

Research Article

Effect of Preparation Parameters on Photoactivity of BiVO_4 by Hydrothermal Method

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Bismuth vanadate (BiVO_4) was synthesized from a mixture of aqueous $\text{Bi}(\text{NO}_3)_3$ and NH_4VO_3 solutions by using hydrothermal method. Via conducting the orthogonal experiments and single-factor experiments, the best synthetic parameters were determined. The physical and photophysical properties of the as-obtained samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and UV-Vis diffusion reflectance spectroscopy (UV-Vis). The result showed that the best experimental parameters of monoclinic BiVO_4 were $\text{pH} = 7$, $T = 195^\circ\text{C}$, and $t = 6$ h. The catalytic performance of BiVO_4 was evaluated by reducing carbon dioxide to methane under visible light irradiation. It was found that the methane production reached $145 \mu\text{g/g-cat}$ after 5 h irradiation with the catalyst dosage of 0.15 g in 200 mL mixed solution of 0.1 M NaOH and 0.1 M Na_2SO_3 .

1. Introduction

Because of the increasing energy crisis and environment problems, more and more scientific research has focused on the utilization of solar light, especially the part of visible light to split water [1, 2], reduce carbon dioxide (CO_2) [3, 4], and degrade pollutants [5–8]. Bismuth vanadate (BiVO_4), an effective photocatalyst for water splitting and pollutant photodegradation under visible light irradiation, has attracted increasing attention in recent years [9–11]. BiVO_4 has three main crystalline structures, the tetragonal zircon, monoclinic scheelite, and tetragonal scheelite structure. Among them, however, only monoclinic scheelite BiVO_4 has the best photocatalytic activity under visible light irradiation [12, 13].

Various methods have been employed to prepare BiVO_4 such as solid-state reactions, sonochemical routes, room-temperature aqueous process, molten salt method, and hydrothermal process [14–17]. Among these methods, hydrothermal synthesis, which is a facile, cost-effective, and controllable synthetic process, has been widely used in preparation of many kinds of functional materials. A. P. Zhang and J. Z. Zhang [18] reported the synthesis of monoclinic BiVO_4 nanosheet by hydrothermal method

which exhibits much high photocatalytic activity for solar photodegradation of methyl orange. Xi and Ye [19] proposed a novel hydrothermal synthetic procedure to obtain monoclinic BiVO_4 nanoplates showing preferential exposition of [001] facets. Zhou et al. [20] reported the preparation of monoclinic BiVO_4 microtubes with flowerlike structures by hydrothermal method, and the catalyst exhibited a prominent improvement in the photocatalytic activity. Thus, as well as the crystalline structures, the photocatalytic property also strongly depends on the surface structure, which is closely related to the synthetic method.

In the present paper, the preparation of BiVO_4 with different structures by the hydrothermal method was reported. The influences of the preparation parameters on the properties of BiVO_4 , including pH, hydrothermal temperature, and hydrothermal time, were discussed intensively. The photocatalytic activity was evaluated by reducing carbon dioxide to methane under visible light irradiation.

2. Experimental

2.1. Synthesis of Photocatalysts. A series of BiVO_4 were synthesized by the following process: stoichiometric amount of

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 were dissolved in the dilute HNO_3 solution and NaOH aqueous solution, separately. Then these two solutions were mixed under magnetic stirring. The NaOH and HNO_3 solutions were used to adjust the pH values to be 6, 7, 8. After stirring for 30 min, the well-mixed mixture was transferred into a Teflon-lined stainless autoclave and sealed. The autoclave was finally put into an oven which was maintained at a certain temperature for a period (2 h, 6 h, 16 h), then was cooled down to the room temperature. The as-obtained samples were centrifuged and washed with deionized water and absolute ethanol for several times and finally dried at 100°C for 2 h.

2.2. Characterization. The X-ray diffraction (XRD) patterns were recorded by a Panalytic X'pert Pro X-ray diffractometer equipped with $\text{CuK}\alpha$ irradiation at a scan rate of 0.02°s^{-1} . The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The morphology and microstructure of the samples were determined by field emission scanning electron microscope (SEM, JEOL JSM-6700F) and transmission electron microscope (TEM, JEM-2100). The UV-Vis absorption spectra were measured by a Hitachi UV-4100 spectrometer, with the scanning range from 300 nm to 800 nm.

2.3. Photocatalytic Activity. Photocatalytic reaction was carried out in a side-irradiation Pyrex cell. The effective irradiation area for the cell is 12.56 cm^2 . 0.15 g photocatalyst powder was dispersed by a stirrer in an aqueous solution (200 mL) consisting of 0.1 M Na_2SO_3 as sacrificial agent, and CO_2 was continuously bubbled into the solution at the rate of 0.1 L/min. Oxygen in Pyrex cell was exhausted by nitrogen bubbling. The photocatalysts were irradiated with visible light through a cutoff filter ($\lambda > 430\text{ nm}$, $T = 65\%$) from a 300 W Xe lamp. The amount of methane gas was determined by an online gas chromatograph equipped with a thermal conductivity detector (TCD) (NaX zeolite column, nitrogen as a carrier gas).

3. Results and Discussion

3.1. Orthogonal Experiments

3.1.1. Taguchi Design. Taguchi's optimization technique is a powerful method to optimize the experimental parameters with minimum number of experiments. We applied Taguchi orthogonal array [21] to study the effect of three important parameters including pH, temperature, and hydrothermal reaction time. And each parameter was tested at three levels (Table 1) with respect to the hydrothermal process. The OA_9 (3^3) matrix employed is shown in Table 2.

3.1.2. Effect of Parameter on the Crystalline Structures of BiVO_4 . The XRD patterns of the as-obtained BiVO_4 are shown in Figure 1. From Figure 1, we can see that these three parameters have great effect on the crystalline structures of BiVO_4 . As is well known, the major diffraction peaks of monoclinic structure (JCPDS NO.14-0688) are 28.6° , 28.8° ,

TABLE 1: Parameters and levels of an orthogonal design (A–C are the respective code for each parameter).

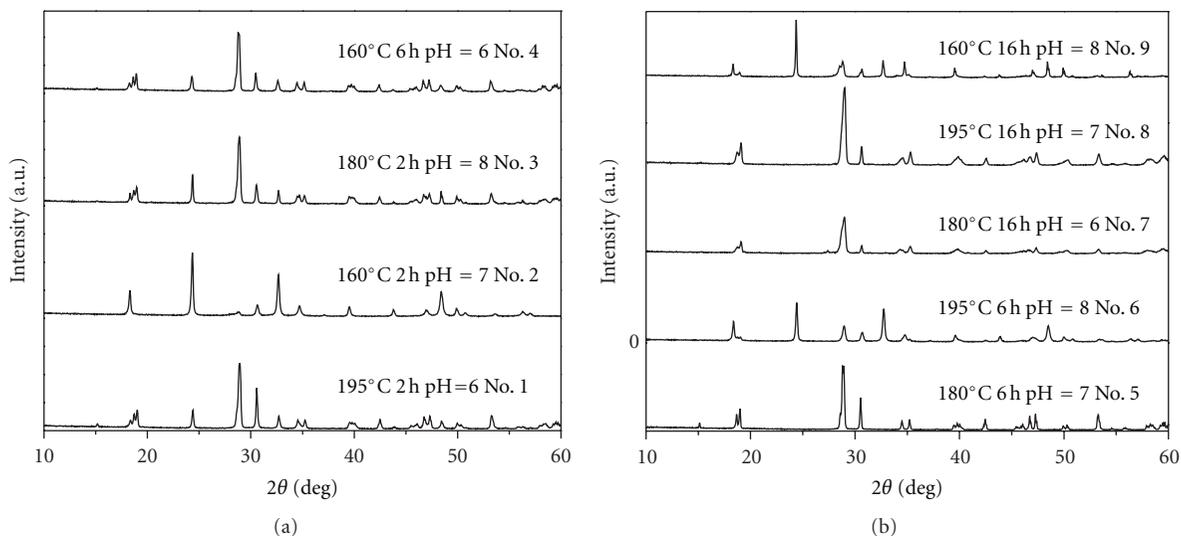
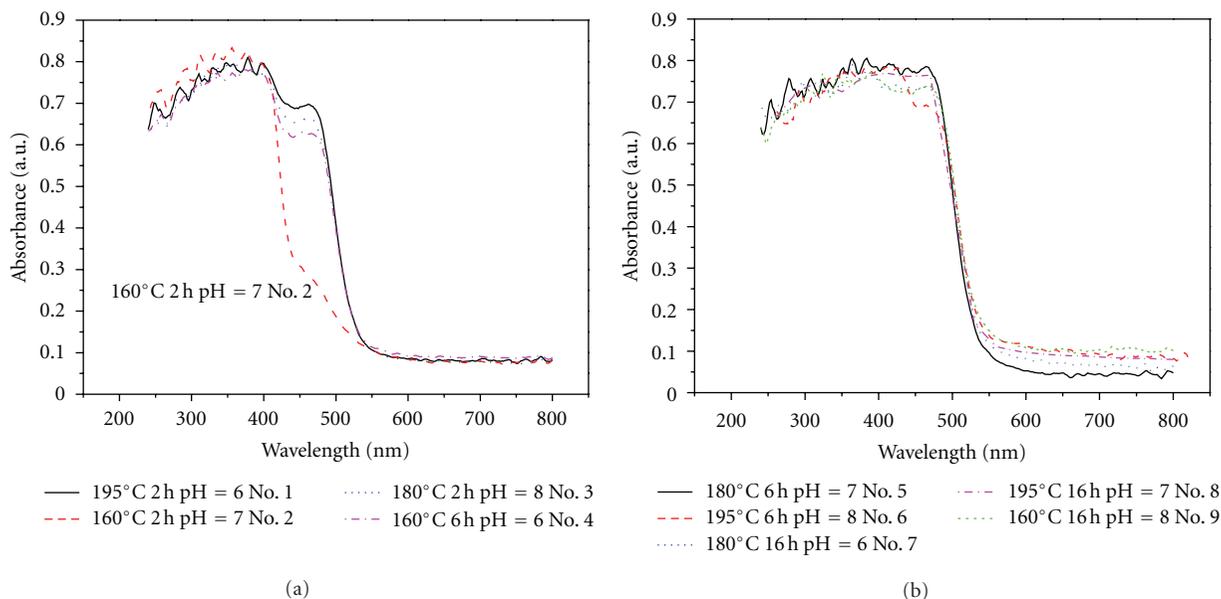
Levels	Parameters		
	A/time (h)	B/pH	C/temperature ($^\circ\text{C}$)
1	2	6	160
2	6	7	180
3	16	8	195

TABLE 2: Design of orthogonal tests.

Test	A/time (h)	B/(pH)	C/temperature ($^\circ\text{C}$)
1	2	6	195
2	2	7	160
3	2	8	180
4	6	6	160
5	6	7	180
6	6	8	195
7	16	6	180
8	16	7	195
9	16	8	160

and 28.9° , which can easily combine to a strong peak around 28.8° , and the major diffraction peak of tetragonal structure (JCPDS NO.14-013) is 24.4° . The other characteristic peaks of monoclinic structure are 30.5° , 34.5° , 47.3° , and 50.0° and those of tetragonal structure are 32.7° and 48.4° . As is shown in Figure 1(a), the XRD pattern of test no. 2 matches well with the pure tetragonal structure according to JCPDS no. 14-013. The others are mixed phases of both monoclinic and tetragonal structure because of peaks appearing in 24.4° and 28.8° . As is exhibited clearly in Figure 1(b), no. 6 and no. 9 are also mixed phases, while no. 5, no. 8 and no. 7 are pure monoclinic structure which are in conformity with JCPDS no. 14-0688. The crystalline structures of BiVO_4 are influenced by these three parameters. Nevertheless, it is obvious to see the intensity of the peaks between no. 5 (pH = 7) and no. 8 (pH = 7) are almost the same, while no. 7 (pH = 6) is a little weaker compared with no. 5 and no. 8. Thus the pH value has the great effect on the degree of crystallinity. It seems that the pure monoclinic structure could be synthesized when pH is 7.

3.1.3. Effect of Parameter on the Optical Property of BiVO_4 . The optical absorption spectra of the as-obtained samples are shown in Figure 2. Their strong absorption lies in visible light region from 400 nm to 550 nm. From Figure 2(a), compared to other samples, a blue shift can be observed in no. 2's absorption edge, whose absorption region is mainly between 400 nm and 450 nm. While the absorption regions of other samples are mainly from 480 nm to 550 nm. It suggests that BiVO_4 which has monoclinic structure has better visible light adsorption. In addition, the absorption region of no. 2 appears a trailing peak at wavelength larger than 450 nm which is caused by the crystalline defects. And there is a small

FIGURE 1: XRD patterns of the as-obtained BiVO_4 .FIGURE 2: UV-Vis spectra of the as-obtained BiVO_4 .

absorption edge at about 460 nm for no. 1, no. 3, no. 4, and no. 6, revealing their tetragonal phase which is in agreement with that of the XRD analysis.

3.2. Single-Factor Experiments. As discussed above, the pure monoclinic structure was synthesized at pH 7. Then the single-factor experiments were carried out to decide the effect of hydrothermal temperature and hydrothermal reaction time. Figure 3 shows XRD patterns of the as-obtained BiVO_4 synthesized as the function of temperature and time. As shown in Figure 3(a), the diffraction peaks of BiVO_4 prepared at pH 7 and time 16 h, match well with pure monoclinic phase BiVO_4 , and the peaks intensity of them

could be arranged in order: $195^\circ\text{C} > 180^\circ\text{C} > 160^\circ\text{C}$. So the best reaction temperature would be 195°C . Fixing pH 7 and temperature 195°C , BiVO_4 was prepared with different hydrothermal reaction time, and the results are shown in Figure 3(b). It is obvious that the pure monoclinic structure was obtained when hydrothermal treated 6 h and 16 h. The XRD intensity for monoclinic structure by treating for 6 h is the strongest. Therefore, the best monoclinic BiVO_4 could be obtained by hydrothermal method at 195°C for 6 h when the pH is 7 in this study.

Figure 4 shows the SEM and TEM images of the as-obtained BiVO_4 as the function of time. Obviously, the morphology of BiVO_4 is notably affected by the hydrothermal time. The BiVO_4 synthesized at 2 h has the regular

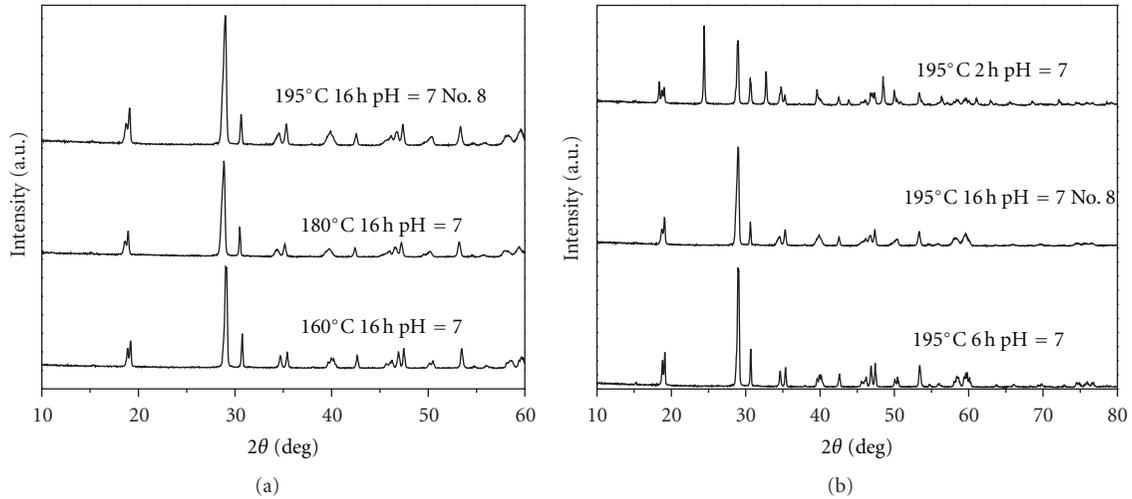


FIGURE 3: XRD patterns of the as-obtained BiVO_4 as the function of (a) temperature and (b) hydrothermal reaction time.

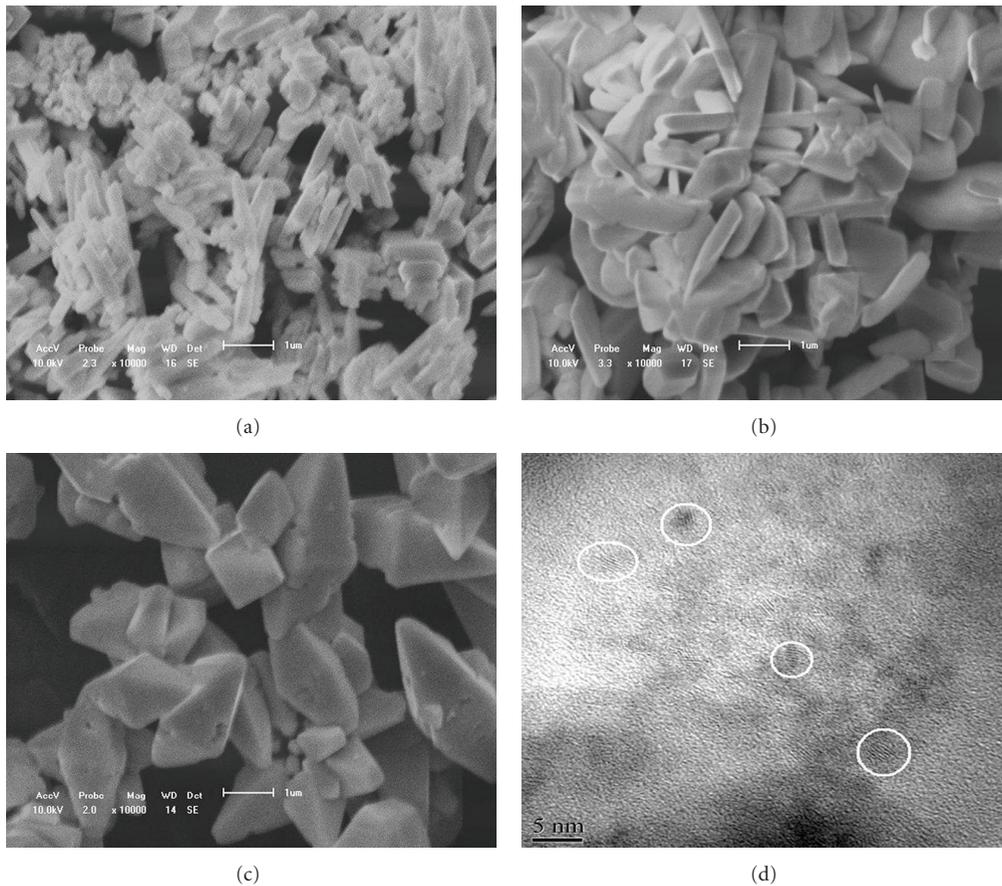


FIGURE 4: SEM images of as-obtained BiVO_4 as the function of hydrothermal reaction time at pH 7 and temperature 195°C : (a) 2 h, (b) 6 h, and (c) 16 h; (d) TEM image of (b).

and complete rodlike morphology as shown in Figure 4(a). Increasing time to 6 h, the as-obtained BiVO_4 is composed of elliptic flake, and the flakes are aggregated to the flower shape as shown in Figure 4(b). At longer hydrothermal time, the flakes seem to collapse and pyramid shape was formed

with defects on the surface as shown in Figure 4(c). This can explain the weakness of its diffraction peak intensity in XRD patterns. In addition, from Figure 4(d), we can see that the flakes are composed of crystal cells of about 5 nm. The difference observed in the morphology can be corrected

by the XRD pattern. Thus, the samples prepared at pH 7, temperature 195°C, and hydrothermal 6 h may have the best photoactivity, which is verified by the reduction of CO₂.

3.3. Verification Tests. Controlled blank experiments were carried out to eliminate inference and improve the precision of analysis. In this case, the blank experiments are divided into four: first, carbon dioxide gas was bubbled into the aqueous solution consisting of 0.1 M Na₂SO₃ and 0.1 M NaOH without photocatalyst under visible light irradiation; second, carbon dioxide gas was bubbled into the aqueous solution consisting of 0.1 M Na₂SO₃ and 0.1 M NaOH with photocatalyst under dark; third, carbon dioxide gas was bubbled into the aqueous solution consisting of only 0.1 M Na₂SO₃ with photocatalyst under visible light irradiation; fourth, nitrogen gas instead of carbon dioxide gas was bubbled into the aqueous solution consisting of 0.1 M Na₂SO₃ and 0.1 M NaOH with photocatalyst under visible light irradiation. Unfortunately, methane, formic acid, methanol, formaldehyde, and formic acid were not detected by liquid chromatogram and gas chromatogram in all the blank experiments. It suggests that CO₂ was not reduced. In this case, only the as-obtained BiVO₄ with monoclinic scheelite structure shows the photoactivity for methane evolution, and the results are shown in Figure 5. Other samples produce much less methane under visible light irradiation. From Figure 5, it can be seen that the amount of methane evolution increases linearly with time but displays a smaller increase after 20 h which may be affected by the concentration of NaOH. Then the effect of NaOH concentration on the amount of methane evolution was studied, and the results are shown in Figure 6.

From Figure 6, we can see that the amount of methane is largest when NaOH concentration is 0.1 M. With the increase of NaOH concentration, the methane evolution reduced. As we know, CO₂ can react with OH⁻ to form CO₃²⁻ and CO₃²⁻ can change to HCO₃⁻ with supersaturation of CO₂. In this case, three forms, as molecular state of CO₂, CO₃²⁻ and HCO₃⁻, coexist and affect each other, resulting in the photo-reduction product of the different amount of methane. It was reported that BiVO₄ could be used to reduce CO₂ to ethanol in water [22]. During the photoreduction of CO₂ to ethanol, many C1 intermediates were generated under visible light irradiation. In our case, due to the existing of sacrificial reagent, the C1 intermediates may be converted to methane directly. Obviously, BiVO₄ has the potential for use in CO₂ reduction. However, the photocatalytic mechanism of the as-obtained BiVO₄ is too complex to be clarified in the present work, and more research needs to be conducted in future.

4. Conclusion

A series of BiVO₄ were synthesized by hydrothermal method. The optimal parameters for monoclinic scheelite BiVO₄ preparation were pH 7.0, hydrothermal temperature 195°C, and time 6 h. Photocatalytic methane evolution by carbon oxide reduction can take place on the as-obtained monoclinic scheelite BiVO₄ under visible light irradiation.

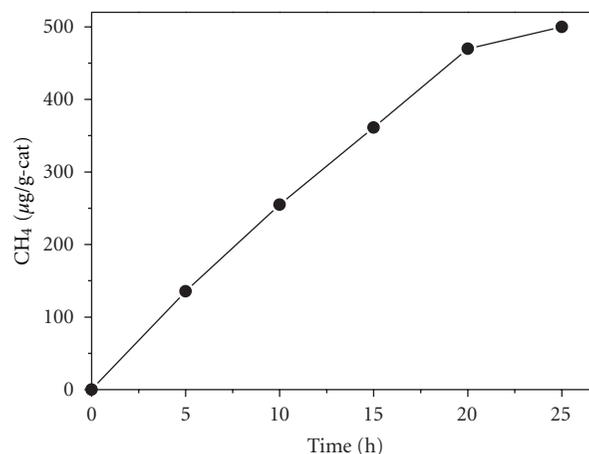


FIGURE 5: Amount of methane evolution over BiVO₄ prepared under the optimized conditions.

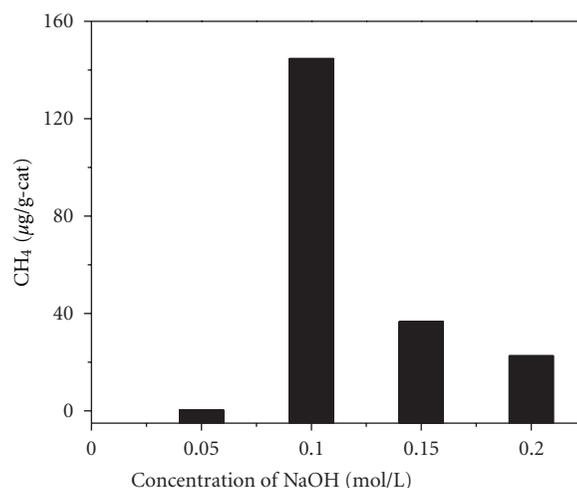


FIGURE 6: Amount of methane evolution over BiVO₄ irradiated for 5 h as the function of concentration of NaOH.

Methane evolution reached to 145 μg/g-cat after 5 h irradiation with the catalyst dosage of 0.15 g in 200 mL mixed solution with 0.1 M NaOH and 0.1 M Na₂SO₃. This as-obtained BiVO₄ is a potential photocatalyst for carbon dioxide reduction under visible light irradiation. However, the photocatalytic mechanism of the as-obtained BiVO₄ is still unclear, and further research needs to be conducted.

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