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Effective use of photogenerated electrons and holes in a system: Photocatalytic selective oxidation of aromatic alcohols to aldehydes and hydrogen production

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ABSTRACT

Effective utilization of photogenerated electrons and holes in a system is always a research hotspot. Photocatalysis has been identified as a promising solution to tackle the current environmental and energy issues. However, photogenerated holes or electrons were wasted in the traditional photocatalytic process. In the paper, a dual-function photocatalytic reaction system was constructed using dispersed Pt_x-modified 2D-3D $Zn_3In_2S_6$ hierarchical structures (x = 1–4). In the system, aromatic alcohols were photocatalytically selectively oxidated into aldehydes and protons were reduced to hydrogen by photogenerated holes and electrons, respectively. In the reaction process, one aromatic alcohol is first dehydrogenated into aromatic aldehyde and two H^+ via the corresponding carbon-centered radical by consuming of two holes, and then two H^+ ions dehydrogenated from OH group and α C—H of alcohol are evolved into H_2 by depleting of two electrons. Atomically dispersed Pt_x could offer the maximum atom efficiency and significantly promote visible light absorption and separation of photogenerated electron-hole pairs. The cooperative photoredox system exhibits remarkable photocatalytic activity for visible light-driven splitting of aromatic alcohols. Under visible light irradiation for 6 h, The H_2 output over 2.14% $Pt/Zn_3In_2S_6$ reaches up to 950 μmol, which is around 7.5, 5.3 and 3.8 times higher than that over $Zn_3In_2S_6$, Pt-nanoparticle/$Zn_3In_2S_6$ and $MoS_2/Zn_3In_2S_6$, respectively. The apparent quantum efficiency (AQE) of 2.14% $Pt/Zn_3In_2S_6$ at 400 nm is about 4.6%. The utilization rate of photogenerated electrons to holes could be achieved 98.2%. Moreover, $Pt/Zn_3In_2S_6$ hybrid shows high stability even when $Zn_3In_2S_6$ was stored for 12 months. Compared with two half-reactions: the photocatalytic selective organics transformation under O_2 atmosphere and the water splitting with sacrificial reagents, such designed dual-purpose photocatalytic reaction not only could effective use of photogenerated electrons and holes for organics transformation and hydrogen production simultaneously but also shows much higher photocatalytic activity than two half-reactions. At the same time, the work also expands the research field of photocatalysis, such as N_2 fixation and CO_2 reduction by using of the as-produced H^+.

1. Introduction

To address the challenges of impending global energy needs and worsening environmental problems, conversion of solar energy into sustainable H_2 by photocatalytic splitting of water has been identified as a promising solution and has attracted more and more global attention [1–7]. Although great progress has been achieved in designing photocatalyst and understanding the microscopic mechanism, photocatalytic H_2 evolution still faces many challenges for practical application [8–17]. For example, the use of sacrificial reagents undesirably wastes the energy of holes, increases the system cost and brings along some oxidation products such as CO_2 [18–20]. How to realize highly efficient production of H_2 along with its intrinsic clean, non-carbon feature and effective use of holes is still a huge challenge.

Recent progresses on photocatalytic selective organic transformations have demonstrated that this green and promising technology can obtain diversiform fine chemicals by selecting appropriate photocatalysts and fine control of reaction conditions [21–24]. For instance, aromatic alcohols could be efficaciously converted into aldehydes by holes photogenerated on visible-light-driven photocatalyst with appropriate conduction band position under mild

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conditions [24–29]. It is preferable to the conventional synthetic pathways (strong chemical oxidants (e.g., Cr^{IV}, ClO^- and Cl_2), environment unfriendly heavy metal catalysts, and harsh reaction conditions such as high temperature and high pressure) [27–35].

Consequently, construction of a dual-function photocatalytic reaction system composed of a dehydrogenation of alcohols and a H_2 evolution may be an ideal approach to solve the above problems. In the system, the photogenerated holes are utilized for selective dehydrogenation of alcohols into corresponding aldehydes and H^+, and the produced H^+ are reduced by the photogenerated electrons to form H_2. This cooperative photoredox reaction not only offers us a promising avenue to reducing the overall cost of water spitting by simultaneously recovering sustainable energy H_2 and high-value fine chemicals, but also provides a new horizon for direct use of photogenerated electrons and holes. Moreover, this reaction (ΔG = 28 kJ mol^{-1}) requires much less energy than water splitting reaction (ΔG = 238 kJ mol^{-1}) [36]. Therefore, compared to the photocatalytic selective organic transformation under O_2 atmosphere and the water splitting with sacrificial reagents, such designed dual-purpose photocatalytic reaction system could be more feasible and practical in the perspective of the sustainable development of the whole human society. However, little success has been realized because of the difficulty in controlling the selectivity of hole-induced oxidation [18,19,36–40]. For example, under sunlight irradiation, Pt/CdS favored dehydrogenation (88.9%) over hydrogenolysis to produce H_2, whereas Pd/$CdS_{0.4}Se_{0.6}$ favored hydrogenolysis (75%) over dehydrogenation to form toluene [36]. Although Pt/TiO_2 [18,37,38] and Pd-nanocubes/TiO_2-nanosheets [19] showed high selectivity for simultaneous 2,3-butanediol (1,1-dibutoxybutane or 1,1-diethoxyethane) production and H_2 evolution under 300 W high-pressure Hg-lamp (λ = 365 nm) and UV–vis light (300 nm $\leq \lambda \leq$ 800 nm), respectively, up to now, few of literatures have been reported visible-light-driven heterogeneous photocatalytic splitting alcohols into corresponding aldehydes and H_2 in a stoichiometric manner [40]. Therefore, to realize simultaneously photocatalytic dehydrogenation of alcohols into H_2 and corresponding aldehydes with high selectivity under visible light irradiation in one photocatalytic reaction system is still a worthy research area. Moreover, exploring the reaction mechanism is also necessary to design photocatalysts with high performance (selectivity, quantum efficiency and stability) for practical applicationas early as possible and expand the research field of photocatalysis such as reduction of carbon dioxide and nitrogen fixation.

Herein, we report a multi-function photocatalytic reaction system for simultaneous decorating atomic Pt_x (x = 1–4) onto 2D-3D $Zn_3In_2S_6$ hierarchical structure and visible-light-driven splitting of aromatic alcohols into hydrogen and corresponding aldehydes at room temperature. $Zn_3In_2S_6$ is a visible-light-absorbing semiconductor with a bulk electronic band gap of about 2.8 eV [41,42]. The $Zn_3In_2S_6$ valence band (VB) has a potential of 1.9 V (vs. NHE), providing adequate oxidizing capacity for selective oxidation of aromatic alcohols (taking p-methoxybenzyl alcohol as an example, the oxidative potentials of p-methoxybenzyl alcohol/p-methoxybenzaldehyde and p-methoxybenzaldehyde/oxidized p-methoxybenzaldehyde are about 1.56 V and 2.01 V (vs. NHE), respectively) [25,42]. The $Zn_3In_2S_6$ conduction band (CB) located at about −0.9 V (vs. NHE) has sufficient driving force for H^+ reduction [42,43]. In addition, 3D $Zn_3In_2S_6$ microspheres assembled by 2D nanosheets are conducive to the deposition of metallic nanoparticles and harvest the induced visible light via multilayers reflection [44]. Atomically dispersed Pt could offer the maximum atom efficiency and significantly promote separation of photogenerated electron-hole pairs. Therefore, Pt/$Zn_3In_2S_6$ hybrids exhibit remarkable photocatalytic activity for visible light-driven splitting of aromatic alcohols into hydrogen and corresponding aldehydes at room temperature. The rates of H_2 evolution and PhCHO production for Pt/$Zn_3In_2S_6$ are much higher than that of the individual $Zn_3In_2S_6$, Pt-nanoparticle/$Zn_3In_2S_6$ and noble metal-free photocatalysts ($MoSe_2$/$Zn_3In_2S_6$, MoS_2/$Zn_3In_2S_6$ and TiN/$Zn_3In_2S_6$). Moreover, this approach is also suitable for other metal sulfide (such as $ZnIn_2S_4$ and CdS). The high photocatalytic performance of Pt/$Zn_3In_2S_6$ hybrids toward visible-light-driven splitting of aromatic alcohols into hydrogen and corresponding aldehydes was investigated by a series of control experiments. The possible mechanism was proposed and proved by electron paramagnetic resonance (EPR) and isotopic tracing experiments.

2. Experimental

2.1. Preparation of photocatalysts

All chemicals used in the experiments were analytical grade and used without further purification. $Zn_3In_2S_6$ was prepared by a hydrothermal method. In a typical procedure, 0.86 g $ZnSO_4{\cdot}7H_2O$, 0.58 g $InCl_3{\cdot}4H_2O$, 0.65 g cetyltrimethylammonium bromide and a double excess of CH_3CSNH_2 were dissolved in 70 mL of deionized water. The solution was then transferred into a 100 mL Teflon-lined autoclave and heated at 160 °C for 12 h. After being cooled down to room temperature, the yellow precipitate was washed with absolute ethanol and deionized water for several times. Finally, the obtained sample was dried at 60 °C in a vacuum oven. Pt/$Zn_3In_2S_6$ photocatalyst was prepared by an in situ photodeposition method. The preparation procedure was the same as that in the activity test.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the as-prepared photocatalysts were tested by a Bruker D8 advance X-ray powder diffractometer with Cu Kα radiation at room temperature. The morphologies and microstructures of the photocatalysts were studied by scanning electron microscopy (SEM, FEI Nova Nano 450), transmission electron microscopy (TEM, FEI Tecnai G2 F20) and high-resolution transmission electron microscopy (HRTEM). The X-ray photoelectron spectroscopy (XPS) spectra were measured on a Thermo Scientific ESCA Lab250 spectrometer with an Al Kα X-ray beam. Additionally, the binding energies were corrected with reference to C 1s peak at 284.6 eV. UV–vis diffuse reflectance spectroscopy test (DRS) was performed to measure the optical properties of the photocatalysts by a UV–VIS-NIR spectrophotometer (UV-3600, SHIMA-DZU, Japan) with $BaSO_4$ as a reflectance standard. Photoluminescence (PL) properties were analyzed using a fluorescence spectrometer (RF530, Shimadzu Scientific Instruments Inc., Japan). The values of Pt amount in Pt/$Zn_3In_2S_6$ photocatalysts were detected by inductively coupled plasma-mass spectrometry (ICP-MS, X-Series 2, Thermo Fisher Scientific, Germany). Electron paramagnetic resonance (EPR) spectra were measured on an EPR Spectrometer (A300, Bruker, Germany). High-angle annual dark-filed scanning transmission electron microscopy (HAADF-STEM) images were obtained on a FEI Titan Themis 200 equipped with a Bruker super-X EDS. The photoelectrochemical tests were carried out on a three-electrode system (CHI-660E, Chenhua Instruments Co., China). A Pt wire and Ag/AgCl were used as counter electrode and reference electrode, respectively. The catalyst powder was deposited on the fluoride tin oxide (FTO) substrate to serve as working electrode (The 4-mg sample was dispersed in 500 μL of deionized water by sonication to get uniform slurry. Then, the 20 μL slurry was deposited as a film on a 0.5 cm × 0.5 cm FTO substrate. After dry at room temperature, the working electrode was obtained.). A quartz cell