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# Efficient visible-light-driven selective conversion of glucose to high-value chemicals over Bi<sub>2</sub>WO<sub>6</sub>/Co-thioporphyrazine composite in aqueous media

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# ABSTRACT

Selective photocatalytic oxidation of glucose to high-value chemicals in aqueous media using atmospheric oxygen as oxidant and solar light as driving force is a greatly attractive topic. Herein, Bi<sub>2</sub>WO<sub>6</sub>/CoPz (cobalt tetra (2,3-bis(butylthio)maleonitrile) porphyrazine) composite was served as a visible-light photocatalyst towards selective oxidation of glucose to high-value arabinose and formic acid in aqueous media, which was performed under visible light ( $\lambda \ge 420$  nm) irradiation using atmospheric oxygen as oxidant. The reactive parameters for glucose oxidation, such as light intensity, CoPz content, glucose concentration and active species, were studied. The highest activity for Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite was obtained when the CoPz content was 0.25 %. Under the optimum reaction conditions, 96.8 % of total selectivity towards arabinose and formic acid at 45.3 % of glucose conversion was obtained after reacting 3 h. The critical role of CoPz and the rationale behind the high photocatalytic performance for Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite were further investigated using various techniques.

#### 1. Introduction

With the growing concerns about fossil fuel depletion and environmental pollution, developing renewable and sustainable energy resources becomes more and more urgent [1-4]. As is known to all, biomass and solar energy are two abundant and renewable sources in nature, thus the combined utilization of biomass and solar energy represents one of the most promising sustainable approaches for solving above problems in future development. Many attempts have been devoted to the transformation of biomass into high-value chemicals by photocatalysis with solar energy [5-8]. Glucose, a C6 monosaccharide, represents an ideal feedstock for the sustainable production of high-value chemicals. Notably, photocatalytic oxidation of glucose can provide various forms of high-value chemicals from C1 to C6 products [9-14]. Among the high-value chemicals obtained from glucose conversion, arabinose (C5 compound) and formic acid (C1 compound) have attracted much attention recently, because both compounds are valuable platform chemicals. Arabinose is an important biobased precursor to produce arabinoxine, vitamin B2 and DNA [15]. While formic acid is a commodity chemical in various industrial fields, especially its applications in hydrogen storage and fuel cell have received a lot of attention in

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# recent years [16-19].

Photocatalytic oxidation of glucose to arabinose and formic acid could be performed by using TiO<sub>2</sub>-based photocatalyst [20-25]. Under UV light irradiation, bare TiO<sub>2</sub> can catalyze glucose oxidation to produce arabinose, formic acid and other products in aqueous phase, and introducing heteropolyacid on TiO2 surface can change the reaction mechanism [20]. The crystalline phase of  $TiO_2$  has an effect on the glucose oxidation, the glucose conversion was enhanced and a good selectivity towards arabinose, erythrose and formic acid was obtained using rutile TiO<sub>2</sub>, and the presence of Pt can increase the glucose conversion [21]. Though TiO<sub>2</sub> is not photoactive under visible light owing to its large bandgap, visible light can also drive the glucose oxidation to produce arabinose, formic acid and other oxidation products in a mixture of water and acetonitrile maybe because of the formation of TiO<sub>2</sub>-glucose LMCT complex [22]. In addition, the visible light activity of TiO<sub>2</sub> towards glucose oxidation could be enhanced by adding Ag nanoparticles in a mixture of water and acetonitrile [23]. Ideally, arabinose and formic acid could be directly produced through the cleavage of C1-C2 bond in glucose molecule. However, the control of selectivity to specific products with targeted C-C bond cleavage remains a challenge, because the glucose molecule has multiple C-C

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bonds, any C—C bond can be cleaved in the photocatalytic process. Therefore, it is very fascinating to explore an efficient strategy for high selective production of arabinose and formic acid from glucose through the C1—C2 bond cleavage.

As a simple aurivillius oxide with a layered structure, bismuth tungstate (Bi<sub>2</sub>WO<sub>6</sub>) has recently attracted considerable attention in photocatalytic organic transformation [26-29]. Especially, it was discovered that Bi<sub>2</sub>WO<sub>6</sub> can serve as a highly selective photocatalyst for organic transformation in water, such as oxidizing glycerol and benzylic alcohol to dihydroxyacetone and benzaldehyde, respectively [26,27]. Water is deemed to be a desirable green solvent, this unique property of Bi<sub>2</sub>WO<sub>6</sub> inspired us that it might be used as a potential photocatalyst towards selective oxidation of glucose to high-value chemicals in water. However, pure Bi<sub>2</sub>WO<sub>6</sub> can only adsorb UV light or visible light with a wavelength less than 450 nm, this makes up only a small fraction of solar spectrum, thus the solar energy cannot be fully utilized. In addition to this, pure Bi<sub>2</sub>WO<sub>6</sub> still suffers from low separation efficiency of photogenerated carriers, which limits its photocatalytic efficiency [30-33]. Metallothioporphyrzine (MPz) has recently attracted considerable attention as a biomimetic photocatalyst, for MPz has a strong ability to absorb visible light so as to utilize solar energy [34–36]. However, MPz as a macrocyclic compound is prone to aggregation, so MPz is usually loaded on a support to fabricate a composite photocatalyst to overcome this problem. In a word, coupling MPz and semiconductor to form a composite photocatalyst can address their shortcomings at the same time. It is also an efficient strategy to fabricate an efficient photocatalytic system for oxidizing glucose to organic acids in aqueous phase [37-39].

In this work, coupling  $Bi_2WO_6$  with cobalt tetra(2,3-bis(butylthio) maleonitrile) porphyrazine (CoPz) to fabricate a composite photocatalyst  $Bi_2WO_6$ /CoPz was designed. Enhancing the visible light absorption and promoting the separation of photogenerated carriers for  $Bi_2WO_6$  were realized by introducing CoPz, and the  $Bi_2WO_6$ /CoPz composite exhibited an excellent visible-light photocatalytic activity for selective oxidation of glucose to arabinose and formic acid in water.

#### 2. Experimental

#### 2.1. Materials

In this work, all chemical reagents were analytical grade, which were supplied by commercial companies. For example, bismuth(III) nitrate pentahydrate (Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) and histidine were supplied by J&K Scientific Ltd. and Shanghai Yuanye Bio-Technology Co., Ltd., respectively. Glucose, arabinose, formic acid and *p*-benzoquinone were supplied by Aladdin Chemistry Co., Ltd. Sodium tungstate hexahydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), sodium hydroxide, dichloromethane, potassium io-dide and isopropanol were supplied by Sinopharm Chemical Reagent Co., Ltd. All of them were used directly in the experiment.

#### 2.2. Preparation of Bi<sub>2</sub>WO<sub>6</sub>

Bi<sub>2</sub>WO<sub>6</sub> was prepared according to the reported hydrothermal method [40]. In a typical procedure, 7.5 mmol of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 3.75 mmol of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were respectively dissolved in 50 mL and 100 mL of deionized water under magnetic stirring. The obtained Bi (NO<sub>3</sub>)<sub>3</sub> solution and Na<sub>2</sub>WO<sub>4</sub> solution were then mixed, producing a white precipitate. After 10 min of ultrasonication, the pH value of system was adjusted to 7 with 0.2 mol·L<sup>-1</sup> of NaOH solution under magnetic stirring. The resulting system was subsequently transferred into a 200 mL of Teflon-lined stainless-steel autoclave. The reaction was allowed to react at 160°C for 24 h, and then the autoclave was cooled naturally. The precipitate was collected through centrifugation, which was washed successively with deionized water and ethanol. Finally, the obtained product was dried at 80°C for overnight under vacuum.

#### 2.3. Preparation of Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite

The synthesis of CoPz was accomplished according to the previous report [41]. The molecular structure of CoPz was shown in Fig. S1. Its XPS analysis was presented in Fig. S2.  $Bi_2WO_6/CoPz$  composite made of  $Bi_2WO_6$  and CoPz was prepared as follows: a homogeneous solution was firstly prepared through dissolving 2.5 mg of CoPz into 50 mL of dichloromethane. Afterwards, 1 g of  $Bi_2WO_6$  powder was added into the above solution under magnetic stirring, which was continually stirred for 12 h. The products were collected through removing dichloromethane with reduced pressure distillation, followed by drying at 80°C for 12 h under vacuum. The loading amount of CoPz was 0.25 %, the prepared composite was denoted as  $Bi_2WO_6/CoPz(0.25 \%)$ . By tuning the loading amount of CoPz,  $Bi_2WO_6/CoPz(0.1 \%)$ ,  $Bi_2WO_6/CoPz(0.5 \%)$  and  $Bi_2WO_6/CoPz(1 \%)$  composites were also prepared according to this approach.

#### 2.4. Characterization

The phase composition of obtained sample was analyzed by X-ray diffraction (XRD), which was conducted on a Bruker D8 Advanced X-ray diffractometer using Cu Ka radiation. To investigate the optical absorption properties of obtained sample, the ultraviolet-visible diffuse reflection spectra (UV-vis DRS) of obtained sample was measured on a Hitachi F-7000 UV-vis spectrophotometer with an integrated sphere accessory, and BaSO<sub>4</sub> was employed as a reference. The chemical states of elements were investigated by means of X-ray photoelectron spectroscopy (XPS) with a VG Multilab 2000 spectrometer, and the binding energy was calibrated with the adventitious C1 s peak at 284.8 eV in XPS analysis. The determination of composite composition was carried out with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with the corresponding elemental mapping, which was acquired using a FEI Talos F200X STEM. The photocurrent measurements were carried out using a Corrtest CS350 electrochemical workstation, which were conducted in a three-electrode system. An LED lamp emitted mainly at 420 nm was utilized as the light source during the photocurrent measurements. Electron spin resonance (ESR) spectra were measured with a JES-FA200 spectrometer to investigate the active species.

# 2.5. Photocatalytic experiments

A cylindrical vessel attached with a circling water-cooled jacket was employed as the reactor for glucose oxidation. The water could be circulated within the jacket when the reaction proceeded, which can ensure that the reaction performs at ambient temperature. The light source was a 300 W Xe lamp equipped with a 420 nm cutoff filter, providing the visible light ( $\lambda \ge 420$  nm) for photocatalytic reaction. For the photocatalytic experiment, 50 mL of glucose aqueous solution was taken into the reactor, its concentration was 3 mmol·L<sup>-1</sup> unless specified otherwise. Then 30 mg of catalyst was added to the glucose aqueous solution. The obtained suspension was magnetically stirred for 30 min in the dark to ensure the adsorption/desorption equilibrium between the glucose and the photocatalyst powders. After that, the suspension was exposed to visible light irradiation, and the light intensity was 1.5 W·cm <sup>2</sup> unless specified otherwise. Because the oxidant was the atmospheric dioxygen, the reactor was directly opened to the air. The sample solution was withdrawn from the reactor at regular intervals during the irradiation, and the filtrate was subsequently obtained through filtration. The filtrate was used to high-performance liquid chromatography (HPLC) analysis.

Glucose and its products were identified and quantitatively analyzed by a DionexUltiMate 3000 HPLC system, which was equipped with a refractive index detector. HPLC separation was examined by using a Shodex SUGAR SH-1011 column. 0.4 mmol·L<sup>-1</sup> of sulfuric acid aqueous solution was served as the mobile phase, and its flow rate was 0.6



Fig. 1. XRD patterns of  ${\rm Bi_2WO_6},$  CoPz and  ${\rm Bi_2WO_6/CoPz}$  composites with different CoPz content.

mL·min<sup>-1</sup>. The injection volume for detection was  $25 \mu$ L. The following formulae were used to calculate the glucose conversion and product selectivity.

 $\frac{Conversion = \frac{[glucose]_0 - [glucose]_i}{[glucose]_0} \times 100\%}{Selectivity = \frac{[product]_i}{[glucose]_0 - [glucose]_i} \times 100\%}$ 

[glucose]<sub>0</sub> indicates the initial molar concentration of glucose.

 $[glucose]_t$  and  $[product]_t$  indicate the molar concentration of glucose and product after *t* time of reaction, respectively.

### 3. Results and discussion

### 3.1. Catalyst characterization

The XRD patterns of pure Bi<sub>2</sub>WO<sub>6</sub> and Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite are displayed in Fig. 1. As shown in Fig. 1, the characteristic diffraction peaks centered at 20 values of 28.4, 32.9, 47.2, 55.9, 58.6, 68.7, 76.0 and  $78.5^{\circ}$  were observed for pure Bi<sub>2</sub>WO<sub>6</sub>, which were indexed to the orthorhombic  $Bi_2WO_6$  [32,33]. Weak diffraction peaks with  $2\theta$  values between 17 and 30° were observed for the XRD pattern of CoPz. In the XRD patterns of Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite, only the diffraction peaks of Bi<sub>2</sub>WO<sub>6</sub> are observed. Furthermore, the intensity of diffraction peaks of Bi<sub>2</sub>WO<sub>6</sub> became slightly weaken with the increase in the CoPz content [42]. The typical TEM image of Bi<sub>2</sub>WO<sub>6</sub> was displayed in Fig. 2(A), it was observed that Bi<sub>2</sub>WO<sub>6</sub> had a nanoflake morphology. The TEM image of Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite (Fig. 2(B) and 2(C)) was not the same as that of pure Bi<sub>2</sub>WO<sub>6</sub>, a transparent thin layer coated on its surface was observed, indicating that the presence of CoPz molecules on the Bi<sub>2</sub>WO<sub>6</sub> surface. The HAADF-STEM with the corresponding elemental mapping analysis was used to further study the composition of the Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite, as shown in Fig. 3. It can be observed that the CoPz distributed uniformly on the surface of Bi<sub>2</sub>WO<sub>6</sub>, this result clearly indicates the successful formation of Bi2WO6/CoPz composite by introducing CoPz on the Bi<sub>2</sub>WO<sub>6</sub> surface.

The chemical states of elements in Bi2WO6 and Bi2WO6/CoPz





Fig. 2. TEM images of Bi<sub>2</sub>WO<sub>6</sub> (A) and the Bi<sub>2</sub>WO<sub>6</sub>/CoPz(0.25 %) composite (B and C).



Fig. 3. HAADF-STEM image of  $Bi_2WO_6/CoPz(0.25 \%)$  composite (A) and its corresponding elemental mapping of Bi, W, O, Co, N and S (B-G).

composite were further determined by XPS. Fig. 4 shows the high resolution XPS spectra in Bi 4f, W 4f and O 1s regions for  $Bi_2WO_6$  and  $Bi_2WO_6$ /CoPz composite. In Fig. 4(A), two peaks with binding energies at 159.3 and 164.7 eV are ascribed to Bi  $4f_{7/2}$  and Bi  $4f_{5/2}$  of  $Bi^{3+}$  in  $Bi_2WO_6$ , respectively [33,43,44]. Fig. 4(B) displays the high resolution XPS spectrum of W 4f, the peaks with binding energies at 35.5 and 37.7 eV originate from W  $4f_{7/2}$  and W  $4f_{5/2}$  of  $W^{6+}$  in  $Bi_2WO_6$ , respectively [32,33,45]. As shown in Fig. 4(C), the XPS spectrum of O 1s may be divided into two peaks at about 530.3 and 532.3 eV, which could be assigned to the crystal lattice oxygen and adsorbed oxygen, respectively [32,33,45]. However, when the CoPz was composited to  $Bi_2WO_6$ , the peaks of Bi 4f, W 4f and O 1s for  $Bi_2WO_6$  were shifted to lower binding energy, it indicated that there existed the strong interaction between CoPz and  $Bi_2WO_6$ . The binding energy values in the  $Bi_2WO_6$ /CoPz composite are different from that of pure  $Bi_2WO_6$ , which is because of

the change in the electron density of the elements at the interface. Therefore, by combining HAADF-STEM with the corresponding elemental mapping as well as XPS investigation, the results confirmed that the  $Bi_2WO_6/CoPz$  composite was formed.

A comparison of the optical properties of Bi<sub>2</sub>WO<sub>6</sub>, CoPz and Bi<sub>2</sub>WO<sub>6</sub>/ CoPz composite was further investigated by UV-vis DRS. As observed in Fig. 5, the UV-vis DRS of pure Bi<sub>2</sub>WO<sub>6</sub> only exhibited the absorption at the wavelength ranging from UV light to visible light at about 450 nm, which originated from intrinsic band-gap transition [32]. There was no absorption of visible light with a wavelength more than 450 nm for pure Bi<sub>2</sub>WO<sub>6</sub>. Three types of characteristic bands of porphyrazine including B-band, Soret-band and Q-band were observed for the UV-vis DRS of CoPz. It also exhibited that CoPz had strong absorption in visible light region. When Bi<sub>2</sub>WO<sub>6</sub> was coupled with CoPz, the light absorption ability of the Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite was obviously different from that of pure Bi<sub>2</sub>WO<sub>6</sub>. The Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite shows an obviously enhancement of visible light absorption ranging from about 400 nm to 800 nm, and the intensity of visible light absorption for Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite in this range increases with higher content of CoPz, this can be attributed to the presence of CoPz. The above results manifest that coupling Bi<sub>2</sub>WO<sub>6</sub> with CoPz can effectively extend the absorbance spectrum of Bi<sub>2</sub>WO<sub>6</sub>. Considering that the visible light constitutes a large fraction of the solar spectrum, thus this composite maybe an attractive photocatalyst for the effective utilization of solar light.

# 3.2. Photocatalytic oxidation of glucose

The photocatalytic performance of catalysts for glucose oxidation was performed in an aqueous medium under visible light irradiation at ambient temperature, and the results are shown in Table 1. Despite the presence of visible light, no conversion of glucose was observed without any catalysts (Table 1, entry 1), indicating that the catalyst plays a vital role in glucose oxidation. By contrast, 25.3 % of glucose conversion was obtained in presence of Bi<sub>2</sub>WO<sub>6</sub> after 3 h reaction under visible light irradiation. It is worth noting that the main products of glucose oxidation are arabinose and formic acid, and the total selectivity of two products is up to 94.5 % (Table 1, entry 2). Beyond that, a small quantity of gluconic acid was detected for the glucose oxidation. These results show that the Bi<sub>2</sub>WO<sub>6</sub> is a highly selective photocatalyst for oxidation of glucose to arabinose and formic acid. As expected, the Bi2WO6/CoPz composite exhibited excellent catalytic activity towards glucose oxidation. After the irradiation of visible light for 3 h, 45.3 % of glucose conversion can be achieved over the Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite, which is about 1.8 times as much as that of Bi<sub>2</sub>WO<sub>6</sub> (Table 1, entry 3). Compared to pure Bi<sub>2</sub>WO<sub>6</sub>, a slight reduction in the selectivity towards arabinose and a slight increase in selectivity towards formic acid were observed in the Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite photoctalytic system. The high selectivity with 96.8 % towards arabinose and formic acid can still be obtained along with high conversion (Table 1, entry 3). Obviously, the introduction of CoPz on Bi<sub>2</sub>WO<sub>6</sub> surface can significantly enhance the photocatalytic activity. These results further demonstrated that coupling Bi<sub>2</sub>WO<sub>6</sub> with CoPz can promote the glucose conversion under the condition of keeping the selectivity of the products unchanged.

In addition, the oxidation of glucose in N<sub>2</sub> atmosphere exhibits no significant progress, which approves the pivotal role of O<sub>2</sub> in the conversion of glucose to arabinose and formic acid (Table 1, entry 4). The oxidation of glucose cannot take place under dark conditions (Table 1, entry 5). The dependence of photocatalytic activity of Bi<sub>2</sub>WO<sub>6</sub>/CoPz (0.25 %) composite for glucose oxidation on the light intensity were further examined, the light intensity of visible light was increased from 0.5 to 1.5 W·cm<sup>-2</sup> when other experimental conditions were unchanged, the results were depicted in Fig. 6. It was found that the conversion of glucose increased with the increase in light intensity (black column), such a tendency reveals that this photocatalytic oxidation is dependent on the light intensity. The selectivity of arabinose decreased with the increase of the light intensity (red column), while the selectivity of



Fig. 4. High resolution XPS spectra in Bi 4f (A), W 4f (B) and O 1s (C) regions for Bi<sub>2</sub>WO<sub>6</sub> and Bi<sub>2</sub>WO<sub>6</sub>/CoPz(0.25 %) composite.



Fig. 5. UV–vis DRS of  $Bi_2WO_6$ , CoPz and  $Bi_2WO_6$ /CoPz composites with different CoPz content.

formic acid appeared a reverse tendency (blue column), but the total selectivity was basically unchanged. These results confirm that the oxidation of glucose was driven by visible light. Therefore, the  $Bi_2WO_6/$ CoPz composite could be served as a highly selective and photoactive visible-light photocatalyst for oxidation of glucose to arabinose and formic acid. In particular, the present reaction conditions, such as water as the solvent, atmospheric oxygen as the oxidant, ambient temperature and atmospheric pressure, make the oxidation of glucose be a highly more desirable green reaction process.

For a deeper understand this photocatalytic system, it is important to correlate the dependence of glucose oxidation with the amount of loading CoPz and the substrate concentration. Therefore, the effect of such parameters was further investigated in the following work, and the

 Table 1

 Oxidation of glucose under different reaction conditions.<sup>a</sup>

Entry	Catalyst	Conversion / %	Selectivity / %	
			Arabinose	Formic acid
1	Without	<1	_	_
2	Bi <sub>2</sub> WO <sub>6</sub>	25.3	66.6	27.9
3	Bi2WO6/CoPz(0.25%)	45.3	60.6	36.2
4 <sup>b</sup>	Bi2WO6/CoPz(0.25%)	3.6	73.2	trace
5 <sup>c</sup>	Bi <sub>2</sub> WO <sub>6</sub> /CoPz(0.25%)	<1	-	-

 $^a$  Reaction conditions: aqueous glucose (3 mmol·L<sup>-1</sup>, 50 mL), 30 mg of catalyst, reacting for 3 h, visible light ( $\lambda \geq$  420 nm) irradiation, light intensity of 1 W·cm<sup>-2</sup>.

<sup>b</sup> N<sub>2</sub> atmosphere.

<sup>c</sup> Without light irradiation.

results are illustrated in Figs. 7 and 8. The dependence of glucose conversion and product selectivity on the CoPz content in the  $Bi_2WO_6/CoPz$  composite is presented in Fig. 7. Four loading amounts, such as 0.1 %, 0.25 %, 0.5 % and 1 %, were taken for this study. It was found that the highest conversion of glucose was achieved when the  $Bi_2WO_6/CoPz$  composite has the loading amount of 0.25 % for CoPz. When the loading amount of CoPz further increased to 0.5 % and 1 %, the photocatalytic activity of the  $Bi_2WO_6/CoPz$  composite decreased as compared to that of 0.25 %, but still higher than that of bare  $Bi_2WO_6$  (Table 1, entry 2). At higher loading amount of CoPz than 0.25 %, the decrease of conversion in the oxidation efficiency was observed, maybe owing to the aggregation of CoPz over  $Bi_2WO_6$  [46,47]. These results manifested that the glucose conversion was strongly dependent on the CoPz amount. Furthermore, the selectivity towards arabinose and formic acid does not change much as the change in the loading amount of CoPz.

Fig. 8 shows the dependence of glucose oxidation on the initial glucose concentration. The related experiments were carried out in the concentration range from 1 to 7 mmol· $L^{-1}$ , whereas other experimental conditions were not varied. Increasing the glucose amount means the



Fig. 6. Dependence of photocatalytic activity of Bi<sub>2</sub>WO<sub>6</sub>/CoPz(0.25 %) composite for glucose oxidation on the light intensity. Reaction conditions: aqueous glucose (3 mmol·L<sup>-1</sup>, 50 mL), 30 mg of catalyst, reacting for 3 h, visible light ( $\lambda \geq$  420 nm) irradiation. (Note: Black column represents the glucose conversion. Red column and blue column represent the selectivity towards arabinose and formic acid, respectively.)



**Fig. 7.** Dependence of photocatalytic activity on the loading amount of CoPz for glucose oxidation. Reaction conditions: aqueous glucose (3 mmol·L<sup>-1</sup>, 50 mL), 30 mg of catalyst, reacting for 3 h, visible light ( $\lambda \ge 420$  nm) irradiation, light intensity of 1 W·cm<sup>-2</sup>. (Note: Black column represents the glucose conversion. Red column and blue column represent the selectivity towards arabinose and formic acid, respectively.)



Fig. 8. Dependence of photocatalytic activity of Bi<sub>2</sub>WO<sub>6</sub>/CoPz(0.25 %) composite on different glucose concentrations for glucose oxidation. Reaction conditions: aqueous glucose (50 mL), 30 mg of catalyst, reacting for 3 h, visible light ( $\lambda \ge 420$  nm) irradiation, light intensity of 1 W·cm<sup>-2</sup>. (Note: Black column represents the glucose conversion. Red column and blue column represent the selectivity towards arabinose and formic acid, respectively.)



Fig. 9. Transient photocurrent response for  $Bi_2WO_6$ , CoPz and  $Bi_2WO_6$ /CoPz (0.25 %) composite.

decrease in the ratio of catalyst to glucose. From Fig. 8, a reduction in the glucose conversion with the increasement of its initial concentration was observed, for example, the glucose conversion from 57 % for 1 mmol·L<sup>-1</sup> decreased to 21.3 % for 7 mmol·L<sup>-1</sup>. In addition, the initial glucose concentration made a different effect on the selectivity of different products. The selectivity of arabinose showed an increase tendency with the increasement of initial glucose concentration, whereas a reverse variation tendency for formic acid was observed, but the total selectivity of these two products was less affected by initial glucose concentration.

The recyclability of Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite was further evaluated with five times of cycling uses, and the results were shown in Fig. S3. The slight decline of glucose conversion was observed after five cycles. Meanwhile, the selectivity of arabinose basically remained unchanged for five cycles, and there was little change in the selectivity of formic acid after five cycles. It demonstrates that the Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite serves as a photocatalyst for glucose oxidation possesses good stability.

### 3.3. Mechanism of enhanced photocatalytic activity

On the basis of the above results, it could be summarized that CoPz makes a big contribution to the enhancement of photocatalytic activity for glucose oxidation. Therefore, a series of experiments were performed



**Fig. 10.** The adsorption of glucose on the  $Bi_2WO_6$  and  $Bi_2WO_6/CoPz$  composite. The photocatalyst (30 mg) was immersed into 50 mL of aqueous glucose (1 mmol·L<sup>-1</sup>), then the suspension system was stirred for 24 h in the dark at ambient temperature. Afterwards, the filtered solution was obtained by centrifugation and then used to analyze.

#### Table 2

Effects of a series of scavengers on photocatalytic oxidation of glucose using  $Bi_2WO_6/CoPz(0.25~\%)$  composite.<sup>a</sup>

Entres	Scavenger	Conversion / %	Selectivity / %	
Entry			Arabinose	Formic acid
1	Without	45.3	60.6	36.2
$2^{b}$	KI	<1	-	-
3 <sup>c</sup>	His	<1	-	-
4 <sup>d</sup>	BQ	3.7	38.3	30.3
5 <sup>e</sup>	IPA	30.8	68.8	30.3

 $^a$  Reaction conditions: aqueous glucose (3 mmol·L<sup>-1</sup>, 50 mL), 30 mg of catalyst, reacting for 3 h, visible light ( $\lambda \geq$  420 nm) irradiation, light intensity of 1 W·cm<sup>-2</sup>.

<sup>b</sup> KI (11.9 mmol·L<sup>-1</sup>).

<sup>c</sup> IPA (11.9 mmol·L<sup>-1</sup>).

<sup>d</sup> BQ (11.9 mmol·L<sup>-1</sup>).

<sup>e</sup> His (11.9 mmol·L<sup>-1</sup>).

to obtain deeper insight into the role of CoPz. First, transient photocurrent responses of Bi<sub>2</sub>WO<sub>6</sub>, CoPz and Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite were measured under visible light irradiation. The photocurrent can directly reflect the mobility of photogenerated electrons, and the rate is directly related to the catalytic activity of photocatalyst [48,49]. As shown in Fig. 9, pure Bi<sub>2</sub>WO<sub>6</sub> and pure CoPz exhibit a weak photocurrent performance, indicating low mobility of the photogenerated charge in pure Bi<sub>2</sub>WO<sub>6</sub> and pure CoPz. In contrast, the photocurrent density of Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite is significantly higher than that of Bi<sub>2</sub>WO<sub>6</sub> and CoPz, which could be assigned to more efficient charge transfer and separation. This result proves that the separation efficiency of photogenerated charges for Bi<sub>2</sub>WO<sub>6</sub> remarkably increases by coupling with CoPz. As a consequence, the enhancing in photocurrent of Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite can remarkably increase the photocatalytic activity. Second, the influence of CoPz for glucose adsorption was studied by adsorption experiments. Fig. 10 shows the adsorption capacities of Bi<sub>2</sub>WO<sub>6</sub> and Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite for glucose at ambient temperature. It was clearly observed that Bi2WO6/CoPz composite presented a higher adsorption capacity towards glucose in comparison to Bi<sub>2</sub>WO<sub>6</sub>, indicating that the introduction of CoPz can promote the adsorption of glucose. The increase in the adsorption capacity manifests that the mass-transfer process is accelerated, and the conversion of glucose was necessarily accelerated [50-52]. Thus Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite with high adsorption capacity towards glucose is more benefit for the oxidation of glucose. The results obtained from photoelectrochemical and adsorption experiments were in well agreement with the above results of photocatalytic activity, which clearly illustrated the reason of high activity of Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite.

To further investigate the mechanism of glucose oxidation in Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite photocatalytic system, the contributions of different active species to this oxidation reaction were determined by active species trapping experiments. For this study, the chemical reagents potassium iodide (KI), isopropanol (IPA), p-benzoquinone (BQ) and histidine (His) were used as scavengers to capture the photogenerated hole ( $h^+$ ), hydroxyl radical (OH), superoxide radical ( $O_2^{-}$ ) and singlet oxygen  $({}^{1}O_{2})$ , respectively. Each scavenger was added into the Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite photocatalytic system for glucose oxidation, and the results are shown in Table 2. A remarkable suppression in glucose conversion was presented after adding KI, His and BQ, suggesting that  $h^+$ ,  ${}^{1}O_2$  and  $O_2^{-}$  play an important role in glucose oxidation. Whereas, the glucose conversion also decreased from 45.3 % to 30.8 % when IPA was added to the reaction, it was indicated that ·OH was also involved in glucose oxidation though it did not contribute as much as other three active species. The production of active species in the Bi<sub>2</sub>WO<sub>6</sub>/CoPz composite photocatalytic system was further confirmed by ESR technique, as summarized in Fig. S4. As presented in Fig. S4, characteristic peaks for <sup>1</sup>O<sub>2</sub>, O<sub>2</sub><sup>--</sup> and ·OH were emerged under visible light irradiation. This result is well consistent with that obtained from



Scheme 1. The plausible reaction route of glucose oxidation reaction with  $Bi_2WO_6/CoPz$  composite photocatalyst.

### the active species trapping experiments.

According to the literatures [16,53], glucose could be transformed to arabinose and formic acid through the C1-C2 bond cleavage. In special, the above experimental results demonstrated that a high selectivity towards arabinose and formic acid was obtained from photocatalytic oxidation of glucose based on Bi<sub>2</sub>WO<sub>6</sub>, implying that the photocatalysis of Bi<sub>2</sub>WO<sub>6</sub> was beneficial to the cleavage of C1-C2 bond. The XPS analysis was performed for the adsorption behavior of glucose on Bi<sub>2</sub>WO<sub>6</sub> surface. Fig. S5 presents high resolution XPS spectra in Bi 4f and W 4f for Bi<sub>2</sub>WO<sub>6</sub> before and after adsorbing glucose. After adsorbing glucose, the shift of Bi 4f and W 4f of Bi<sub>2</sub>WO<sub>6</sub> was observed, suggesting that there exists a specific interaction between the Bi<sub>2</sub>WO<sub>6</sub> and glucose molecule. It was speculated that this specific interaction may be related to the C1 and C2 of glucose. Thereafter, the active species generated in the photocatalytic process can attack the C1-C2 bond of glucose, producing arabinose and formic acid (Scheme 1).

# 4. Conclusions

In brief, a new composite photocatalyst  $Bi_2WO_6/CoPz$  was fabricated by combining  $Bi_2WO_6$  with CoPz. The  $Bi_2WO_6/CoPz$  composite shows excellent photocatalytic activity of selective oxidation of glucose to arabinose and formic acid in an aqueous solution under the irradiation of visible light, which results from the synergistic effect between  $Bi_2WO_6$ and CoPz. The total selectivity towards arabinose and formic acid can reach up to about 96.8 % at 45.3 % of glucose conversion under visible light irradiation for 3 h under the optimum reaction conditions. A possible explanation was presented for high photocatalytic activity for glucose oxidation over the  $Bi_2WO_6/CoPz$  composite using various techniques. It is hoped that this study can deliver some new insights for designing high efficient photocatalyst for selective organic transformation in aqueous media using solar light as driving force under mild conditions.

#### CRediT authorship contribution statement

Yanchun Ge: Investigation, Formal analysis, Data curation, Writing - original draft. Quanquan Zhang: Investigation, Formal analysis, Data curation. Changjun Yang: Conceptualization, Resources, Writing - review & editing, Supervision. Bingguang Zhang: Conceptualization, Validation, Formal analysis, Data curation. Kejian Deng: Project administration.

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118265.

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