



Short Communication

Hydrogen production under visible light by photocatalytic reforming of glucose over an oxide solid solution photocatalyst

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ABSTRACT

Hydrogen production under visible light by photocatalytic reforming of glucose over an oxide solid solution photocatalyst $\text{Bi}_x\text{Y}_{1-x}\text{VO}_4$ (BYV) was demonstrated for the first time. It was found that a certain amount of Y doping would promote the transition of BiVO_4 from monoclinic to tetragonal phase and finally lead to the formation of tetragonal BYV solid solution. BYV with a B/Y ratio of 1:1 showed the highest activity for hydrogen production. The amount of photoproducted hydrogen lowered after several hours of reaction. However, when the gas product was replaced with N_2 atmosphere, hydrogen production recovered. It is supposed that the generated CO_2 might participate in the redox reaction and in some way inhibit the hydrogen production. Therefore, for photocatalytic reforming of glucose, removal of gas product in time is indispensable.

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1. Introduction

Photocatalytic water splitting under solar light has been considered as one of the most promising routes for renewable hydrogen production [1–6]. The photocatalytic process is initiated by the absorption of a photon with energy equal to or larger than the band gap of the semiconductor. When light irradiates, photogenerated electrons are excited to the conduction band, where they reduce H_2O to H_2 . Photogenerated electrons are also very easy to recombine with holes in the semiconductor. This recombination leads to the lower quantum efficiency of photocatalysis. Adding sacrificial reagents, such as methanol, Na_2S , Na_2SO_3 , and EDTA, can effectively restrain this recombination process and improve quantum efficiency whereas it is at the cost of nonrenewable sacrificial agents [7–12].

Biomass, such as glucose, the most versatile renewable resource, can be utilized for the sustainable production of hydrogen. A number of processes have been developed for this purpose (e.g., steam gasification [13], fast pyrolysis [14], and supercritical conversion [15]). However, these processes require rigorous conditions, such as high temperature or high pressure, and therefore, are of high cost. The pioneer study, conducted in 1980 by Kawai et al. [16], reported that hydrogen could be generated from the carbohydrate under UV light irradiation. Subsequently, they indicated that hydrogen could also be acquired from some other biomasses, such as cellulose, starch, dead insects, and waste materials using the same process [17]. These reports showed the feasibility of producing hydrogen from biomass by the photocatalytic process. However, all these studies have been

conducted under UV light, which accounts for only ca. 4% of the solar spectrum. Photocatalytic reforming of biomass under visible light has been more desired.

Fu et al. [18] have reported photocatalytic hydrogen production using biomass glucose over Pt/TiO_2 under UV light irradiation. Most recently Li et al. reported photocatalytic reforming of glucose under visible light over $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ and ZnIn_2S_4 [19,20]. This is the first report of photocatalytic reforming of biomass under visible light. From the viewpoint of thermodynamics and compared with sulfides and nitrides, oxide photocatalysts would be more favored considering that they are generally more stable and have more positive valence band positions suitable for biomass oxidation. Unfortunately, most of oxide semiconductors either have a wide band gap or lower conduction band, and these drawbacks restrict their availability for this purpose.

Recently, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ [2], $(\text{Zn}_{1-x}\text{Ge})(\text{N}_2\text{O}_x)$ [21] and BiYWO_6 [22] solid solutions have been designed to split water under visible light. Shangguan et al. reported a novel $\text{Bi}_{0.5}\text{Dy}_{0.5}\text{VO}_4$ solid solution which can also split water, indicating that solid solution design is a feasible and effective method to obtain oxide photocatalyst with suitable band structures [23]. In this communication, we demonstrated photocatalytic reforming of glucose under visible light over an oxide solid solution $\text{Bi}_x\text{Y}_{1-x}\text{VO}_4$ (BYV) for the first time and the mechanism for hydrogen production was also investigated.

2. Experimental sections

2.1. Preparation and characterization

All reagents were of analytical-grade purity and were used without further purification. Bi_2O_3 , Y_2O_3 and NH_4VO_3 were used as

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raw materials and mixed in stoichiometric proportions. BYV with various Bi/Y ratios were prepared by calcining the mixture at 1073 K in air for 12 h and then at 1123 K for 12 h with an intermediate regrinding, as reported for the preparation of $\text{Bi}_{0.5}\text{Dy}_{0.5}\text{VO}_4$ [23]. The BYV samples are denoted as Bi (x), where x represents the molar ratio of Bi in BYV.

X-ray diffraction (XRD) patterns of the as-prepared photocatalysts were recorded by an X'Pert PRO diffractometer using $\text{Cu K}\alpha$ radiation. Diffuse reflectance UV–vis Spectra of the photocatalysts were measured on a HITACHI UV4100 instrument equipped with lab sphere diffuse reflectance accessory. The crystallite morphology was observed by a JEOL JSM-6700F field emission scanning electron microscopy (SEM).

2.2. Photocatalytic hydrogen production

Photocatalytic hydrogen evolution under visible light was performed in a side irradiation pyrex cell. A PLS-SXE300/300UV Xe lamp (350 W) from Beijing Changtuo Co., Ltd was used as light source along with a 430 nm cut-off filter for removal of the UV light. The gas phase sampled with a syringe was analyzed with a TCD SP2100 gas chromatograph (TDX-01 column, nitrogen as carrier gas). In all experiments, 0.2 g of catalyst was suspended in a 100 mL aqueous solution containing 0.1 M glucose. Various concentrations of NaOH or HCl were added in the reaction solution for pH control. 1 wt.% Pt as co-catalyst was photo-deposited in situ on the photocatalyst from precursor of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. After 2 h of illumination, the photocatalytic hydrogen production test started. N_2 was flushed for 30 min before the photo-deposition and the photocatalytic hydrogen production tests.

3. Results and discussion

3.1. Characterization of BYV samples

XRD patterns for BYV with various molar ratios of Bi in BYV are shown in Fig. 1. For a pure BiVO_4 sample (Bi 1.0), most of the diffraction peaks were attributed to monoclinic phase BiVO_4 (space group, I2/b ; JCPDS No. 00-014-0688), except for some weak diffraction peaks stemming from V_2O_5 [24]. The refined lattice constants for this BiVO_4 phase were as follows: $a = 5.1970 \text{ \AA}$, $b = 5.0960 \text{ \AA}$, $c = 11.7020 \text{ \AA}$. The most intensive peak was at 28.8° corresponding to the diffraction of (-121) plane. When 20% of Y was doped, the XRD patterns significantly changed. A new peak at ca. 24.4° was found. This peak was attributed to (200) plane of the tetragonal phase YVO_4 (JCPDS 72-0861). The diffraction peaks of the solid solutions shifted to lower angles as the

value of x was increased. The successive shift of the XRD pattern indicated that the crystals obtained were not simple mixtures of YVO_4 and BiVO_4 phases but the $\text{Bi}_x\text{Y}_{1-x}\text{VO}_4$ (BYV) solid solutions. It can be inferred from our XRD results that a pure BYV solid solution could be formed when Bi:Y ratios were smaller than 0.6. At higher Bi contents, both tetragonal BYV solid solution and monoclinic BiVO_4 existed.

UV–vis diffuse reflectance spectra of various BYV samples are given in Fig. 2. The absorption onset for YVO_4 was found to be around 400 nm corresponding to a band gap of 3.1 eV. The absorption tail extending to 500 nm might be attributed to the impurities such as V_2O_5 that could not be detected by XRD. With the doping of Bi in YVO_4 , the absorption edge shifted to longer wavelength. For Bi 0.5 (Bi/Y = 1:1), the absorption onset was around 460 nm corresponding to a band gap of 2.7 eV. For Bi 0.6 (Bi/Y = 3:2) and Bi 0.8 (Bi/Y = 4:1), the shoulders were found, which could be attributed to the monoclinic phase BiVO_4 existing in separated state and not forming solid solution with YVO_4 .

The SEM image shown in Fig. 3(a) revealed that the as-prepared BYV particles had a relative uniform shape with size around 500 nm. These nano-scale particles further aggregated into large bundles of several micrometers. Fig. 3(b) with higher resolution showed that the surfaces of the BYV particles were smooth and no impurity existed at their surfaces.

Specific surface area of the various samples was also investigated. The results are listed in Table 1. It was seen that the surface areas for all the as-prepared samples were quite small. The surface area of the BYV solid solution decreased with increasing doping of Y. As would also be shown by our hydrogen production results in the following section, no clear correlation between the surface area and the photocatalytic activity could be found.

3.2. Photocatalytic activity evaluation

Photocatalytic hydrogen production under visible light over various BYV samples was conducted. The amount of hydrogen was determined after 2 h of photocatalytic reaction at $\text{pH} = 3$ and all the BYV samples were loaded with 1 wt.% Pt by in situ photo-reduction. In all experiments, hydrogen was not detected in the absence of glucose, which excluded the possibility that Pt loaded BYV could split pure water. Here, Pt can trap photogenerated conduction electron, and electron acceptor H^+ obtains the electron to produce hydrogen on Pt. As shown in Fig. 4, hydrogen production can hardly be detected for pure YVO_4 (Bi 0.0) sample. With the increasing contents of Bi, the hydrogen production rate increased, reaching the maximum when

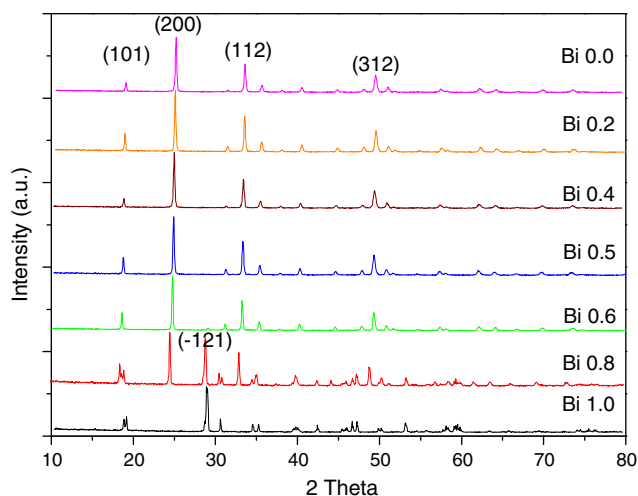


Fig. 1. X-ray diffraction (XRD) patterns of BYV with various molar ratio of Bi in BYV.

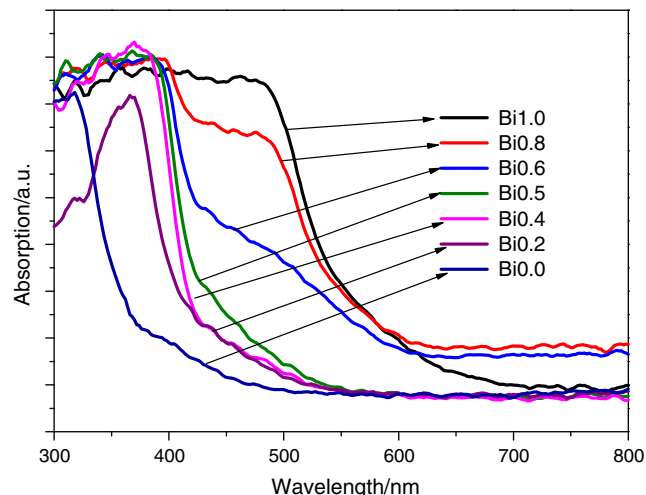


Fig. 2. UV–vis diffuse reflectance spectra of BYV with various molar ratio of Bi in BYV.

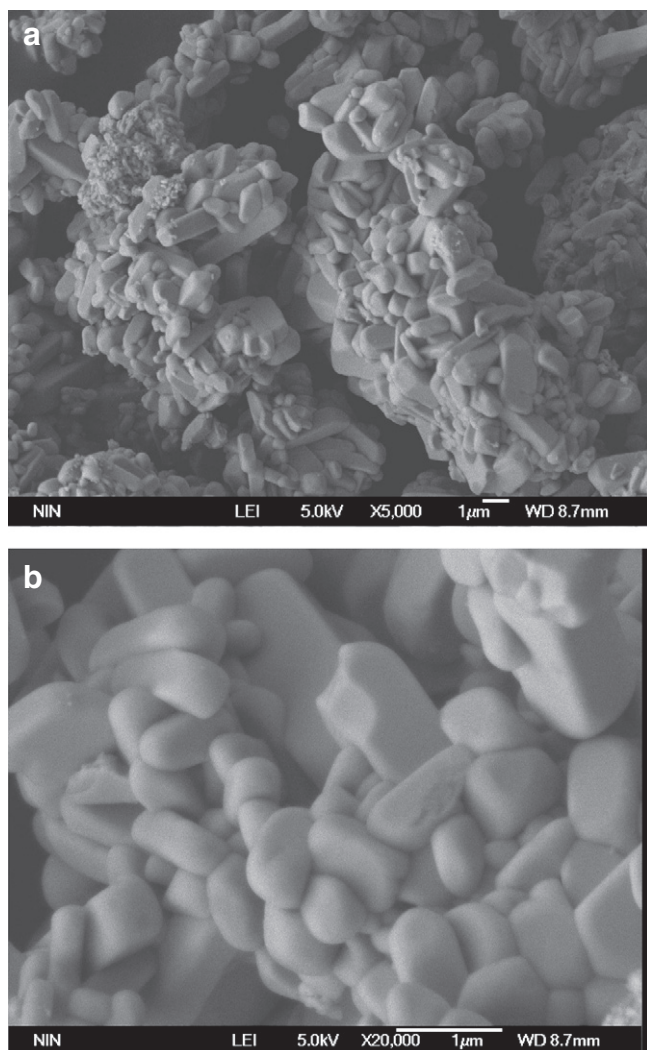


Fig. 3. SEM image of $\text{Bi}_{0.5}\text{Y}_{0.5}\text{O}_4$ (Bi 0.5) (a) $\times 5000$; (b) $\times 20000$.

the Bi/Y ratio was 1 (Bi 0.5). At higher Bi/Y ratios, the hydrogen production rate decreased again. BYV (Bi 0.5) thus seemed to be the optimal composition for hydrogen production. In our case, both the metal cations (Bi, Y) are supposed to hold A sites in ABO_4 metal oxide. Different Bi/Y ratios must affect the band structure of the solid solution photocatalyst, which in turn impacts the migration of photogenerated charges. For BYV (Bi 0.5), the formation of a single phase pure solid solution and the intimate interaction of Bi and Y are expected. The intimate interaction of Bi/Y is believed to be beneficial for charge transportation and separation, as has been suggested in the literature [25,26].

For further investigation, the time courses of photocatalytic hydrogen production under visible light over BYV (Bi 0.5) at different pH values were recorded, as shown in Fig. 5. The pH values were adjusted by adding certain amounts of HCl or NaOH. Again, control experiment confirmed no hydrogen production in the absence of light irradiation or glucose. It was found that after 2 h of reaction, the hydrogen production at both pH = 3 and pH = 11 were higher than at

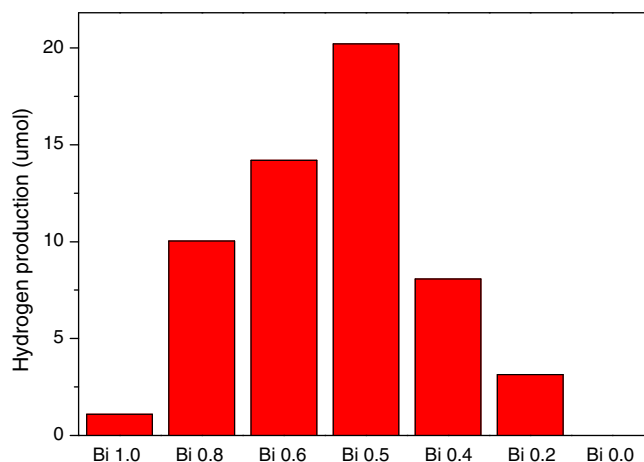


Fig. 4. The amount of hydrogen determined after 2 h of photocatalytic reaction (pH = 3), all BYV sample were loaded with 1% Pt.

other pH values. To our surprise, the hydrogen production was the lowest at neutral condition of pH = 7. Both acidic and basic conditions seemed favorable for photocatalytic reforming of glucose. The effects of solution pH value on the hydrogen generation are considered to be quite complicated, involving the changes of the chemical state of glucose and redox potential of H^+/H_2 . The pK_a of glucose is ca. 12.3 [27]. When the $\text{pH} < \text{pK}_a$, the glucose in the solution is mainly in molecular form. In basic solution, glucose can dissociate into H^+ and $\text{C}_6\text{H}_{11}\text{O}_6^-$. Li has studied photocatalytic hydrogen generation in the presence of glucose over ZnS-coated ZnIn_2S_4 under visible light irradiation and found that when the pH value of the reaction solution was lower than 8.0, no hydrogen was produced. The hydrogen production reached the maximum at pH = 12.68 [20]. In our case, it is assumed that at higher pH value (pH = 11), the dissociated $\text{C}_6\text{H}_{11}\text{O}_6^-$ can act as a hole scavenger, facilitating hydrogen production. At lower pH values, for example at pH = 3, the redox potential of H^+/H_2 would become more positive that is advantageous to efficient hydrogen generation. For sulfide such as ZnS-coated ZnIn_2S_4 , however, the poor stability and hence negligible activity in acidic solution is expected.

It should also be noted in Fig. 5 that after 2 or 3 h of reaction, the hydrogen production at all the pH values, almost stopped or even decreased. However, when the gas product was removed by flushing

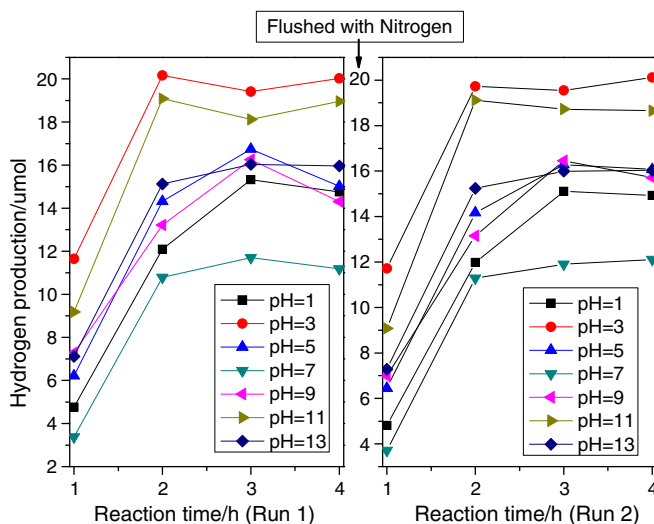


Fig. 5. The time courses of photocatalytic hydrogen production over BYV (Bi 0.5) under visible light at various pHs, pH = 1, 3, 5, 7, 9, 11, and 13, respectively.

Table 1

Sample	Bi(1.0)	Bi(0.8)	Bi(0.6)	Bi(0.5)	Bi(0.4)	Bi(0.2)	Bi(0.0)
BET(m^2/g)	0.31	0.30	0.26	0.22	0.19	0.18	0.15

with nitrogen, the hydrogen production almost recovered. It has been proposed [18] that for photocatalytic reforming of glucose over TiO₂ under UV light, the gas product is only CO₂ and H₂. However, in our gas product, trace amount of methane was also detected. It was reported by Sakata that during photocatalytic hydrogen production from ethanol–water mixture, methane was detected as a by-product [28]. It was also known that CO₂ in the presence of water could be reduced to methane [29,30]. In fact, our further experiment revealed that, when the gas product was replaced with nitrogen and hydrogen mixture, the hydrogen production was not influenced as significantly as in the presence of CO₂. Gratzel et al. has found in their study on visible light induced water cleavage in colloidal solutions of chromium-doped titanium dioxide particles that a photostationary state would eventually be reached where H₂ generation and recombination occur at the same rate [31], indicating that hydrogen production in their case was also stopped. In our case, it is supposed that the generated CO₂ might participate in the redox reaction, possibly forming CH₄, and in some way inhibit the hydrogen production. The co-catalyst Pt might also catalyze this reaction. When the gas product was removed by flushing with nitrogen, the hydrogen production could be recovered. Therefore, for photocatalytic reforming of glucose at least in our condition, the timely removal of gas product is indispensable.

4. Conclusion

Photocatalytic reforming of glucose under visible light was demonstrated for the first time over an oxide solid solution Bi_xY_{1-x}VO₄ (BYV), prepared by a solid state reaction method. It was found that a certain amount of Y doping could promote the phase transition of BiVO₄ from monoclinic to tetragonal phase and finally led to the formation of a single phase solid solution.

For B/Y ratio of 1:1, a well crystallized BYV solid solution with absorption edge at around 460 nm formed, which possessed the highest activity for photocatalytic reforming of glucose when loaded with Pt and at pH = 3. Hydrogen production at various pH values showed that both at pH = 3 and pH = 11 hydrogen production was higher than at other pH values. It was also noted that after 2 or 3 h of reaction, the hydrogen production stopped and even decreased. However, when the gas

product was replaced with fresh N₂ atmosphere, hydrogen production recovered. It is supposed that in our reaction condition, the generated CO₂ might in some way inhibit the hydrogen production. Therefore, for photocatalytic reforming of glucose at least in our condition, the timely removal of gas product is indispensable.

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