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# Electronic Supplementary Information (ESI)

## A Green and Efficient Photocatalytic Route for the Highly-Selective Oxidation of Saturated Alpha-carbon C–H Bond in Aromatic Alkanes over Flower-like $Bi_2WO_6$

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## Experimental Details

### Preparation of catalysts

**Synthesis of flower-like $Bi_2WO_6$:** Flower-like $Bi_2WO_6$ in the form of powder was prepared by a simple hydrothermal method. Typically, 0.6 g L-lysine and 1.65 g sodium tungstate dehydrate were completely dissolved in 60 mL deionized water. A bismuth nitrate solution (20 mL, 0.5 $mol \cdot L^{-1}$) prepared by dissolution of 4.85 g bismuth nitrate pentahydrate in 1.5 M nitric acid was added into the above mixture. After stirring for 4 h at room temperature, the mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 160°C for 8 h. The final products were collected by centrifugation, then washed with deionized water and dried in air at 60°C.

**Synthesis of CdS:** CdS in the present work was synthesized according to the reported procedure [S1]. Briefly, cadmium acetate, $Cd(Ac)_2 \cdot 2H_2O$, was dissolved in 200 mL deionized water and placed in a bath ultrasonicator for 10 min to achieve the desired 5.0 mM $Cd(Ac)_2$ solution (denoted as A). Sodium sulfide, $Na_2S \cdot 9H_2O$, was dissolved in 200 mL deionized water by ultrasonication to obtain the desired 6.0 mM $Na_2S$

solution (denoted as B). Solution B was slowly added into solution A in a drop-by-drop process for 4 h, and was aged for 36 h with vigorous stirring. Then, the products were collected by filtration, washed with water, and fully dried at 60°C in an oven.

**Synthesis of $Bi_2WO_6$ nanoparticles:** The preparation of nanoparticle $Bi_2WO_6$ was according to the previous report [S2]. Briefly, 11.15 g of $Bi(NO_3)_3{\cdot}5H_2O$ and 3.80 g of $Na_2WO_4{\cdot}2H_2O$ were dissolved in 50 mL distilled water separately. A precipitation was obtained when the two solutions were mixed together under magnetic stirring at room temperature for 1 h. After being filtered out, the precipitate was washed with distilled water and then dried at 80°C for 2 h. And the resulting powder was calcined at 500°C for 2 h.

**Synthesis of $Bi_2WO_6$ nanoplates:** $Bi_2WO_6$ nanoplates were synthesized according to the reported procedure [S3]. Briefly, 2.5 mmol $Na_2WO_4$ and 5 mmol $Bi(NO_3)_3$ were mixed together, and 100 mL of deionized water was added. White precipitates appeared immediately, and the beaker was put in ultrasonic bath for 10 minutes in order to complete the precipitate reaction. After being washed for several times, the collected precipitate was added into a 50 mL Teflon-lined autoclave. And the autoclave was filled with deionized water up to 80% of the total volume. After that, the autoclave was sealed into a stainless steel tank and kept at 160°C for 20 h.

**Synthesis of nestlike $Bi_2WO_6$:** The rodlike $Bi_2WO_6$ was synthesized according to the reference [S4]. Typically, 0.2425 g (0.5 mmol) of $Bi(NO_3)_3{\cdot}5H_2O$ and 0.0824 g (0.25 mmol) of $Na_2WO_4{\cdot}2H_2O$ were dissolved in 40 mL of deionized water by ultrasonic treatment and magnetic stirring. Then 3 g of $Na_2SO_4$ was added into the above mixture. After the pH was adjusted to 1, the mixture was transferred into a Teflon-lined stainless steel autoclave and maintained at 180°C for 24 h. The final products were collected by centrifugation, washed several times with deionized water and ethanol, and dried in air at 60°C for 12 h.

## Catalyst characterizations

The powder X-ray diffraction (XRD) pattern of the prepared $Bi_2WO_6$ was collected on a Bruker D8 Advance X-ray diffractometer with mono-chromatized Cu-Kα radiation (λ=0.15406 nm). The morphology and microscopic structure were obtained over a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) and high-resolution transmission electron microscope (HR-TEM, JEM-2100F). X-ray photoelectron spectroscopy (XPS) was used to determine the Bi4f, W4f and O1s binding energies (BEs) of surface bismuth, tungsten and oxygen species, using Mg-K**α** (hν = 1253.6 eV) as excitation source (XPS, SSX-100, Mg-K**α**). The UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded over a Cary-100 spectrophotometer, using $BaSO_4$ as background reference.

## Photocatalytic activity

Briefly, 8 mmol substrate and 50 mg photocatalyst were mixed uniformly in a round bottom flask with a condenser pipe on top. Then $O_2$ was bubbled through the mixture at a rate of 3 mL·min$^{-1}$. The suspension was stirred for 30 min before illumination. Then the reaction was carried out under visible light originated from a 300 W Xe lamp (PLS-SXE 300C, Perfectlight) with a 400 nm cutoff filter. After reaction, the catalyst was removed by centrifugation, and the products were directly analyzed with an SHIMADZU Gas Chromatograph (GC-2010, with a capillary SH-Rtx-1701 analysis column). Control photoactivity experiments with different radical scavengers 1 mmol (tetra-methylpiperidine N-oxide (TEMPO) as radical scavenger, ammonium oxalate (AO), potassium persulfate ($K_2S_2O_8$), *tert*-butyl alcohol (TBA) and benzoquinone (BQ) as scavengers for photogenerated holes, photogenerated electrons, hydroxyl radicals, and superoxide radical specials, respectively) were performed under similar reaction condition. Time-dependent scale-up experiment of 80 mmol toluene over 500 mg flower-like $Bi_2WO_6$ was carried out using ten times the amount of toluene and catalyst adopted in experiments performed under the standard reaction condition. Conversion of aromatics and selectivity to the corresponding aldehydes is defined as follows:

$$Conversion\ (\%) = \frac{\sum content\ (mmol) of\ each\ product\ analyzed\ via\ GC}{Substrat\ (mmol)} \times 100\%$$

$$Selective\ (\%) = \frac{content\ of\ corresponding\ aldehyde\ (mmol)}{\sum content\ (mmol) of\ each\ product} \times 100\%$$

## Supporting Figures

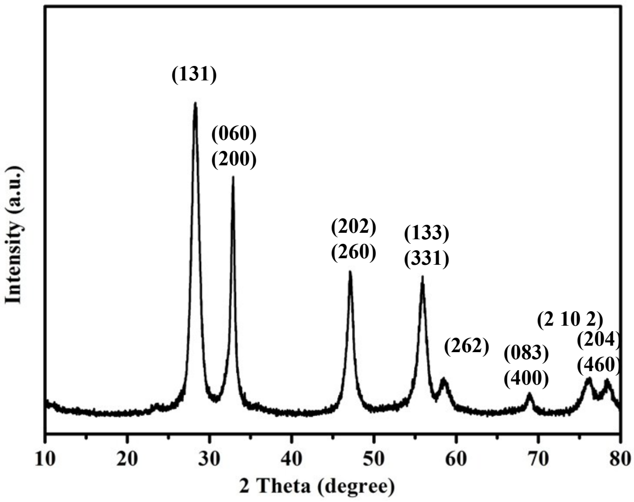

**Figure S1** Powder XRD patterns of the flower-like $Bi_2WO_6$ microspheres.

The X-ray diffraction peaks of the as-prepared flower-like $Bi_2WO_6$ in Figure S1 exhibit an orthorhombic structure with lattice parameters a = 0.5457 nm, b = 1.6436 nm, and c = 0.5438 nm (JCPDS 39-0256).

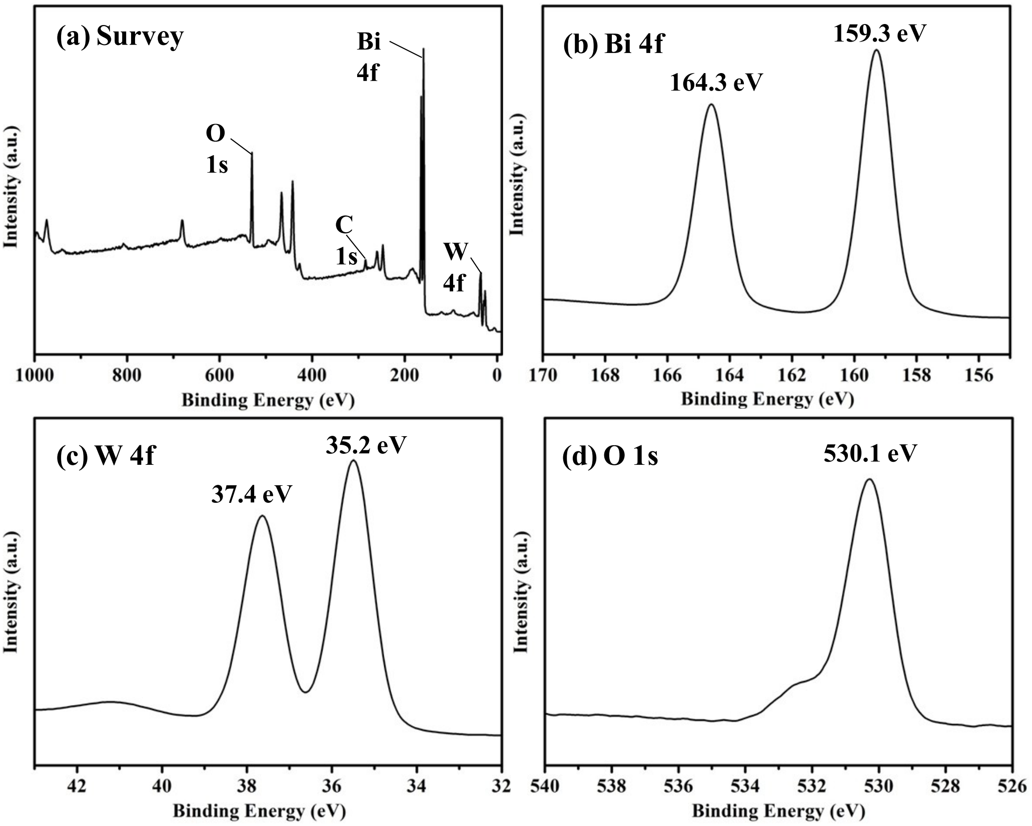

**Figure S2** XPS results: (a) survey, (b) Bi 4f, (c) W 4f, and (d) O 1s spectrum of flower-like $Bi_2WO_6$.

In Fig. S2b, the peaks at 164.3 and 159.3 eV binding energy are attributed to the 4f $_{5/2}$ and 4f $_{7/2}$ of $Bi^{3+}$, respectively. In Fig. S2c, the peaks at 37.4 and 35.2 eV are corresponding to W4f$_{5/2}$ and W4f $_{7/2}$ signals of $W^{6+}$ oxidation state.

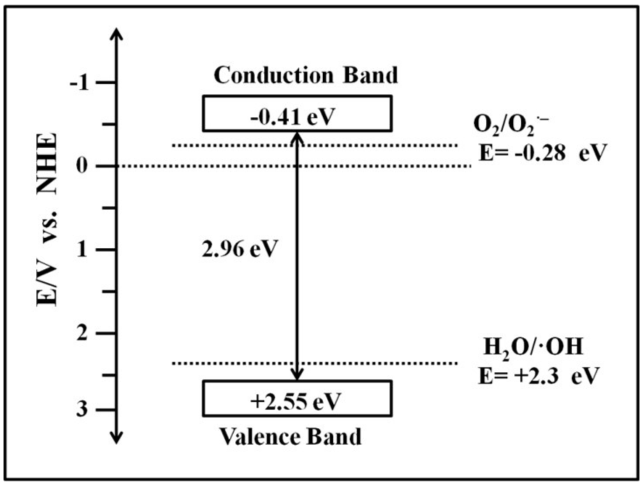

**Figure S3** Schematic of the band gap structure of flower-like $Bi_2WO_6$.

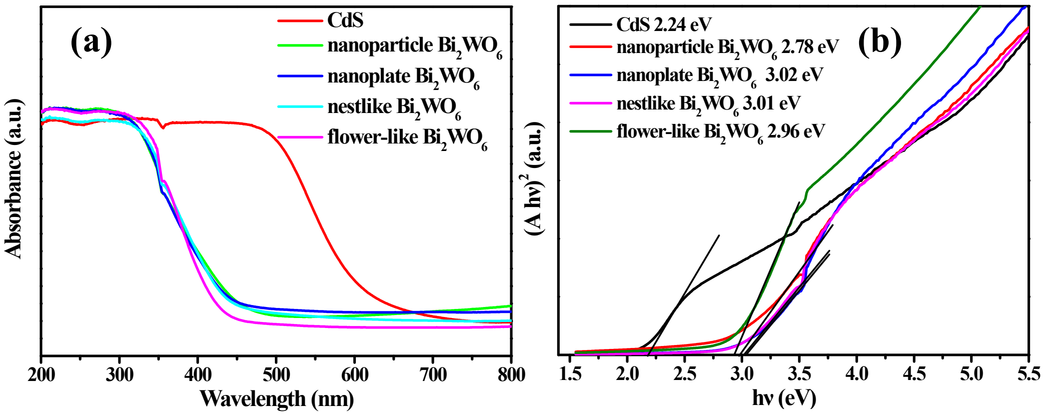

**Figure S4** (a) UV-vis diffuse reflectance spectra (DRS), and (b) the corresponding $(Ahv)^2$ versus photon energy plot of CdS and $Bi_2WO_6$ of different morphologies.

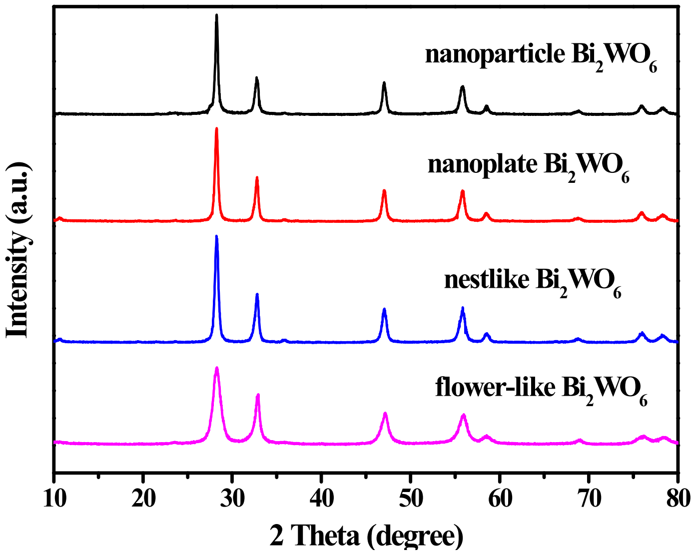

**Figure S5** Powder XRD patterns of the as-prepared $Bi_2WO_6$ samples with different morphologies.

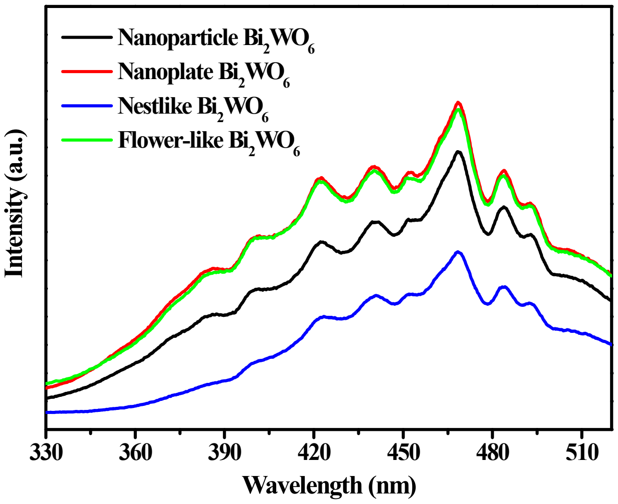

**Figure S6** PL emission spectra of $Bi_2WO_6$ with different morphologies ($\lambda_{Ex}$=270 nm)

**Table S1** Nitrogen adsorption-desorption isotherms of as-prepared $Bi_2WO_6$ samples

| Sample | $S_{BET}$ ($m^2 \cdot g^{-1}$) | Pore Volume ($cm^3 \cdot g^{-1}$) | Average Pore Size (nm) |
|---|---|---|---|
| Nanoparticle $Bi_2WO_6$ | 158.56 | 0.40 | 10.20 |
| Nanoplate $Bi_2WO_6$ | 174.84 | 0.37 | 8.52 |
| Nestlike $Bi_2WO_6$ | 19.12 | 0.09 | 19.68 |
| Flower-like $Bi_2WO_6$ | 30.33 | 0.23 | 30.96 |

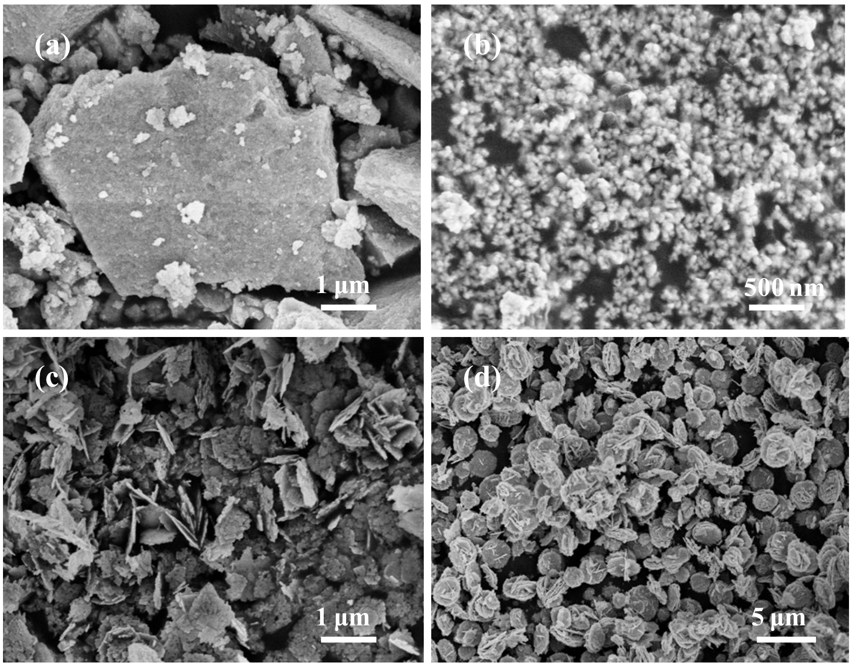

**Figure S7** SEM images of the as-prepared samples: (a) CdS, (b) nanoparticle $Bi_2WO_6$, (c) nanoplate $Bi_2WO_6$, and (d) nestlike $Bi_2WO_6$.

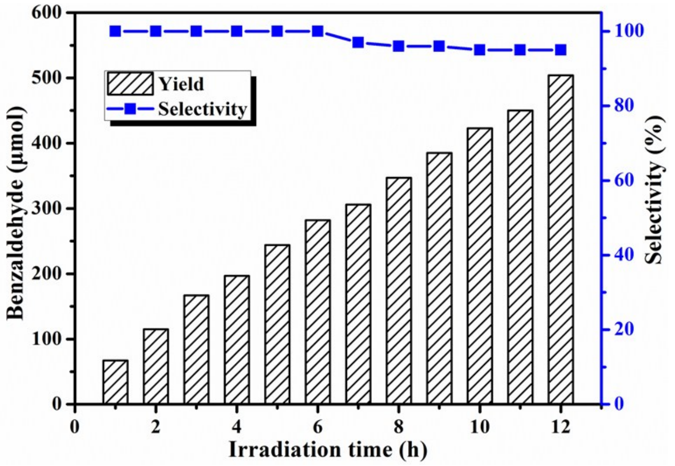

**Figure S8** Time-dependent photocatalytic performance toward selective oxidation of toluene over flower-like $Bi_2WO_6$ under visible-light irradiation using ten times the amount of toluene and catalyst adopted in experiments performed under the standard reaction condition.

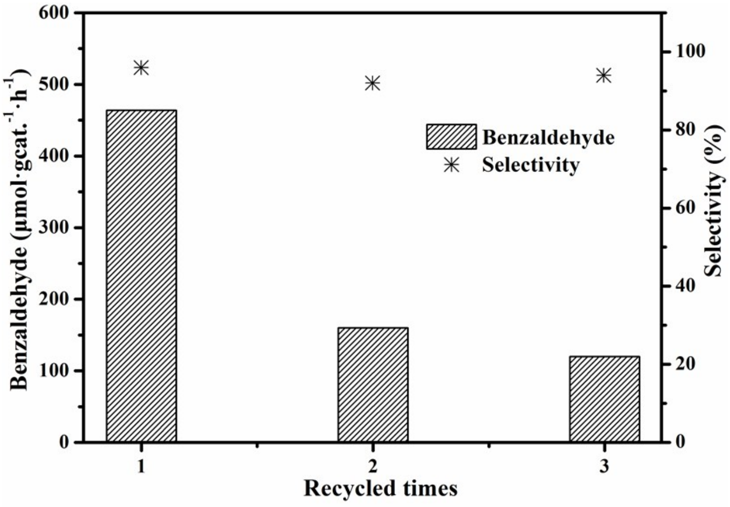

**Figure S9** Photoactivity recycled experiments of flower-like $Bi_2WO_6$ toward the selective oxidation of toluene to benzaldehyde under visible light for 5 h.

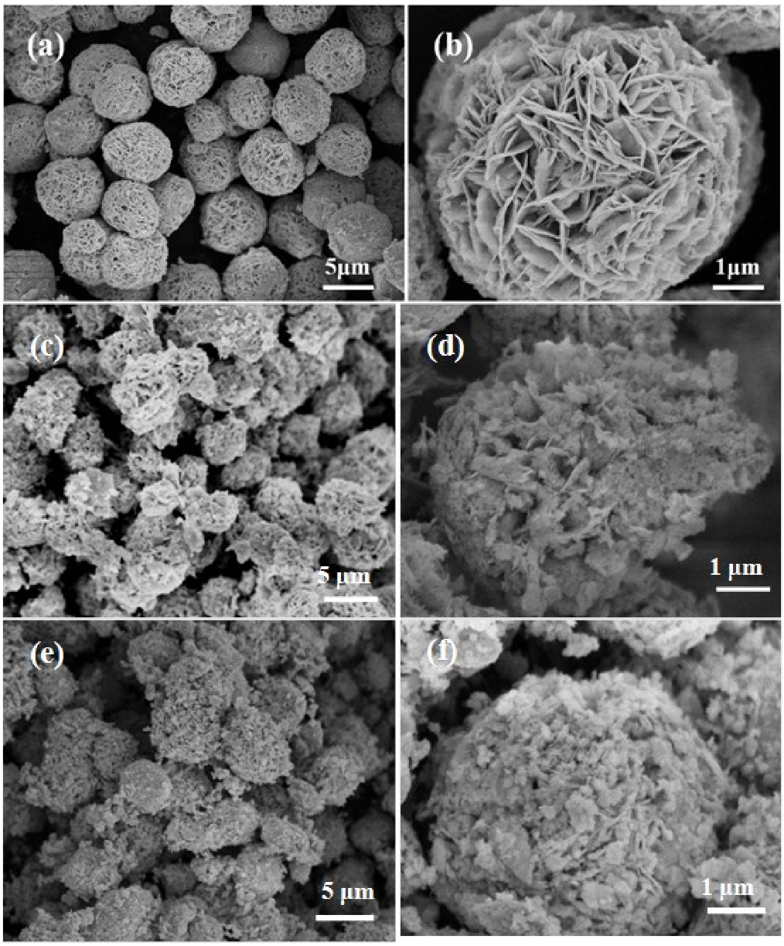

**Figure S10** SEM images of fresh flower-like $Bi_2WO_6$ (a, b), collected catalyst after first recycle (c, d), and collected catalyst after second recycle (e, f).

## Reference

S1. Y. H. Zhang, N. Zhang, Z. R. Tang and Y. J. Xu, *Chem. Sci.*, 2012, **3**, 2812-2822.

S2. H. G. Yu, R. Liu, X. F. Wang, P. Wang and J. G. Yu, *Appl. Catal. B: Environ.*, 2012, **111-112**, 326-333.

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