



# Synergistic effect of photocatalysis and thermocatalysis for selective oxidation of aromatic alcohols to aromatic aldehydes using Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO composite



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## ABSTRACT

Selective oxidation of aromatic alcohols to corresponding carbonyl compounds under mild conditions has a promising prospect in industry. In the paper, we successfully prepared a new mode of photothermocatalyst, Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO composite, which shows dramatically enhanced activity for selective oxidation of benzyl alcohol to benzaldehyde compared with single Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> and ZnO under visible light illumination. The enhancement is due to a synergistic effect of low-temperature thermocatalysis on ZnO and photocatalysis on Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>. ZnO could weaken bonds of the C–H<sub>α</sub> and the O–H. Then the reactive species (<sup>•</sup>O<sub>2</sub><sup>-</sup> and h<sup>+</sup>) generated on Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> could be easy for selective oxidation of benzyl alcohol to produce benzaldehyde. The photoelectrochemical and photoluminescence (PL) results and a series of control experiments (e.g. reaction temperature and radical scavenger) prove this synergistic effect and proposed mechanism. Moreover, the stable performance and high activity of Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO for other aromatic alcohols indicate its applicable potential. This study provides a promising way to combine photocatalysis and thermocatalysis for the design of novel and efficient visible-light-driven catalyst for selective oxidation of aromatic alcohols or other organics under mild reaction conditions.

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## 1. Introduction

Since Fujishima and Honda found that water can be split into H<sub>2</sub> and O<sub>2</sub> by a TiO<sub>2</sub> electrode under UV-light irradiation in 1972 year [1], numerous types of materials have been developed as photocatalysts, such as metallic oxides [2], metal sulfides [3], metal-free semiconductors [4], composites [5], etc. [6,7]. Many reports published had proved that the photocatalysis method has a great promise for environmental remediation [2], solar energy conversion [3,7], and organics transformation [8,9] and so on [7,10]. In recent years, the photocatalytic selective oxidation of aromatic alcohols to corresponding aldehydes has attracted extensive attention [10], because such aromatic aldehydes and their derivatives are crucial raw materials for the synthesis of fine chemicals and pharmaceuticals [11]. The traditional preparation methods of aromatic

aldehydes (chemical oxidation treatment and thermocatalysis) have serious drawbacks (using toxic or corrosive stoichiometric oxidants such as KMnO<sub>4</sub>, Cr<sup>IV</sup>, ClO<sup>-</sup> and Cl<sub>2</sub>, expending vast energy to provide the unavoidable temperature and pressure, causing environment pollution, etc.) [12]. It is known that the photocatalysis method can remedy these defects efficiently, because of its high selectivity, use of solar light as the driving force and O<sub>2</sub> as an oxidant, the milder reaction conditions and environmentally friendly properties [12]. However, in order to achieve the industrialization, the prepared photocatalysts excited by visible-light and with high activity is the key factor for the photocatalytic selective organic transformation.

It has been reported that TiO<sub>2</sub> is one of the most promising photocatalysts because of its low costs, easy availability, high photocatalytic activity, and so on [1–3]. However, it has been confirmed that benzyl alcohol could be oxidized immoderately to yield benzoic acid or carbon dioxide because of its powerful oxidizing capacity [12,13]. Meanwhile, the wide band gap (3.2 eV) is another factor to limit the application [5], because the UV-light that only occupied 7% in sunlight can be absorbed by TiO<sub>2</sub>. Therefore, great efforts have been devoted in order to enhance the utilization of

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visible light and improve the selectivity to target product. For example, modifying TiO<sub>2</sub> through doping ions [14] and coupling with noble metals [15] or other semiconductors [16], and developing non-TiO<sub>2</sub> photocatalysts such as ZnIn<sub>2</sub>S<sub>4</sub> [17], In<sub>2</sub>S<sub>3</sub> [18], g-C<sub>3</sub>N<sub>4</sub> [19], Bi<sub>12</sub>O<sub>17</sub>Cl<sub>2</sub> [13], MVO<sub>4</sub> (M=In, Bi) [8] etc. [9,10]. In despite of these advances in the photocatalytic selective transformation of aromatic alcohols, the design of an efficient and stable photocatalyst for selective oxidation of aromatic alcohols into aromatic aldehydes under visible light has remained challenges so far.

It is well known that transformation of aromatic alcohols into corresponding aldehydes is a dehydrogenation process. It has been reported that ZnO was frequently studied as a promising thermocatalyst for dehydrogenation of alcohols [20–22]. For example, Antonio Guerrero-Ruiz et al. [21] reported that ZnO showed high activity (selectivity of 94%) for the thermocatalytic dehydrogenation of ethanol into acetaldehyde at 623 K for 1 h. Y. Shinohara et al. [22] studied the dehydrogenation of 2-propanol by experiments and theory. The results showed that the selectivity of ZnO for the dehydrogenation of 2-propanol could reach up to 97.8% at 523 K. On the other hand, Zn-In-S (e.g. ZnIn<sub>2</sub>S<sub>4</sub> and Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>), an important ternary semiconductor, is of great interest to applications such as energy conversion and the photocatalysis due to its direct band gap (2.4–2.8 eV for bulk materials) and outstanding optical and electrical properties [23]. For example, ZnIn<sub>2</sub>S<sub>4</sub> and Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> showed high activities for H<sub>2</sub> evolution under visible light irradiation [24]. Moreover, ZnIn<sub>2</sub>S<sub>4</sub> could be employed as catalyst to activate O<sub>2</sub> for selective oxidation of aromatic alcohols into aromatic aldehydes under visible light [17a]. Therefore, Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> may be an excellent photocatalyst for selective oxidation of aromatic alcohols. However, few of the literature about the properties of Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> as a photocatalyst have been reported for photocatalytic selective organic transformation. According to the above analysis, if a dehydrogenation catalyst (e.g. ZnO) is combined with a photocatalyst (e.g. Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>), a visible-light excited, efficient and stable catalyst for selective oxidation of aromatic alcohols to corresponding aldehydes may be produced. This is first time to report the synergistic effect of the photocatalysis and thermocatalysis for selective oxidation of aromatic alcohols into aromatic aldehydes.

In this paper, a novel mode of catalysts of Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO composite for selective oxidation of aromatic alcohols to corresponding aldehydes, which possess both photocatalytic and thermocatalytic activities, was prepared by a hydrothermal method and a solvent assisted interfacial reaction. The composite Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO exhibits an efficient synergistic effect for selective oxidation of aromatic alcohols to corresponding aromatic aldehydes under mild conditions by photothermocatalytic reaction. In the Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO composite, Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> as a photocatalyst was motivated under visible light illumination to generate the reactive species (electrons, holes and superoxide radical), and ZnO as a thermocatalyst loaded on the surface of Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> could weaken the bonds of C–H<sub>α</sub> and O–H of benzyl alcohol (PhCH<sub>α2</sub>OH) by low-temperature thermocatalysis [22]. The physical, chemical and photoelectric properties of Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO composite were characterized by XRD, UV–vis DRS, SEM, TEM, EDS-mapping, XPS and BET techniques. The photothermocatalytic synergistic effect was thoroughly investigated by photoelectrochemical, PL and a series of control experiments. A possible reaction mechanism was proposed.

## 2. Experimental

### 2.1. Materials

Indium chloride tetrahydrate (InCl<sub>3</sub>·4H<sub>2</sub>O), thiacetamide (CH<sub>3</sub>CSNH<sub>2</sub>), zinc sulfate heptahydrate (ZnSO<sub>4</sub>·7H<sub>2</sub>O), zinc acetate (ZnAc<sub>2</sub>), potassium hydroxide (KOH) and methanol (CH<sub>3</sub>OH) were

purchased from by Aladdin Chemistry Co. (Shanghai, China). All chemicals used in the experiments were analytical pure grade and used directly without further purification.

### 2.2. Preparation of samples

#### 2.2.1. Synthesis of Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> sample

Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> was prepared by a modified hydrothermal method [24]. In a typical procedure, 2 mmol InCl<sub>3</sub>·4H<sub>2</sub>O, 3 mmol ZnSO<sub>4</sub>·7H<sub>2</sub>O and a double excess of CH<sub>3</sub>CSNH<sub>2</sub> were dissolved in 70 mL of deionized water. The mixed solution was further transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed and heated at 433.15 K for 12 h, and then cooled down to room temperature. A light yellow precipitate was washed with absolute ethanol and deionized water for several times. Finally, the obtained product was dried in a vacuum oven at 333.15 K for 8 h.

#### 2.2.2. Synthesis of Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO composites and ZnO sample

The as-prepared Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> powder was added into 15 mL methanol, then 0.1 M ZnAc<sub>2</sub> methanol solution was added dropwise into the Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub> suspension to form mixed suspension under continuous stirring at 333.15 K. After vigorous stirring for 30 min, double stoichiometric ratio of KOH was added into the above suspension and maintained at 333.15 K for 2 h. Then the mixed suspension was allowed cooling to room temperature. The yellowish product was collected by a centrifugal machine, washed thoroughly with deionized water, and dried in a vacuum oven at 333.15 K for 8 h. For comparison, ZnO was prepared by the similar procedure without adding Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>.

### 2.3. Characterization

X-ray diffraction (XRD) was recorded by a Bruker D8 advance X-Ray powder diffractometer with Cu K $\alpha$  radiation and a scanning speed of 3° min<sup>-1</sup> at room temperature. UV–vis diffuse reflectance spectroscopy (DRS) was carried out to measure the optical properties of the as-prepared samples by a UV–VIS–NIR spectrophotometer (UV-3600, SHIMA-DZU, Japan) with BaSO<sub>4</sub> as a reflectance standard. The morphologies and microstructures of the photocatalysts were investigated by scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20). N<sub>2</sub> adsorption-desorption isotherms and the Brunauer-Emmett-Teller (BET) surface areas were measured with an ASAP 3020 system (Micromeritics Instrument Corp.). The X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific ESCA Lab250 spectrometer with an Al K $\alpha$  X-ray beam, and the binding energies were corrected with reference to C 1s peak at 284.6 eV. Photoluminescence (PL) experiments were carried out by the FP-6500 fluorescence spectrometer. The value of ZnO amount in Zn<sub>3</sub>In<sub>2</sub>S<sub>6</sub>@ZnO composites was measured by inductively coupled plasma-mass spectrometry (ICP-MS, X-Series 2, Thermo Fisher Scientific, Germany.).

The photoelectrochemical experiments were performed in a three-electrode system (CHI-660E, Chenhua Instruments Co. Shanghai, 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. A quartz cell filled with 0.1 M Na<sub>2</sub>SO<sub>4</sub> or 0.1 M KCl electrolyte containing 0.1 M K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] was used as the reaction system. A 300 W Xenon lamp (PLS-SXE 300C, Beijing Perfect Light Co. Ltd) equipped with a 420 nm cutoff filter ( $\lambda > 420$  nm) was applied as a visible light source.

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