes and reduction of nitrobenzene to aniline by photogenerated electrons in a coupled system has been realized by our group [24–26]. Moreover, we also know that aromatic aldehydes and aniline in a reaction system can further interact to generate Schiff base compounds. The Schiff bases are covalent —RC=N— linkage compounds produced by condensation polymerization of amine and active carbonyl compounds, which can be widely used in various fields, such as medical science and chemical industry [27,28]. If Schiff base compounds can be produced by photocatalytically technology, a green synthesis method in the field of organic synthesis is established. The challenge for achieving the goal is to develop photocatalysts that can selective oxidation of aromatic alcohols to aldehydes and reduction of nitrobenzene to aniline effectively. Very recently, metal chalcogenide as photocatalysts for hydrogen production from H_2O, reduction of CO_2 and selective oxidation of organics have been investigated extensively because of its appropriate band gap, positions of valence band (VB) and conduction band (CB) [29–31]. The solid solution $Cd_XZn_{1-X}S$ semiconductor catalyst is also widely studied because of its excellent photocatalytic performance and chemical stability [32–36]. More importantly, the appropriate band edges and band gap of $Cd_XZn_{1-X}S$ provide a possibility for photocatalytically producing Schiff base in the coupled system of aromatic alcohols and nitrobenzene.

In this paper, $Cd_XZn_{1-X}S$ photocatalysts were successfully fabricated by a simple wet chemistry process at room temperature. The as-synthesized $Cd_XZn_{1-X}S$ samples exhibit outstanding photocatalytic performance for the photocatalytic selective synthesis of Schiff bases in a coupled system of aromatic alcohols and nitrobenzene using N_2 and visible light. When $Cd_{0.78}Zn_{0.22}S$ sample is used as a photocatalyst, the highest yield of Schiff base reaches up to 55.2% under visible light irradiation for 4 h. The changes of intermediate products (aromatic aldehydes and aniline) produced in the reaction process are also investigated. To the best of our knowledge, one-pot synthesis of Schiff base compounds in the coupled system of aromatic alcohols and nitrobenzene instead of aldehydes and aniline by photocatalysis method has not been reported.

2. Experimental

2.1. Materials

Cadmium nitrate tetrahydrate [$Cd(NO_3)_2{\cdot}4H_2O$], zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$], sodium sulfide ($Na_2S{\cdot}9H_2O$), benzotrifluoride (BTF), methanol (MeOH), ethanol (EtOH), ethylene glycol (EG) and other chemicals used in the experiments were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used throughout the experiments.

2.2. Preparation of photocatalysts

A series of $Cd_XZn_{1-X}S$ (X = 0, 0.2, 0.4, 0.6, 0.8, 0.9 and 1.0) samples were synthesized *via* a simple wet-chemical method using $Cd(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Na_2S{\cdot}9H_2O$ as Cd, Zn and S sources, respectively. In a typical procedure, 5× mmol $Cd(NO_3)_2{\cdot}4H_2O$ and 5(1 − X) mmol $Zn(NO_3)_2{\cdot}6H_2O$ were dissolved in 20 mL of deionized water by constantly stirring to form a homogeneous solution. After that, 20 mL of 0.25 M $Na_2S{\cdot}9H_2O$ aqueous solution was added dropwise into the above solution with vigorous stirring for about 30 min. Then the reaction was further stirred for 2 h under ambient conditions. The resulted yellow slurry was centrifuged, washed several times with water, and then dried in an oven under 80 °C for 24 h. The as-prepared $Cd_XZn_{1-X}S$ powders were ground in the mortar before further use.

2.3. Characterization of samples

The crystallographic structures of $Cd_XZn_{1-X}S$ samples were analyzed by powder X-ray diffraction (XRD) using a Bruker D8 advance X-ray diffractometer with Cu Kα radiation (λ = 0.154056 nm), and a scanning speed of 3°/min. The crystallite size of the samples can be calculated by X-ray line broadening analysis according to the Scherrer formula. The elemental analysis was carried out on an inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, ELAN9000). The UV–Vis absorption spectra of synthesized samples were obtained on a UV–vis spectrophotometer (Lambda850). Microcrystalline structure and surface characteristics of the samples were analyzed by scanning electron microscopy (SEM) (S4800/FEI-quanta-200F). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were performed with a FEI-G2 transmission electron microscope with an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) was used to determine the specific surface and pore size distribution of the as-prepared samples by ASAP2020 instrument. X-ray photoelectron spectroscopy (XPS) measurement was carried out on a Thermo Scientific ESCA Lab250 spectrometer, which consists of monochromatic Al Kα as the X-ray source, a hemispheric analyzer, and a sample stage with multiaxial adjustability to obtain the surface composition of the sample. The (photo)electrochemical experiments were conducted in a three-electrode system (CHI-660D, Chenhua Instruments Co., Shanghai, China), and a 300 W Xe lamp (CEL-HXF300E7, Beijing China Education Au-light Co., Ltd) with a cutoff filter ($\lambda > 420$ nm) was used as a photo source in the experiments.

2.4. Photocatalytic tests

The photocatalytic performance of the as-prepared samples was evaluated by selective photocatalytic synthesis of Schiff base compounds in an autoclave fitted with a top Pyrex window. The detail procedure was implemented as follows: 0.1 g catalyst was dispersed in 15 mL benzotrifluoride (BTF) containing aromatic alcohol (0.0255 M) and nitrobenzene (0.0085 M), and then the mixture was transferred into a closed 100 mL autoclave, which was filled with a 0.1 MPa pressure of nitrogen. Before the visible light irradiation, the autoclave was placed on magnetic stirrer and was stirred for 30 min to reach adsorption-desorption equilibrium between the photocatalyst and the reactants. The suspension reaction solution was irradiated by a 300 W Xe arc lamp (CEL-HXF300E7, Beijing China Education Au-light Co., Ltd) with cutoff filter ($\lambda > 420$ nm). The temperature of the reactant solution was maintained at 50 °C by a flow of cooling water during the reaction. After the reaction, the mixture was centrifuged at 12,000 rmp for 10 min to completely remove the catalyst particles. The obtained reaction solutions were analyzed qualitatively by gas chromatography–mass spectrometer (GC–MS, Agilent 5975C-7890A) and were determined quantitatively with a gas chromatograph (Shimadzu GC-2014C, Japan) equipped with an SE-30 capillary column. Conversion, yield and selectivity for Schiff base product, selective oxi-