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# Short Communication

# Selective methanol production from photocatalytic reduction of CO<sub>2</sub> on BiVO<sub>4</sub> under visible light irradiation

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# 1. Introduction

Large-scale emission of CO<sub>2</sub> has become a global environmental issue due to its greenhouse effect, and converting CO<sub>2</sub> efficiently to useful fuels is known as a feasible way to solve the environmental problem [1–3]. Since the photoelectrocatalytic reduction of CO<sub>2</sub> to organic compounds in semiconductor suspension was first reported in 1979 [4], the focus has been on the use of  $TiO_2$  and water in order to provide an approach to the photocatalytic reduction of CO<sub>2</sub> to fuels such as CH<sub>4</sub>, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH [5–9]. However, the photocatalytic efficiency of CO<sub>2</sub> reduction to fuels such as CH<sub>4</sub> over TiO<sub>2</sub> is very low (<0.1%) due to its bandgap wider than 3.0 eV [5–9]. Therefore, the majority of research is aimed at designing novel photocatalysts for the CO<sub>2</sub> reduction in order to improve conversion efficiency, selectivity and/or harvesting visible light [10–17]. For example, Jia and co-workers [10] have found that C-doped LaCoO<sub>3</sub> is able to reduce CO<sub>2</sub> into HCOOH under visible-light irradiation. Selective methanol production over NiO/InTaO<sub>4</sub> was also observed under visible light [11]. Moreover, the improved efficiency was also demonstrated for some novel titaniabased nanomaterials [6,7], coupling TiO<sub>2</sub> to dyes [8] or quantum dots [9]. Still, it remains as challenging tasks to find novel photocatalysts to efficiently reduce  $CO_2$  under visible light [5,12–14].

Bismuth vanadate (BiVO<sub>4</sub>) has inspired a great deal of interest because of its low toxicity and excellent visible-light-responsive photoactivity [18,19]. For example, Liu and co-workers [18] found that the visible-light-driven photocatalytic CO<sub>2</sub> reductions in monoclinic BiVO<sub>4</sub> suspension can selectively produce  $C_2H_5OH$  under continuously bubbling

# ABSTRACT

Lamellar  $BiVO_4$  was prepared through a surfactant-assisted hydrothermal process. The obtained lamellar  $BiVO_4$  with monoclinic phase was used as photocatalyst for the reduction of  $CO_2$ , and exhibited a selective methanol production under visible-light irradiation. It is found that the methanol yield can be significantly enhanced by adding NaOH solution in the  $BiVO_4$  suspension because the caustic solution can dissolve more  $CO_2$  and the  $OH^-$  serves as a stronger hole-scavenger as compared to water. The possible mechanism for the selective methanol production from the present photocatalytic  $CO_2$  reduction system was also discussed.

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CO<sub>2</sub>. Recently, microspheric or lamellar BiVO<sub>4</sub> was selectively prepared through a hydrothermal process by using cetyltrimethylammonium bromide (CTAB) as a template-directing reagent in our group [19]. The microspheric BiVO<sub>4</sub> with mixed tetragonal and monoclinic crystals was derived from a relatively low hydrothermal temperature ( $\leq$ 160 °C), while the lamellar BiVO<sub>4</sub> with a pure monoclinic phase was obtained at 200 °C, and showed a better visible-light-driven photoactivity for O<sub>2</sub> production than the microspheric product [19].

During the  $O_2$  production over the monoclinic BiVO<sub>4</sub>, the byproducts are photogenerated electrons and H<sup>+</sup> ions because these H<sup>+</sup> cannot capture the electrons to produce H<sub>2</sub> due to the unmatched energy levels between the conduction band of BiVO<sub>4</sub> and the reduction potential of water [18,19], whereas it is possible to convert CO<sub>2</sub> to fuels by using the above electrons and H<sup>+</sup> in the BiVO<sub>4</sub> suspension [11,18]. Herein, the lamellar BiVO<sub>4</sub> with a pure monoclinic phase was prepared and used as a catalyst for photocatalytic CO<sub>2</sub> reduction in a CO<sub>2</sub>/NaOH suspension, and the effects of the photoreaction conditions on the photoactivity and stability were investigated. Moreover, the possible mechanism for the selective methanol formation from the CO<sub>2</sub> reduction system is also discussed.

# 2. Experimental section

# 2.1. Material preparation

Monoclinic BiVO<sub>4</sub> was prepared by a CTAB-assisted hydrothermal process. More details on the material preparation and characterization can be found in our previous report [19]. The obtained product hydrothermally treated at 200 °C shows well-defined lamellar structure with



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dimension in the range of 0.08–0.12  $\mu m$  and pure monoclinic phase as shown in Fig. S1 (see Supplementary data for details).

# 2.2. Photocatalytic activity test

Photocatalytic CO<sub>2</sub> reduction was carried out in a homemade closed gas system. Supercritical fluid-grade CO<sub>2</sub> was used as the reactant to avoid any hydrocarbon contamination. Photoreaction was performed in a Pyrex glass cell containing photocatalyst (0.2 g) and 1.0 M NaOH solution (100 mL) with magnetic stirring. Prior to the light irradiation, the above suspension was thoroughly degassed to remove air, and then CO<sub>2</sub> gas was introduced continuously into the reactor for 30 min to establish an adsorption–desorption balance and a saturated CO<sub>2</sub> solution. The reactor was tightly closed during the reaction with internal pressure maintained at ~1.0 atm, and then was irradiated by 300 W Xe-lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.). If necessary, a cutoff filter (Kenko L-42) was employed for the visible-light ( $\lambda \ge 420$  nm) irradiation. The photoreaction temperature was kept at 20 °C.

The products in the solution were qualitatively identified by gas chromatography (SP6800A with GDX-502 columns) equipped with a flame ionization detector (FID), and the outlet gases were sampled through a sampling value and analyzed by gas chromatography (SP6800A with TDX-01 columns) equipped with thermal conductivity detector (TCD). All peaks were checked with their corresponding standards, and each experiment was repeated at least 5 times in parallel to obtain an average value. After measuring the methanol production amount under the same photoreaction condition, apparent quantum efficiency (AQE) was calculated from the relationship  $6 \times$  number of evolved methanol molecules/number of incident photons [20–23] (see Supplementary data for details).

# 3. Results and discussion

# 3.1. Effect of photoreaction conditions on the photocatalytic CO<sub>2</sub> reduction

Control experiments showed no appreciable reduced C1 or C2 product in the absence of either photocatalyst or light irradiation, illustrating that both photocatalyst and light irradiation are necessary for the photocatalytic CO<sub>2</sub> reduction. In addition, commercial TiO<sub>2</sub> nanoparticles (P25) were used as reference for the CO<sub>2</sub> reduction, and no obvious reduced C1 or C2 product can be detected. Therefore, photo-induced CO<sub>2</sub> reduction in the BiVO<sub>4</sub> suspension was firstly performed under the full spectrum irradiation of Xe-lamp, it was found that CH<sub>3</sub>OH can be produced from the reaction system, and concomitant traces of C<sub>2</sub>H<sub>5</sub>OH are too small to be quantified. Moreover, no obvious other compounds such as HCOOH are detectable, and the outlet gases are determined to be O<sub>2</sub> and CO<sub>2</sub> but not CH<sub>4</sub> or H<sub>2</sub>. Furthermore, there is also no obvious CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH or other products detectable from the BiVO<sub>4</sub> suspension by introducing N<sub>2</sub> instead of CO<sub>2</sub>, demonstrating the organic products are generated from the reduction of CO<sub>2</sub>.

Generally, the photocatalytic  $CO_2$  reduction efficiency and selectivity mainly depend on the photocatalyst property and reaction condition [5,6]. It has been reported that  $C_2H_5OH$  can be selectively produced from BiVO<sub>4</sub> suspension with continuously bubbling  $CO_2$  at the rate of 0.4 L min<sup>-1</sup> [18]. In this continuously bubbling  $CO_2$  system, large amount of C1 intermediates can be produced due to the sufficient carbon source, which can facilitate the dimerization of C1 intermediates to form  $C_2H_5OH$  [6,18]. Therefore, the selective formation of CH<sub>3</sub>OH in the present closed gas system may be ascribed to the limited carbon source. More importantly, the different catalyst structures may be another key reason for obtaining the different products in the present system [7]. The corresponding overall reaction might be described as follows.

$$BiVO_4 + h\nu \to h^+ + e^- \tag{1}$$



**Fig. 1.** Time course of the CH<sub>3</sub>OH and  $O_2$  production from the photocatalytic CO<sub>2</sub> reduction system. Conditions: BiVO<sub>4</sub> (0.2 g), 1.0 M NaOH solution (100 ml), and full spectrum irradiation of Xe-lamp.

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ + 4e^-$$
 (2)

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$
(3)

To further confirm the above assumption, the effects of the photoreaction conditions on the CH<sub>3</sub>OH production from the CO<sub>2</sub>/BiVO<sub>4</sub> system containing 1.0 M NaOH solution were investigated. Fig. 1 shows the CH<sub>3</sub>OH and O<sub>2</sub> evolution amount as the functions of the irradiation time. As can be seen, CH<sub>3</sub>OH yield increases markedly with prolonging the irradiation time to 6 h, and then a steady CH<sub>3</sub>OH yield remains at ~35 µmol upon further prolonging the irradiation time, indicating the oxidation of the formed CH<sub>3</sub>OH occurring on the catalyst surface or the coverage of intermediates on the active site [21]. According to our previous report [19], the monoclinic BiVO<sub>4</sub> is an efficient photocatalyst for O<sub>2</sub> production. As can be seen from Fig. 1, the ratio of O<sub>2</sub>/CH<sub>3</sub>OH generation rate is approximately constant, ~1.22 rather than 1.5, which may be ascribed to the fact that only the  $O_2$ that existed in the outlet gas can be detected, and a part of the generated O<sub>2</sub> is dissolved in the reaction solution. Again, O<sub>2</sub> yield also increases slowly after 6 h light irradiation, implying that the re-oxidation of the formed CH<sub>3</sub>OH may occur [21].

Fig. 2 shows the effect of photocatalyst amount on  $CH_3OH$  production in the  $CO_2$  reduction system. As can be seen, no appreciable  $CH_3OH$  can



**Fig. 2.** Effects of the amount of  $BiVO_4$  on the  $CH_3OH$  production from the photocatalytic  $CO_2$  reduction system. Conditions: 1.0 M NaOH solution (100 ml) and full spectrum irradiation of Xe-lamp for 6 h.



**Fig. 3.** Effects of NaOH concentration on the CH<sub>3</sub>OH production from the photocatalytic CO<sub>2</sub> reduction system. Conditions: BiVO<sub>4</sub> (0.2 g), NaOH solution (100 ml), and full spectrum irradiation of Xe-lamp for 6 h.

be detected in the absence of photocatalyst, illustrating  $BiVO_4$  is necessary for the photocatalytic  $CO_2$  reduction. Usually, a higher photocatalyst amount is expected to correspond to greater light absorption, and thus a higher  $CH_3OH$  yield. However,  $CH_3OH$  yield obviously increases with enhancing the photocatalyst dosage from 0.1 to 0.2 g, and then decreases when the addition amount exceeds 0.2 g (Fig. 2). It can be concluded that the light penetration is blocked by the aggregation of nanoparticles owing to the large quantity of photocatalyst in the suspension [21].

Fig. 3 shows the effect of NaOH concentration on CH<sub>3</sub>OH production in the CO<sub>2</sub> reduction system. As can be seen, traces of CH<sub>3</sub>OH can be detected even without NaOH, which is ascribable to the limited CO<sub>2</sub> dissolved in the suspension. Whereas CH<sub>3</sub>OH yield substantially increases with enhancing the NaOH concentration, indicating NaOH solution is crucial in the present system. This phenomenon may be due to the following reasons: Firstly, NaOH solution can dissolve more CO<sub>2</sub> than water. The pH value decreased from 14 (1.0 M NaOH) to 7.5 after bubbling  $CO_2$ , indicating the solution mainly contains  $HCO_3^-$  or with a small amount of  $CO_3^{2-}$ , which might accelerate the photocatalytic CO<sub>2</sub> reduction [6,11]. In addition, OH<sup>-</sup> can act as hole-scavenger to promote the carrier separation, and resulting in an improved CO<sub>2</sub> reduction efficiency. Moreover, CH<sub>3</sub>OH yield increases slowly once the NaOH concentration is higher than 1.0 M, which can be ascribed to the formation of the saturated  $HCO_3^-$  solution after bubbling  $CO_2$ . Since the alkaline substance with excessive concentration would damage the chromatographic column, 1.0 M NaOH solution was chosen for the following experiments.

#### 3.2. Photocatalytic CO<sub>2</sub> reduction efficiency and stability

Table 1 summarizes the CH<sub>3</sub>OH production rate and apparent quantum efficiency (AQE) over the monoclinic BiVO<sub>4</sub> under full spectrum or visible-light ( $\lambda \ge 420$  nm) irradiation of Xe-lamp for 6 h. As can be seen, the CH<sub>3</sub>OH production rate is 3.76 µmol h<sup>-1</sup> under visible-light irradiation, with ~31% reduction as compared to that under full spectrum, indicating UV-light also contributes to the selective methanol production. Moreover, there is still no other than

# Table 1 Photocatalytic $CH_3OH$ production rates and AQE values from $BiVO_4$ suspension.<sup>a</sup>

Light source	Full spectrum	Visible light
CH <sub>3</sub> OH yield rate ( $\mu$ mol h <sup>-1</sup> )	5.52	3.76
AQE (%)	0.24	0.22

 $^a$  Condition: BiVO<sub>4</sub> (0.2 g), 1.0 M NaOH solution (100 ml), and full spectrum or visible-light ( $\lambda{\geq}420$  nm) irradiation of Xe-lamp for 6 h.



**Fig. 4.** Repeated experiments of the photocatalytic CO<sub>2</sub> reduction for CH<sub>3</sub>OH production from  $BiVO_4$  (0.2 g) suspension containing 1.0 M NaOH solution (100 ml) under full spectrum irradiation.

CH<sub>3</sub>OH detected under the visible-light irradiation. The maximum AQE values for the CH<sub>3</sub>OH production achieved 0.24% and 0.22% for the full spectrum and visible-light irradiation, respectively. The less satisfactory visible-light-responsive efficiency can be ascribed to the narrow visible-light absorption band with an absorption edge at ~550 nm (Fig. S2a) [19]. Moreover, the limited increase in the photocatalytic efficiency under the full spectrum can be attributed to the small spectral distribution of UV-light with wavelength <420 nm (Fig. S2b).

Fig. 4 shows the photostability of the present  $CO_2/BiVO_4$  system for  $CH_3OH$  production under 6 h light irradiation of full spectrum for each run. The photocatalyst was recovered every 6 h by centrifugation, washing and drying at 80 °C. As can be seen, the photoinduced  $CO_2$  reduction reaction shows comparatively good reproducibility and consistency in three consecutive repeated runs of accumulatively 18 h. To further check the stability of the photoreaction, the photocatalyst recovered by centrifugation but without washing and drying processes was immediately reused to the repeated experiments. It can be found that the  $CO_2$  reduction reaction still shows good consistency in the repeated runs (Fig. S3). Moreover, XRD pattern (Fig. S1) and XPS spectra (Fig. S4) of the recovered BiVO<sub>4</sub> after the repeated experiment for 18 h are almost identical to that of the as-prepared ones. The above results indicated the BiVO<sub>4</sub> is stable in the present  $CO_2$  reduction system.

Based on the above results and discussion, the possible photocatalytic mechanism is proposed and illustrated in Fig. 5. Accordingly, lots of photogenerated carriers can transfer to the  $BiVO_4$  surfaces under visible-light irradiation. The absence of  $H_2$  in the outlet gases suggests that the proton failed to capture the photogenerated electrons, which confirmed the previous report that  $BiVO_4$  cannot produce  $H_2$  due to



Fig. 5. Proposed mechanism of  $\text{CH}_3\text{OH}$  production from the  $\text{CO}_2$  reduction system containing  $\text{BiVO}_4.$ 

its energy band structures are unmatched with the water reduced potential [18,19]. Considering that the potential can be lowered by nearly 0.7 V when CO<sub>2</sub> was changed to  $CO_3^2$  or  $HCO_3^-$  [11], it is reasonable to think that those  $HCO_3^-$  or  $CO_3^{2-}$  can anchor to the surface Bi<sup>3+</sup> sites through weak Bi...O bonds so that they can efficiently receive the electrons from the V3d-block bands of BiVO<sub>4</sub> to form CO<sub>2</sub>•<sup>-</sup> radical anions, and give rise to methoxyl (•OCH<sub>3</sub>) radicals and then to CH<sub>3</sub>OH after protonation [18,24], while  $O_2$  is produced from  $H_2O$  or  $OH^-$  by scavenging holes on the BiVO<sub>4</sub> surfaces [4,19,21,24]. These procedures can reduce the carrier recombination. Obviously, the photoreduction of CO<sub>2</sub> and the decomposition of H<sub>2</sub>O proceed competitively on the BiVO<sub>4</sub> surfaces, and CH<sub>3</sub>OH is preferentially produced since the protons in water are difficult to capture the photogenerated electrons due to their unmatched energy band structures [19,24]. However, it still is not clear if the BiVO<sub>4</sub> surface state can be restored during the photocatalytic CO<sub>2</sub> reduction, which needs further investigation.

#### 4. Conclusions

Lamellar BiVO<sub>4</sub> was prepared through a surfactant-assisted hydrothermal process, and methanol can be selectively produced from a suspension containing the obtained BiVO<sub>4</sub> and CO<sub>2</sub>/NaOH solution under full spectrum or visible-light irradiation of Xe-lamp. Since BiVO<sub>4</sub> is inexpensive, stable and visible-light responsive, the present visible-light-driven photocatalytic CO<sub>2</sub> reduction system may become one of the promising methods for the fixation and removal of CO<sub>2</sub> because of its simplicity, easy controlling and low cost. However, higher conversion efficiency is still expected for the practical application of the present CO<sub>2</sub> reduction system. The optimization of the present reaction condition and the investigation of the detailed mechanism are in progress.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.08.008.

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