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A Green and Efficient Photocatalytic Route for High-Selective Oxidation of Saturated Alpha-Carbon C–H Bond in Aromatic Alkanes over Flower-like Bi<sub>2</sub>WO<sub>6</sub>

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A green and efficient route for high-selective oxidation of saturated alpha-carbon C-H bond in aromatic alkanes under visible-light irradiation and solvent-free condition is developed using flower-like Bi<sub>2</sub>WO<sub>6</sub> microspheres as catalyst.

Among the oxidation reactions of hydrocarbon, the efficient and selective activation of saturated C-H bonds in alkanes or aromatics for the generation of value-added products such as aldehydes and ketones is a significant challenge both in organic synthesis and chemical industry.<sup>1</sup> Because of the low selectivity and/or conversion, the conventional processes are unsatisfactory. In addition, the systems are usually environment-unfriendly. Since the saturated C-H bonds are thermodynamically strong and dynamically inert, the reaction conditions are usually harsh, requiring high temperature, high pressure, and extra initiators or toxic reagents.<sup>2-5</sup> From the viewpoint of green chemistry, it is desirable to develop an environment-benign route that is highly efficient for the conversion of alkanes or aromatics to value-added products.

It was demonstrated that heterogeneous photocatalysis has huge potential in the oxidation of hydrocarbons.<sup>6-10</sup> So far, only a limited amount of catalysts, e.g.  $TiO_2$  or  $TiO_2$ -based, <sup>11-15</sup> CdS or CdSbased materials, <sup>16, 17</sup> and Nb<sub>2</sub>O<sub>5</sub>, <sup>18</sup> were researched for the selective photo-oxidation of alkanes or aromatic alkanes using O<sub>2</sub> as oxidant. However, the application of these catalysts is hampered by ill factors such as low selectivity, poor efficiency, and the need of using ultraviolet light or organic solvents. As far as the use of visible light is concerned, the works on photocatalytic selective oxidation of alkanes or aromatic alkanes are rare, especially for those without the use of noxious solvents.<sup>19, 20</sup> Furthermore, for the few known cases there are shortcomings such as low selectivity, extra-initiator involvement, above room temperature (60°C) and use of noble metal. Hence, it is necessary to design high-efficiency photocatalysts for the oxidation of saturated C-H bonds. As a simple Aurivillius oxide, bismuth tungstate ( $Bi_2WO_6$ ) shows good performance in the degradation of organic compounds under visible-light irradiation, owing to its suitable band location and unique layered structure.<sup>21-25</sup> The  $Bi_2WO_6$  materials are low-cost and easily prepared. Recent reports demonstrated that  $Bi_2WO_6$  exhibits appreciable results for the selective oxidation of alcohols under visible-light irradiation.<sup>26-30</sup>

Herein, we report for the first time the use of flower-like  $Bi_2WO_6$  as photocatalyst for highly selective and efficient oxidation of aromatic alkanes using  $O_2$  as oxidant under visible-light irradiation and solvent-free condition. We reveal the pivotal roles of photogenerated holes ( $h^+$ ) and superoxide radicals, and propose a possible mechanism for the reaction.

The flower-like Bi<sub>2</sub>WO<sub>6</sub> microspheres were prepared by a simple hydrothermal method, and the details are provided in the Electronic Supplementary Information (ESI).<sup>†</sup> According to the SEM images (Fig. 1a and b), the flower-like microspheres are 6-7  $\mu$ m in diameter and are made up by nano-sheets. Based on the results of XRD and XPS analysis (Figure S1 and S2), the microspheres are identified as orthorhombic Bi<sub>2</sub>WO<sub>6</sub>.<sup>31, 32</sup>

In UV-Vis DRS study, the flower-like  $Bi_2WO_6$  microspheres exhibit intense absorption in both ultraviolet and visible-light regions (Fig. 1d). The band gap energy ( $E_g$ ) is estimated to be 2.96 eV based on the absorption spectrum and the  $(Ahv)=K(hv-E_g)^n$ formula.<sup>33</sup> The calculated position of conduction and valence band is at -0.41 and 2.55 eV, respectively (Fig. S3), implying a relatively strong oxidation ability of the material. Since  $H_2O/\cdotOH$  and  $O_2/O_2^$ display a standard redox potential (vs. NHE) of 2.3 and -0.28 eV that are within the redox capability of the flower-like  $Bi_2WO_6$ , the band structure provides the feasibility and theoretical basis for the formation of hydroxyl radicals ( $\cdotOH$ ) and superoxide radicals ( $O_2^-$ ).

The selective oxidation of typical primary aromatic alkanes was carried out at room temperature in the absence of solvent over various catalysts under visible-light irradiation for 5 h. Under  $N_2$  atmosphere or in the absence of a photocatalyst and/or light

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<sup>+</sup>Electronic Supplementary Information (ESI) available: experimental details, photocatalyst characterization figures, photocatalytic activity experiments. See DOI: 10.1039/x0xx00000x

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**Fig. 1** (a-b) SEM images, (c) TEM image, and (d) UV-Vis DRS of flower-like  $Bi_2WO_6$ ; the inset is the corresponding  $(Ahv)^2$  versus photon energy plot

illumination, there is no detection of reactivity. The results of the control experiments suggest that the reaction is photocatalytic, and an oxidant such as  $O_2$  is needed.

The photocatalytic activity of selective oxidation of toluene was examined over CdS <sup>16</sup> and Bi<sub>2</sub>WO<sub>6</sub> of different morphologies <sup>25, 34, 35</sup> (prepared according to the reported literatures) (Table 1). It was observed that the flower-like Bi<sub>2</sub>WO<sub>6</sub> performs the best, showing the highest reaction rate (464  $\mu$ mol·g<sup>-1</sup>·h<sup>-1</sup>) and conversion (1.5%). The only by-product of the reaction is benzyl alcohol. Since all the prepared samples exhibit good response of visible light and the band gaps of Bi<sub>2</sub>WO<sub>6</sub> with different morphologies are similar (Fig. S4), the high performance of flower-like Bi<sub>2</sub>WO<sub>6</sub> is unlikely to be due to the good response of visible light or the appropriateness of band gap. Besides, the structure properties and photoluminescence (PL) results of the as-prepare Bi<sub>2</sub>WO<sub>6</sub> samples (Fig. S5 and S6, and Table S1) do not suggest that the better photoactivity of flower-like Bi<sub>2</sub>WO<sub>6</sub> can be ascribed to factors such as surface area, pore volume or separation ability of photogenerated charge carries. Considering

**Table 1** Selective oxidation of toluene over different photocatalysts

 under visible-light irradiation <sup>a</sup>

Catalyst	Benzaldehyde (µmol∙g <sup>-1</sup> ∙h <sup>-1</sup> )	Conv. (%)	Sel. (%)
CdS	240	0.7	98
Nanoparticle Bi <sub>2</sub> WO <sub>6</sub>	172	0.6	97
Nanoplate Bi <sub>2</sub> WO <sub>6</sub>	160	0.5	95
Nest-like Bi <sub>2</sub> WO <sub>6</sub>	140	0.4	96
Flower-like Bi <sub>2</sub> WO <sub>6</sub>	464	1.5	96

<sup>a</sup> Photocatalyst (50 mg), substrate (8 mmol), no solvent, room temperature,  $O_2$  flow rate (3 mL·min<sup>-1</sup>), visible-light irradiation ( $\lambda$  > 400 nm, 5 h).





<sup>a</sup> Substrate (8 mmol), catalyst (50 mg), O<sub>2</sub> flow rate (3 mL·min<sup>-1</sup>)
 <sup>b</sup> P-cresol (8mmol), catalyst (50 mg), benzotrifluoride (2 mL), O<sub>2</sub> flow rate (3 mL·min<sup>-1</sup>)

<sup>c</sup> P-methoxytoluene (1 mmol), catalyst (50 mg), acetonitrile (2 mL),  $O_2$  flow rate (3 mL·min<sup>-1</sup>)

that the as-prepared  $Bi_2WO_6$  samples are greatly different in morphology (Fig. S7), it is deduced that the high performance is ascribable to the unique flower-like structure of  $Bi_2WO_6$ , and the enhancement of visible light absorption as a result of multi-reflection of light across the structure.

It was found that the selective oxidation of toluene derivatives over flower-like  $Bi_2WO_6$  is also effective (Scheme 1). It is noted that the oxidation of ethylbenzene or n-propylbenzene produces ketones rather than aldehydes. Thus, only the alpha-carbon of C-H bond is activated in this photocatalytic system. Compared with the oxidation of xylenes, the lower transformation of chlorotoluenes can be associated with the presence of electron withdrawing group (–Cl) that inhibits the oxidation activity of the methyl. That is, the methyl of xylenes is more active than that of chlorotoluenes. For the same reason, the selectivity to chlorobenzaldehydes is 100%, Published on 18 November 2015. Downloaded by Nanyang Technological University on 19/11/2015 11:33:30



Fig. 2 Kinetic-experiments for selective oxidation of toluene under visible light in the presence or absence of various radical scavengers over flower-like  $Bi_2WO_6$  (AO as hole scavenger,  $K_2S_2O_8$  as electron scavenger, and TBA as hydroxyl radical scavenger).

whereas in the oxidation of xylenes, there is the generation of the corresponding alcohols as by-product.

Furthermore, time-dependent scale-up experiments on toluene oxidation over flower-like  $Bi_2WO_6$  show that there is effective increase of benzaldehyde yield but no significant change of the high selectivity upon the extension of irradiation time (Fig. S8). With such performance, it is clear that the flower-like  $Bi_2WO_6$  is a photocatalyst effective for the oxidation of aromatic alkanes to the corresponding aldehydes. In all cases of using flower-like  $Bi_2WO_6$ , there is no detection of carbon dioxide, indicating the absence of over oxidation during the photocatalytic processes.

We performed experiments to prove that the photocatalytic oxidation of toluene over Bi<sub>2</sub>WO<sub>6</sub> involves free radicals. By adding 0.01 mmol tetra-methylpiperidine N-oxide (TEMPO) which is a typical radical scavenger, we quench the transformation of toluene to benzaldehyde almost completely. Furthermore, the effects of different active species in the reaction system were explored. Kinetic-experiments were performed with an appropriate amount of ammonium oxalate (AO), potassium persulphate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and tert-butanol (TBA) as scavenger for holes (h<sup>+</sup>), photogenerated electrons (e<sup>-</sup>) and hydroxyl radicals (·OH), respectively.<sup>36-38</sup> As shown in Fig. 2, the conversion of toluene is almost prohibited in the presence of AO, and there is no increase of conversion with reaction time. The results indicate that the holes are vital for the activation of toluene. Besides, both the addition of TBA and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> results in a certain decrease of toluene conversion. The results suggest that •OH and e<sup>-</sup> are also involved in the reaction, but their influences are apparently moderate. Since O<sub>2</sub> accepts photogenerated electrons easily to produce superoxide radical (02 ), <sup>39</sup> it was considered as oxidant for the transformation of toluene. <sup>16</sup> In this study, the conversion of toluene increase with time in the presence of electron scavenger  $K_2 S_2 O_8. \ \mbox{In other words, the}$ oxidation by  $O_2$  is unlikely to occur or only plays a minute role in this system.



Fig. 3 Schematic of the plausible mechanism for photocatalytic selective oxidation of toluene to benzaldehyde over flower-like  $Bi_2WO_6$  under visible-light irradiation

Based on the above results, it is deduced that the major active species for the photocatalytic selective oxidation of toluene is h<sup>4</sup> rather than  $\cdot \text{OH}$  or  $\text{e}^-\!\!.$  To a certain degree the deduction is in agreement with the active species commonly found in systems for the oxidation of hydrocarbons.<sup>16, 27, 28</sup> Accordingly, we propose a plausible mechanism for the catalytic reaction (Fig. 3). Before the start of visible light illumination, toluene gets in touch with Bi<sub>2</sub>WO<sub>6</sub>. After then, the photogenerated holes from valence band and electrons from conduction band are transferred to the Bi<sub>2</sub>WO<sub>6</sub> surface under visible light irradiation. The direct oxidation of toluene for the formation of toluene cationic radicals as facilitated by the holes is a vital step. This step involves the activation of saturated C-H bond and is often regarded as the rate-determining step for selective oxidation of alkanes.<sup>1</sup> Finally, the O<sub>2</sub> dissolved in toluene combines with the toluene cationic radicals to generate the target product benzaldehyde. In this reaction system the holes play a key role in the direct dehydrogenation of toluene to the radical intermediate, and O<sub>2</sub> is the main oxidizing species.

In summary, a green and efficient system has been developed for the selective oxidation of aromatic alkanes into valuable products under mild conditions. This is the first report on the use of easily synthesized flower-like Bi<sub>2</sub>WO<sub>6</sub> as active photocatalyst for the selective oxidation of aromatic alkanes under visible-light irradiation without the need of any solvents. The good performance of flower-like Bi<sub>2</sub>WO<sub>6</sub> toward the oxidation of aromatic alkanes is attributed to its unique morphology. We investigated the specific functions of active intermediate species, and proved that the photogenerated holes are significantly involved in the oxidation process. A plausible reaction mechanism is proposed. The visiblelight driven method using flower-like Bi<sub>2</sub>WO<sub>6</sub> opens an environment-friendly way for efficient synthesis of organic compounds that requires the activation of saturated alpha-carbon C-H bonds.

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### Notes and references

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