



# Optimizing Pd and Au-Pd decorated Bi<sub>2</sub>WO<sub>6</sub> ultrathin nanosheets for photocatalytic selective oxidation of aromatic alcohols



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## ARTICLE INFO

### Article history:

Received 16 March 2018

Revised 16 May 2018

Accepted 16 May 2018

### Keywords:

Metal nanoparticles  
Ultrathin nanosheets  
Photocatalytic reaction  
Selective oxidation  
Interfacial cooperation

## ABSTRACT

Ultrathin semiconductor nanosheets decorated with metallic nanoparticles (NPs) are promising in photocatalysis due to the multi-component interactions. The materials with a series of monometallic Pd and bimetallic Au-Pd NPs anchored on Bi<sub>2</sub>WO<sub>6</sub> ultrathin nanosheets were synthesized and developed as photocatalysts for selective oxidation of aromatic alcohols to aromatic aldehyde. By optimizing the metallic contents, a typical sample of Au(0.25)Pd(0.25)-Bi<sub>2</sub>WO<sub>6</sub> exhibited the highest photocatalytic activity among all the prepared photocatalysts including Au(0.5)-Bi<sub>2</sub>WO<sub>6</sub>, Pd(*x*)-Bi<sub>2</sub>WO<sub>6</sub>, Au(*x*)Pd(*x*)-Bi<sub>2</sub>WO<sub>6</sub> (*x* represents the weight percentage of metal in the photocatalyst), along with the improved selectivity for producing benzaldehyde. The extended absorption in visible range, higher efficiency for the transfer and separation of photogenerated charge carriers, and the superior ability for generating active radicals of Au(0.25)Pd(0.25)-Bi<sub>2</sub>WO<sub>6</sub> were demonstrated by DRS spectra, photoelectrochemical measurements, and ESR detection. The effect of the active species for selective oxidation of aromatic alcohols was proved to follow the order of  $h^+ + \cdot O_2^- > h^+ \gg \cdot O_2^-$ . Accordingly, a possible mechanism based on the interfacial cooperation between bimetallic Au-Pd NPs and Bi<sub>2</sub>WO<sub>6</sub> ultrathin nanosheets was proposed to illustrate the photocatalytic process, where the holes accumulated in Bi<sub>2</sub>WO<sub>6</sub> ultrathin nanosheets and  $\cdot O_2^-$  produced on metallic NPs synergistically promote the selective oxidation of aromatic alcohols.

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## 1. Introduction

The development of green and sustainable chemistry to partially oxidize alcohols into carbonyl compounds (ketones/aldehydes) has attracted significant attention [1,2], because the carbonyl compounds (ketones/aldehydes) are widely applied as the precursors for producing drugs, vitamins and fragrances, and also important intermediates for many complex syntheses. Traditionally, the selective oxidation of alcohols using stoichiometric oxidizing agents such as chromate (Cr<sup>6+</sup>) or permanganate (Mn<sup>7+</sup>) are hazardous, delivering considerable amounts of toxic waste [3,4]. Recently, the photocatalytic processes have shown great potential in organic synthesis because of the remarkable advantages such as inexhaustible solar energy, environmentally benign process, and sustainability [5,6]. Typically, the selective oxidation reactions driven by photocatalysis have been demonstrated at atmospheric pressure and room temperature by several types of substrates such as alcohols, amines, and sulfides [7–10]. To further improve the conversion and selectivity of the reactions, the devel-

opment of high-efficiency photocatalysts has gained considerable attention of researchers [11].

As one of the typical members of the Aurivillius family, bismuth tungstate (Bi<sub>2</sub>WO<sub>6</sub>) consisting of perovskite-like slabs of [WO<sub>4</sub>]<sup>2-</sup> sandwiched between bismuth oxide [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> units [12–14] has shown good photocatalytic performance in organic contaminant decomposition, water splitting, photoreduction of carbon dioxide, organic transformations, due to the relatively narrow bandgap of ~2.7 eV, appropriate energy band positions and favorable separation of photogenerated electron-hole pairs induced by internal electric fields between the slabs [12,15–17]. In recent years, the ultrathin two dimensional (2D) nanosheets with mono- or several atomic layer thicknesses have sparked widespread interests due to their unique characteristics, such as higher specific surface areas, more active sites, and fast charge separation, endowing them enhanced performance in heterogeneous photocatalysis compared to most of the other nanostructures [18,19]. Xie and co-workers synthesized the single-unit-cell Bi<sub>2</sub>WO<sub>6</sub> layers for the photo-reduction of CO<sub>2</sub> to methanol, and achieved a methanol formation rate of 125-times higher than that of bulk Bi<sub>2</sub>WO<sub>6</sub> owing to the larger CO<sub>2</sub> adsorption capacity, higher photoabsorption, and increased electron-hole separation efficiency [20]. Simultaneously, the monolayer Bi<sub>2</sub>WO<sub>6</sub> nanosheets were also reported by Wang's

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group [21], demonstrating an excellent photocatalytic activity for  $H_2$  production under visible light where both the highly active surface and the favorable charge separation contributed to the superior photocatalytic performances of the monolayer material. However, the photocatalytic activity of pure  $Bi_2WO_6$  is hard to be further improved only by changing the morphology due to its inherent restrictions such as limited light harvesting ability, rapid recombination of photogenerated carriers, and low mobility of charge carriers [22,23]. In this regard, the hybrid nanostructures of metal-decorated  $Bi_2WO_6$  ultrathin nanosheets are expected to break through the bottlenecks of pure  $Bi_2WO_6$  because of the remarkable synergistic properties arising from the materials combination, and therefore to gain further enhancement in photocatalysis.

Noble metal nanoparticles (NPs), such as Ag, Au, Pd and Pt, are deemed as wonderful co-catalysts for various photocatalytic reactions [24–26]. Many noble-metal decorated semiconductor photocatalysts have exhibited enhanced photocatalysis due to their interfacial synergistic interactions between metal and semiconductor [27–29]. The modification of metal NPs on an n-type semiconductor forms the Schottky barrier at the metal/semiconductor interface, which contributes to the efficient separation and transfer of photogenerated charge carriers [30,31]. Loading metal NPs on semiconductors is also an effective strategy to increase the surface catalytic activity, where metal NPs would trap the charges from semiconductor and act as highly active sites for reactions [32,33]. Furthermore, bimetallic catalysts often show tunable and optimized activity compared to their monometallic counterparts [34,35]. Typically, AuPd NPs exhibit effective activity because of their synergistic electron effect that can improve the catalytic performance [36–38]. As a result, it is prospective that the  $Bi_2WO_6$  ultrathin nanosheets loaded with bimetallic NPs will show improved photocatalysis for selective organic reactions due to the multi-component interactions between metals and between metals and semiconductor. Although there are some literatures have reported the photocatalytic performance of noble metal decorated  $Bi_2WO_6$  nanostructures [39–42], the photocatalysts with optimal bimetallic Au-Pd NPs anchored on  $Bi_2WO_6$  ultrathin nanosheets were rarely exploited yet.

In this work, the  $Bi_2WO_6$  ultrathin nanosheets with thickness of  $\sim 5$  nm were synthesized through a facile solvothermal method, and a series of monometallic Pd and bimetallic Au-Pd NPs were then anchored on the  $Bi_2WO_6$  ultrathin nanosheets by a simple reducing reaction at  $60^\circ C$ . The as-prepared materials were developed as photocatalysts for selective oxidation of aromatic alcohols to aromatic aldehyde under a simulated sunlight. By comparison, the  $Au(0.25)Pd(0.25)-Bi_2WO_6$  sample exhibited the highest photocatalytic activity among the photocatalysts of  $Bi_2WO_6$ ,  $Au(0.5)-Bi_2WO_6$ ,  $Pd(x)-Bi_2WO_6$ ,  $Au(x)Pd(x)-Bi_2WO_6$  ( $x$  represents the weight percentage of metal in the photocatalyst). Finally, a possible mechanism based on the interfacial cooperation effect between bimetallic Au-Pd NPs and  $Bi_2WO_6$  ultrathin nanosheets was proposed to illustrate the improved photocatalysis for the selective oxidation of aromatic alcohols.

## 2. Experimental

### 2.1. Materials

Bismuth chloride ( $BiCl_3$ ), sodium tungstate dihydrate ( $Na_2WO_4 \cdot 2H_2O$ ), hexadecyltrimethylammonium bromide (CTAB), chloroauric acid tetrahydrate ( $HAuCl_4 \cdot 4H_2O$ ), ammonium tetrachloropalladate ( $(NH_4)_2PdCl_4$ ), ethylene glycol (EG), and acetonitrile were purchased from Aladdin Industrial Corporation and used without further purification.

### 2.2. Synthesis of $Bi_2WO_6$ ultrathin nanosheets

The  $Bi_2WO_6$  ultrathin nanosheets were synthesized through a facile solvothermal process. Typically, 3.5 mmol  $BiCl_3$ , 0.503 g CTAB and 1.75 mmol  $Na_2WO_4 \cdot 2H_2O$  were successively dissolved in 30 mL ethylene glycol to form a white suspension. After 30 min stirring, the suspension was transferred into a Teflon-lined stainless steel autoclave with 50 mL capacity, which was kept at  $160^\circ C$  for 5 h and then cooled to room temperature naturally. Finally, the resultant precipitate was collected and washed with deionized water by centrifugation, and dried at  $60^\circ C$  in air overnight. The product is  $Bi_2WO_6$  ultrathin nanosheets.

### 2.3. Noble-metal loading on $Bi_2WO_6$ ultrathin nanosheets

A series of monometallic Pd and bimetallic Au-Pd NPs were loaded on the  $Bi_2WO_6$  ultrathin nanosheets by a moderate reduction reaction with ethanol as the reducing agent. The preparation process is described as follows. 100 mg of  $Bi_2WO_6$  ultrathin nanosheets was dispersed in 40 mL of ethanol-water mixed solvent ( $V_{ethanol}:V_{water} = 1:1$ ) by 30 min sonication to form a suspension. For preparing  $Pd(x)-Bi_2WO_6$  ( $x$  represents the weight percentage of Pd in the material), a certain amount of  $(NH_4)_2PdCl_4$  solution (0.01 M) was added into the  $Bi_2WO_6$  suspension under stirring. The dosage of  $(NH_4)_2PdCl_4$  solution was calculated according to that the theoretical weight percentage of Pd NPs in the targeted material is 0.25 wt%, 0.5 wt% and 1.0 wt%, respectively. After continuously stirred for 1 h at room temperature, the mixture was then stirred at  $60^\circ C$  for 30 min. Finally, the product was collected by centrifugation, washed with absolute ethanol, and dried at  $60^\circ C$  overnight to obtain the samples of  $Pd(0.25)-Bi_2WO_6$ ,  $Pd(0.5)-Bi_2WO_6$ , and  $Pd(1.0)-Bi_2WO_6$ , respectively, for various characterizations and photocatalytic tests.

Similarly, the  $Au(x)Pd(x)-Bi_2WO_6$  materials ( $x$  represents the weight percentage of metal in the material) were prepared by the same procedure with simultaneously adding  $HAuCl_4 \cdot 4H_2O$  (0.01 M) and  $(NH_4)_2PdCl_4$  (0.01 M) solutions according to the theoretically calculated dosages. Two typical samples of  $Au(0.25)Pd(0.25)-Bi_2WO_6$  and  $Au(0.5)Pd(0.5)-Bi_2WO_6$  were obtained for characterizations and photocatalytic studies.

Also,  $Au(0.5)-Bi_2WO_6$  sample with 0.5 wt% of Au loading was also prepared with adding  $HAuCl_4$  (0.01 M) solution.

### 2.4. Characterization

The crystal phase of the materials was analyzed by x-ray diffractometer (Japan Shimadzu XRD-6000) with  $Cu K\alpha$  radiation. The morphology of the samples was observed by a field emission scanning electronic microscope (FESEM, JEOL JSM-6700F, Japan) and a transmission electron microscopy (TEM, JEOL-2010, Japan). AFM images were recorded using Agilent 5500 AFM (Agilent Technologies, USA). The crystal structure and element distribution were analyzed by a high-resolution transmission electron microscopy (HRTEM, Hitachi S4800) associated with the energy-dispersive X-ray (EDX) mapping. The weight percentage of noble metal NPs in the materials was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu, ICPS-8100). The solid sample absorption spectra were measured by UV-Vis diffuse reflection recorded on a spectrophotometer of Perkin Elmer Lambda 950. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo SCIENTIFIC ESCALAB 250Xi X-ray photoelectron spectrometer with an excitation source of  $Al K\alpha$  radiation ( $\lambda = 1486.8$  eV), and the binding energies were normalized to the signal of adventitious carbon at 284.8 eV. The electron spin resonance (ESR) signals of spin-trapped oxidative

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