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Photocatalytic coupling of formaldehyde to ethylene glycol and glycoaldehyde over bismuth vanadate with controllable facets and cocatalysts

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Bismuth vanadate (BiVO₄) single crystals with controllable facets and cocatalysts were synthesized and studied for photocatalytic coupling of formaldehyde into C₂ compounds mainly including ethylene glycol and glycoaldehyde. By using chloride anion as a morphology-controlling agent, we succeeded in synthesizing BiVO₄ single crystals with uniform truncated tetragonal bipyramidal morphology enclosed with {010} and {110} facets. The ratio of exposed {010} and {110} facets could be regulated by changing the concentration of Cl⁻. The BiVO₄ with an equal fraction of exposed {010} and {110} facets exhibited the highest ability of electron-hole separation and the highest C₂-compound yield. The loading of core-shell structured Pt@MoO_x and MnO_x particles onto {010} and {110} facets, respectively, further enhanced the formation of C₂ compounds. Our studies suggested that the Pt core and the MnO_x particles accelerated the separation of photogenerated electron-hole pairs, whereas the MoO_x shell catalyzed the coupling of HCHO possibly via a redox mechanism. The yields of C₂ compounds and ethylene glycol reached 21% and 11%, respectively, under an irradiation with UV-vis light for 12 h. Quantum yields of 11% and 4.8% were achieved for the coupling products under ultraviolet (350 nm) and visible (450 nm) light irradiation, respectively.

1. Introduction

Photocatalysis has attracted much attention not only for the degradation of organic pollutants and the splitting of water but also for the green and sustainable chemical synthesis.¹⁻³ The utilization of solar energy may drive unique catalytic reactions that are difficult to be achieved by using thermal energy. The carbon-carbon (C-C) bond formation is a core process in the synthetic chemistry. Traditionally, the C-C coupling reaction often uses labile reagents or catalysts and is carried out under harsh conditions.⁴ Under light irradiation, high-energy intermediates, which are suitable for the subsequent C-C coupling under mild conditions, may be generated.^{3,4} The photocatalysis by a robust heterogeneous semiconductor catalyst would provide a promising methodology for C-C coupling reactions.

 C_2 compounds such as ethylene glycol (EG, HOCH₂CH₂OH), glycoaldehyde (HOCH₂CHO), and acetaldehyde (CH₃CHO) are important synthetic intermediates. In particular, EG has many applications or potential applications in various fields such as energy

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(e.g., for direct EG fuel cells or as a H_2 source), transportation (e.g., as an antifreeze or coolant for automobiles or aircrafts) and chemical manufacture (e.g., as a precursor for polyesters).⁵ In the current industry, EG is primarily produced from petroleum-derived ethylene via epoxidation and subsequent hydrolysis of ethylene epoxide. Other synthetic routes based on non-petroleum carbon resources such as the hydrogenolysis of dimethyl oxalate and the carbonylation of formaldehyde followed by esterification and hydrogenation have also been investigated.⁵ However, these multi-step processes are not atom- and energy-efficient. The development of new synthetic methods for the production of C₂ compounds directly from C₁ feedstock would be highly attractive.

Thus far, only a few studies have been devoted to the photocatalysis for the synthesis of C_2 compounds through the coupling of C_1 feedstock, such as methanol or formaldehyde.^{6,7} An early study reported the use of ZnS, a UV-responsive semiconductor, for photocatalytic coupling of methanol to EG under UV-light irradiation, but the efficiency of EG formation was very low (EG yield = 0.3% in 60 h).⁶ Recently, we disclosed a novel photocatalytic coupling of HCHO into C_2 compounds mainly including EG, glycoaldehyde and acetaldehyde by using BiVO₄, a visible-light-responsive semiconductor.⁷ We clarified that EG and acetaldehyde was formed through the reductive coupling of HCHO with photogenerated electrons (eqn 1 and 2), whereas the formation of glycoaldehyde required both photogenerated electrons and holes (eqn 3). A part of holes were consumed in the formation of HCOOH



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(eqn 4). The C-C coupling proceeded via radical intermediates such as $\bullet CH_2OH.$

2HCHO + 2H ⁺ + 2e ⁻ → HOCH ₂ CH ₂ OH	(1)
2HCHO + 2H ⁺ + 2e ⁻ → CH ₃ CHO + H ₂ O	(2)
2HCHO + e^- + h^+ → HOCH ₂ CHO	(3)
HCHO + H ₂ O + 2h ⁺ → HCOOH + 2H ⁺	(4)

However, the BiVO4 catalyst used in our previous work was in irregular morphology and was not well designed, resulting in limited C_2 -compound yields. The engineering of crystal facets via morphology control has become an important methodology for the design of semiconductor photocatalysts.⁸ The facet control has been proven to be a useful strategy in enhancing the photocatalytic performance in many systems such as TiO₂,⁹⁻¹¹ BiVO₄,¹²⁻¹⁷ Cu₂O,^{18,19} Ag₃PO₄,^{20,21} BiOCl,^{22,23} and CeO₂²⁴ for organic-pollutant degradation, water splitting, and CO₂ reduction. It is now generally accepted that the exposure of a more reactive facet of a semiconductor can result in higher reactivity. For instance, TiO₂ nanosheets with a higher percentage of reactive {001} facet (up to 89%) exposed showed much better photocatalytic efficiency for the degradation of organic dyes than Degussa P25.9 For BiVO₄, several studies demonstrated that the sheet-like monoclinic crystal with a higher fraction of {010} facet exhibited higher photocatalytic activity for O₂ evolution.^{12,13,15,17} Therefore, it would be helpful to study the effect of exposed facets on catalytic behaviors of BiVO4 for the photocatalytic coupling of HCHO to C₂ compounds.

Cocatalysts are known to play crucial roles in photocatalysis not only by accelerating the separation of photogenerated electron-hole pairs but also by providing genuine catalytically active sites for the activation and conversion of reactants.^{25,26} The loading of oxidative/reductive cocatalysts on different facets of BiVO₄ has been reported to facilitate the activity for O₂ evolution reaction.²⁷ However, so far such a strategy has not been used for the design of BiVO₄ for other photocatalytic reactions.

Recently, we synthesized BiVO₄ single crystals with regular truncated tetragonal bipyramidal morphology enclosed by {010} and {110} facets, and succeeded in controlling the ratio of exposed {010}/{110} by a simple method. The present paper reports our synthesis of the BiVO₄ single crystals with controllable {010}/{110} ratios. We will investigate the effect of exposed facets on catalytic behaviors of BiVO₄ single crystals for the coupling of HCHO. The roles of cocatalysts loaded on different facets of BiVO₄ crystals will also be discussed. The present work aims to offer insights into the rational design of BiVO₄ photocatalysts for C-C coupling reactions.

2. Experimental

2.1. Synthesis of BiVO_4 single crystals with controllable exposed facets

BiVO₄ single crystals with regular truncated tetragonal bipyramidal morphology enclosed by {010} and {110} facets were synthesized by a hydrothermal method. In brief, NH_4VO_3 (50 mmol) and $Bi(NO_3)_3 \cdot 5H_2O$ (50 mmol) were dissolved in an aqueous nitric acid solution (2.0 M, 200 mL), and the pH value of the solution was adjusted to 2.0 with an aqueous ammonia solution. An orange precipitate was formed under stirring. Then, NaCl was added into the mixture and the suspension was further stirred for 15 min. After

aging for 2 h, the suspension was transferred to a Teflon-lined stainless steel autoclave and was subjected 10to 3 Avdrother and treatment at 473 K for 24 h. The obtained powdery sample was recovered by filtration, washing with deionized water and drying at 333 K in air overnight. The sample was finally calcined at 773 K in air for 2 h. We found that the ratio of exposed {010} and {110} facets in the obtained sample could be changed by changing the concentration of NaCl. To clarify whether Na⁺ or Cl⁻ played the determining role in controlling the morphology, we also used several other Na-containing or Cl-containing salts as morphology-controlling agents instead of NaCl and the detailed experimental procedures were described in the electronic supplementary information (ESI). BiVO₄-010 and BiVO₄-110 samples with {010} and {110} facets predominantly exposed, respectively, were synthesized using the methods reported in literature,^{12,17} and the detailed procedures were described in the ESI.

2.2. Loading of cocatalysts

Cocatalysts were loaded onto BiVO₄ single crystals by a stepwise photodeposition technique. As an example, the preparation of BiVO₄ containing Pt, MoO_x and MnO_x cocatalysts (MnO_x - MoO_x -Pt-BiVO₄) are described as follows. Pt particles were first loaded by photoreduction of H₂PtCl₆ in an aqueous suspension under irradiation with a 300 W Xe lamp for 1 h. Then, MoO_x species were deposited onto the obtained Pt-BiVO4 by photoreduction of Na₂MoO₄ in an aqueous solution containing methanol as a sacrificial agent under irradiation with a 300 W Xe lamp for 3 h. The MoO_x -Pt-BiVO₄ sample was subsequently dispersed in an aqueous solution of Mn(NO₃)₂ (0.10 M). After evacuation, the suspension was exposed to irradiation with a 300 W Xe lamp to deposit Mn species. NaIO3 with a concentration of 0.050 M was added into the suspension as an electron acceptor. After 3 h of photodeposition, the obtained sample was washed thoroughly with deionized water and dried overnight in vacuum. The procedures for the loading of cocatalysts other than Pt, MoO_x , and MnO_x were described in the ESI.

2.3. Characterization

The photocatalysts or photocatalytic systems were characterized by a series of techniques including N₂ physisorption, diffuse-reflectance ultraviolet-visible (UV-vis) spectroscopy, photoluminescence (PL) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), high-sensitivity low-energy ion scattering (HS-LEIS) spectroscopy, and photoelectrochemical measurements. N2 physisorption was carried out with a Micromeritics Tristar 3020 Surface Area and Porosimetry analyzer. Diffuse-reflectance UV-vis spectra were recorded on a Varian-Cary 5000 spectrometer equipped with a diffuse-reflectance accessory. The spectra were collected with BaSO₄ as a reference. The PL spectroscopic measurements were performed with Hitachi F-7000 fluorescence spectrophotometer. The SEM measurements were carried out using ZEISS SIGMA scanning electron microscope with 20 kV accelerating voltage. The TEM measurements with selected area electron diffraction (SAED) and line-scan energy-dispersive X-ray spectroscopy (EDS) analyses were performed on a Tecnai F20 electron microscope (Phillips Analytical) operated at an acceleration voltage of 200 kV.

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The XPS measurements were performed on a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al K_a radiation (1846.6 eV) as the X-ray source. For pseudo in situ XPS measurements, the sample was irradiated with Xe lamp (λ = 320-780 nm) under N₂ atmosphere for 6 h in the pretreatment chamber. After evacuation to remove N₂, the sample was directly transferred into the detection chamber for XPS measurements without exposure to air. The HS-LEIS measurements were carried out on an IonTOF Qtac100 low-energy ion scattering analyzer. ⁴He⁺ ions with a kinetic energy of 3 keV were applied at a low ion flux equal to 1325 pA cm⁻², which was necessary to avoid the sputtering of surfaces. ²⁰Ne⁺ ions with a kinetic energy of 5 keV were applied at a low ion flux equal to 445 pA cm⁻². The scattering angle was 145°.

Photoelectrochemical measurements were carried out with CHI 760E using a standard three electrode cell with a working electrode, a Pt plate as the counter electrode and an SCE electrode as the reference electrode. A mixed aqueous solution of 0.5 M NaH₂PO₄ and 0.5 M Na₂SO₃ was used as the electrolyte. The working electrodes were prepared by electrophoretic deposition on cleaning F-doped SnO₂-coated glasses (FTO glass, 1 cm × 2 cm). The electrophoretic deposition was carried out in an acetone solution (100 cm³) containing iodine (30 mg) and BiVO₄ powders ground finely (200 mg), which were dispersed by sonication for 5 min. The FTO electrode was immersed, parallel with the Pt electrode, in the solution with ca. 8 cm of distance, and then 20 V of bias was applied between them for 3 min using a potentiostat (DYY-2C). After this process was repeated for four times, the electrode was dried and calcined at 673 K for 30 min. The BiVO₄-coated area was controlled to be 1.0×1.0 cm, and the typical surface density of the photocatalyst was ca. 2.0 mg cm⁻².

The surface energies of {010} and {110} surfaces of BiVO₄ crystals were evaluated by the density functional theory (DFT) method. The Cl⁻-terminated {010} and {110} surfaces with different Cl⁻ coverages were also calculated by the DFT method. The details of theoretical calculations were described in the ESI.

2.4. Photocatalytic reaction

Photocatalytic reactions were carried out in a sealed quartz-tube reactor (volume, 20 cm³; inner diameter, 16 mm). Typically, the height of the reaction solution was 19 mm. The light source was a 300 W Xe lamp. Typically, 10 mg of solid catalyst was ultrasonically dispersed in 5.0 cm³ aqueous solution containing HCHO. Then, the reactor was evacuated and filled with nitrogen. Photocatalytic reactions were performed at room temperature typically for 12 h. After the reaction, the liquid products were analyzed by a highperformance liquid chromatograph (HPLC, Shimazu LC-20A) with refractive index (RI) and ultraviolet detectors together with a Shodex SUGARSH-1011 column (8 mm \times 300 mm) using a dilute H_2SO_4 aqueous solution as the mobile phase. Gaseous products including H₂, CO and CO₂ were analyzed by an Agilent Micro GC3000 equipped with a molecular sieve 5A column and a high-sensitivity thermal conductivity detector. The details of apparent quantum yield measurements were described in the ESI.

3. Results and discussion

3.1. BiVO₄ single crystals with controllable facets

Although great success has been made on the fabrication of TiO₂ single crystals with controlled facets,^{8a,9} the synthlesis⁶ of ⁰ other semiconductor photocatalysts such as BiVO₄ with well-controlled facets is still challenging.^{8b} Monoclinic BiVO₄ nanosheets with {010} facet preferentially exposed could be obtained by using sodium dodecyl benzene sulfonate or ethanolamine as a morphology-directing agent.^{12,13} The use of TiCl₃ as a morphology-controlling agent could also lead to the formation of BiVO₄ sheets with {010} preferentially exposed.¹⁵ It has been reported that the thickness of plate-like monoclinic BiVO₄ changed with the concentration of nitric acid during the synthesis.^{14,17} However, it is not easy to tune systematically the ratio of different facets for BiVO₄ photocatalyst.

We characterized the BiVO₄ samples synthesized in this work by the hydrothermal method. XRD measurements clarified that these samples were in monoclinic structure (Fig. S1, ESI⁺). However, the intensity of the (040) diffraction peak at ~30.5° depended on the concentration of NaCl. This peak became stronger upon increasing the concentration of NaCl, suggesting that NaCl may influence the morphology of BiVO₄. SEM measurements showed that the BiVO₄ samples we synthesized were composed of uniform single crystals with well-defined decahedral shape (Fig. S2, ESI⁺). The morphology of BiVO₄ single crystals changed gradually with the concentration of NaCl concentration (Fig. S2, ESI⁺). By using a slab model of monoclinic BiVO₄ single crystals with truncated tetragonal bipyramidal morphology, which was enclosed by eight {110} facets on sides and two {010} facets on the top and bottom (Fig. S3, ESI+), we calculated the ratio of {010} to {110} or the fraction of {010} facet. The result clarified that the fraction of {010} facet increased significantly with an increase in the concentration of NaCl (Table S1, ESI⁺). For convenience, hereafter, this series of samples was denoted as BiVO₄-HT-x%, where x represents the percentage of exposed {010}



Fig. 1. Electron microscopy for BiVO₄ single crystals. (a)-(e) SEM images: (a) BiVO₄-HT-23%, (b) BiVO₄-HT-39%, (c) BiVO₄-HT-50%, (d) BiVO₄-HT-62%, (e) BiVO₄-HT-75%. (f) TEM image of BiVO₄-HT-50% and SAED patterns of its {110} and {010} facets.

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Fig. 2. SEM micrographs for BiVO₄ samples synthesized by using other metal chlorides or sodium salts instead of NaCl: (a) none, (b) NaCl, (c) KCl, (d) CaCl₂, (e) ZnCl₂, (f) AlCl₃, (g) NaF, (h) NaBr, (i) NaI, (j) Na₂SO₄.



Fig. 3. Effect of Cl $^-$ coverage on surface energies of {010} and {110} surfaces.

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facet. The fraction of {010} facet could be regulated in ite wide range of 23-75% by controlling NaCl concentration (Fig. 10) The selected area electron diffraction (SAED) patterns confirmed the identity of {010} and {110} facets (Fig. 1f).

These results indicated that NaCl played a key role in tuning the ratio of {010} to {110} facet, and thus functioned as a morphologycontrolling agent. A previous study claimed that the presence of TiCl₃ could also change the morphology of BiVO₄ crystals.¹⁵ To identify the role of Na⁺ or Cl⁻ in directing the morphology, we investigated the effects of other metal chlorides and other sodium salts with different counter anions on the morphology of BiVO₄ crystals. Fig. 2 shows that the morphology of BiVO₄ sample is not uniform without addition of an additive, although some particles already have the decahedral shape. The use of KCl, CaCl₂, ZnCl₂, and AlCl₃ instead of NaCl as an additive during the hydrothermal treatment could also result in uniform truncated tetragonal bipyramidal morphology (Fig. 2 c-f). On the other hand, the employment of NaF, NaBr, NaI, and Na₂SO₄ to replace NaCl led to the generation of irregular morphology of BiVO4 particles (Fig. 2 g-j). Therefore, it becomes clear that Cl⁻ anions function as morphology-controlling agents and play a key role in controlling the ratio of exposed {010} to {110} facets.

It is worth mentioning that fluoride anions could increase the {001} facet of anatase TiO₂ by decreasing the surface energy of the {010} facet as compared to that of the {101} facet.²⁸ To understand the role of Cl⁻ anions in controlling the morphology, we performed DFT calculations. Monoclinic BiVO₄ surfaces were modelled by periodic slabs, and 2×2 surface cells were established for both {010} and {110} surfaces.²⁹⁻³¹ Fig. 3 illustrates the models of clean and Cl-terminated $\{010\}$ and $\{110\}$ surfaces. The surface energies (y) for clean {010} and {110} surfaces were calculated to be 0.27 and 0.28 J m⁻², respectively (Fig. 3). This suggests that the {010} and {110} surfaces possess similar stability. The surface energies for both {010} and {110} surfaces decreased by the presence of Cl⁻, and the increase in Cl⁻ coverage caused drops in the γ values of both facets (Fig. 3). Our computational results further clarified that the surface energies of the two facets became different in the presence of Cl⁻. The termination of the surface with Cl⁻ anions resulted in more significant decreases in the surface energy of the {010} surfaces as compared to that of the {110} surfaces. Moreover, the relative stability of the {010} surface increased with an increase in the coverage of Cl⁻. Thus, it is understandable that the increase in the concentration of Cl⁻ anions increases the fraction of more stable {010} facets during the hydrothermal treatment.

3.2. Effect of exposed facets on photocatalytic coupling of HCHO

The successful control of the ratio of different facets has provided an opportunity to elucidate the effect of crystal facets in photocatalytic coupling of HCHO. Table 1 shows the catalytic behaviours of BiVO₄ single crystals with systematically changed fractions of {010} facet. EG and glycoaldehyde were formed as the major C₂ products along with CH₃CHO. HCOOH was also formed by the oxidation of HCHO. The ratio of electrons and holes consumed by assuming eqn (1)-(4) for the product formation was 1.0±0.1 for each catalyst displayed in Table 1, confirming that the reactions of eqn (1)-(4) occurred on our BiVO₄ catalysts. As compared to the BiVO₄ with irregular morphology, which was synthesized without addition of Cl⁻, the BiVO₄ single crystals with uniform morphology exhibited higher yields of EG,

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Table 1. Effect of fraction of {010} facets on performances of BiVO4 single crystals for photocatalytic conversion of HCHO^a

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Catalyst	Produc	t concentration	(mol dm ⁻³)	Product yield ^c (%)		o ⁻ /b ⁺		
Catalyst	EG	CH₃CHO	HOCH ₂ CHO	Total C ₂	НСООН	EG	Total C ₂	e /ii
BiVO4 ^b	0.22	0.053	0.13	0.40	0.25	3.6	6.5	1.1
BiVO ₄ -HT-23%	0.26	0.055	0.23	0.54	0.35	4.2	8.8	0.93
BiVO ₄ -HT-39%	0.30	0.058	0.26	0.62	0.39	4.9	10	0.94
BiVO ₄ -HT-50%	0.35	0.072	0.30	0.72	0.46	5.7	12	0.93
BiVO ₄ -HT-62%	0.31	0.061	0.26	0.63	0.40	5.0	10	0.94
BiVO ₄ -HT-75%	0.25	0.047	0.20	0.50	0.34	4.1	8.1	0.90
BiVO4-010	0.23	0.040	0.17	0.44	0.29	3.7	7.2	0.95
BiVO ₄ -110	0.18	0.044	0.10	0.32	0.22	2.9	5.3	1.0

^a Reaction conditions: catalyst, 10 mg; reactant solution, HCHO 12.3 mol dm⁻³, 5.0 cm³; light source, Xe lamp with λ = 320-780 nm, 300 W; irradiation time, 12 h. ^b BiVO₄ with irregular morphology. ^cThe yield was calculated on a molar carbon basis.



Fig. 4. Transient photocurrent responses for BiVO₄ single crystals with different frcations of exposed {010} facets. (a) $BiVO_4$ -HT-23%, (b) $BiVO_4$ -HT-39%, (c) $BiVO_4$ -HT-50%, (d) $BiVO_4$ -HT-62%, (e) $BiVO_4$ -HT-75%.

glycoaldehyde, and total C₂ compounds. It is of interest that the photocatalytic behaviour depends on the ratio of {010} to {110} facets. The increase in the fraction of exposed {010} facets from 25% to 50% significantly enhanced the formations of EG, glycoaldehyde and total C₂ compounds (Table 1). However, a further increase in the fraction of {010} facets to $\geq 60\%$ rather decreased the photocatalytic performance. Thus, the maximum performance was achieved on the BiVO₄-HT-50% catalyst with 50% fraction of {010} facets. The yields of EG and C₂ compounds reached 5.7% and 12%, respectively, after 12 h of reaction. For comparison, the catalytic behaviours of the BiVO₄-010 and BiVO₄-110 samples with {010} and {110} facets predominantly exposed (see Figs. S4 and S5, ESI⁺ for their XRD patterns and SEM images), respectively, were also measured. Both

 $BiVO_4\mbox{-}010$ and $BiVO_4\mbox{-}110$ samples showed lower yields of EG and C_2 compounds than the $BiVO_4\mbox{-}HT\mbox{-}50\%$ (Table 1).

Our characterizations clarified that the specific surface areas decreased slightly with an increase in the fraction of {010} facets, while the mean sizes (evaluated by the length *b* in Fig. S3, ESI⁺) increased slightly at the same time. These cannot explain the change in the catalytic behaviours with an increase in the fraction of {010} facets. Furthermore, the bandgap energy values calculated from the UV-vis spectroscopy for this series of catalysts were the same, being 2.3 eV (Table S2, ESI⁺). Thus, the observation that the BiVO₄ single crystal with an equal fraction of {010} and {110} facets shows the highest catalytic performance (Table 1) suggests that both facets play crucial roles in the photocatalytic coupling of HCHO.

It is worth mentioning that our present result that both {010} and {110} facets are required for obtaining a high activity is quite different from those reported previously, where the {010} facet of sheet-like BiVO₄ has been proposed to be the key to photocatalytic degradation of organic pollutants or O2 evolution.12,13,15,17 The coexistence of two facets with a proper ratio has been reported to favour the reduction of CO2 with H2O with single-crystal TiO2 and CeO₂ photocatalysts.^{11,24} Recent studies demonstrated that the photogenerated electrons and holes in the BiVO₄ single crystal would migrate separately to its {010} and {110} facets.^{16,27,32} Thus, it can be expect that the co-existence of {010} and {110} facets with a proper ratio would be beneficial to the separation of photogenerated electrons and holes. To understand the effect of the {010}/{110} ratio on the separation of photogenerated electron-hole pairs, we performed transient photocurrent response and photoluminescence spectroscopy measurements. The result displayed in Fig. 4 reveals that the photocurrent density increases upon increasing the fraction of {010} facets from 23% to 50%, but a further increase in the fraction of {010} facets rather decreases the photocurrent density. This indicates that the BiVO₄ with an equal fraction of {010} and {110} facets possesses the highest ability of electron-hole separation. We performed photoluminescence (PL) spectroscopic studies for the BiVO₄ catalysts with different {010}/{110} ratios. A luminescence band centred at 535 nm was observed for our BiVO4 single crystals (Fig. S6, ESI⁺). It is generally accepted that the photoluminescence

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arises from the recombination of the photogenerated carries on a semiconductor, and thus the higher intensity of the luminescence band means the higher probability of the recombination of photogenerated carriers. For our BiVO₄ single crystals, the intensity of the luminescence band decreased in the order of BiVO₄-HT-75% > BiVO₄-HT-23% > BiVO₄-HT-39% > BiVO₄-HT-62% > BiVO₄-HT-50%, indicating that the BiVO₄-HT-50% has the lowest ability of electronhole recombination. This order agrees well with that obtained from the transient photocurrent response measurement, confirming that the co-existence of {010} and {110} facets with an equal fraction favours the separation of electron-hole pairs. Furthermore, the order of ability of electron-hole separation is the same with that of the C₂ formation activity during the photocatalytic conversion of HCHO (Table 1). Therefore, we conclude that the ability of electron-hole separation is the key parameter that determines the catalytic behaviours for the $BiVO_4$ with different ratios of $\{010\}$ and $\{110\}$ facets. In combination with recent result that the photogenerated electrons and holes in the BiVO4 single crystal migrate separately to {010} and {110} facets, we speculate that the reduction of HCHO to EG and acetaldehyde occurs on the {010} facet, where the photogenerated electrons accumulate, whereas the oxidation of HCHO to HCOOH takes place on the {110} facet, toward which the holes migrate. The formation of glycoaldehyde requires both electrons and holes, and thus may occur at the interface of the two facets. The spatial separation of reduction and oxidation reactions could avoid the reverse reactions and is beneficial to the formation of C₂ compounds.

3.3. Effects of cocatalysts on photocatalytic coupling of HCHO

We studied the effects of cocatalysts loaded onto the BiVO₄-HT-50% catalyst, which showed the best performance among BiVO₄ single crystals with different {010}/{110} ratios, for photocatalytic coupling of HCHO. Pt, a typical reduction co-catalyst, was first loaded onto the BiVO₄-HT-50% through photoreduction of H₂PtCl₆. SEM studies clarified that Pt nanoparticles were selectively deposited onto the {010} facet (Fig. 5a), where the photogenerated electrons accumulated. The same phenomenon has also been observed in previous studies.^{16,27} Our transient photocurrent response measurements showed that the deposition of Pt onto the {010} facets with a loading of 0.50 wt% increased the current density (Fig. 6, curves a and b). The luminescence band at 520-540 nm arising from the recombination of electron-hole pairs became significantly weakened in the presence of Pt nanoparticles (Fig. S7, ESI⁺). These observations clarified that the loading of Pt nanoparticles onto the {010} facets accelerated separation of photogenerated electron-hole pairs. This can be explained by the strong ability of Pt to extract electrons from the {010} facets of BiVO₄. However, our catalytic studies revealed that the enhancement in the yields of C₂ compounds was very limited (Table 2).

To find a cocatalyst having genuine catalytic functions in photocatalytic coupling of HCHO, we examined some redox cocatalysts including CrO_x, MoO_x, WO_x, VO_x, CuO_x, and FeO_x photodeposited on the 0.5 wt% Pt-BiVO₄-HT-50%. These redox cocatalysts except for FeO_x could enhance the formation of C_2 compounds (Table 2). Among these cocatalysts, MoO_x was the most effective in catalysing the coupling of HCHO. The yields of EG and

total C₂ compounds reached 8.5% and 17%, respectively, over the 3 wt% MoOx-0.5 wt% Pt-BiVO4-HT-50% Catalyst039WeCYRAther investigated the effect of MoO_x content on catalytic performances. Table 3 shows that the increase in MoO_x content from 0.5 to 3.0 wt% enhances C-C coupling but a further increase in MoO_x content to 5.0

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Fig. 5. SEM micrographs for BiVO₄-HT-50% with different cocatalysts and the proposed catalyst model. (a)-(e) SEM micrographs: (a) 0.5% Pt-BiVO₄-HT-50%, (b) 3% MoOx-BiVO4-HT-50%, (c) 3% MoOx-0.5% Pt-BiVO4-HT-50%, (d) 3% MnO_x-BiVO₄-HT-50%, (e) 3% MnO_x-3% MoO_x-0.5% Pt-BiVO₄-HT-50%. (f) Proposed catalyst model.



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Table 2. Effect of cocatalysts on performances of BiVO₄-HT-50% for photocatalytic conversion of HCHO^a

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Catalyst ^b	Product	Total C ₂ yield ^c (%)				
	EG	CH₃CHO	HOCH ₂ CHO	total C ₂	нсоон	-
BiVO ₄ -HT	0.35	0.072	0.30	0.72	0.46	12
Pt-BiVO ₄ -HT	0.38	0.084	0.31	0.77	0.44	13
3% MoO _x -Pt-BiVO ₄ -HT	0.52	0.13	0.39	1.0	0.70	17
3% CrO _x -Pt-BiVO ₄ -HT	0.49	0.11	0.39	0.99	0.71	16
3% VO _x -Pt-BiVO ₄ -HT	0.47	0.11	0.38	0.96	0.70	16
3% WO _x -Pt-BiVO ₄ -HT	0.46	0.11	0.38	0.95	0.68	16
3% CuO _x -Pt-BiVO ₄ -HT	0.41	0.10	0.44	0.95	0.60	16
3% FeO _x -Pt-BiVO ₄ -HT	0.37	0.071	0.32	0.76	0.49	13

^{*a*} Reaction conditions: catalyst, 10 mg; reactant solution, HCHO 12.3 mol dm⁻³, 5.0 cm³; light source, Xe lamp (λ = 320-780 nm), 300 W; irradiation time, 12 h. ^{*b*} BiVO₄-HT-50% was used; the Pt loading was 0.5 wt%. ^{*c*} The yield was calculated on a molar carbon basis.

Table 3. Effect of MoO_x contents on performances of MoO_x-Pt-BiVO₄-HT-50% for photocatalytic conversion of HCHO^a

Catalyst ^b	Product o	Total C2 vield ^c (%)				
	EG	CH₃CHO	HOCH ₂ CHO	total C ₂	НСООН	
Pt-BiVO ₄ -HT	0.38	0.084	0.31	0.77	0.44	13
0.5% MoO _x -Pt-BiVO ₄ -HT	0.45	0.10	0.34	0.89	0.61	14
3% MoO _x -Pt-BiVO ₄ -HT	0.52	0.13	0.39	1.0	0.70	17
5% MoO _x -Pt-BiVO ₄ -HT	0.50	0.11	0.38	0.99	0.63	16
3% MoO _x -BiVO ₄ -HT	0.37	0.079	0.30	0.74	0.46	12

^{*a*} Reaction conditions: catalyst, 10 mg; reactant solution, HCHO 12.3 mol dm⁻³, 5.0 cm³; light source, Xe lamp (λ = 320-780 nm), 300 W; irradiation time, 12 h. ^{*b*} BiVO₄-HT-50% was used; the Pt loading was 0.5 wt%. ^{*c*} The yield was calculated on a molar carbon basis.



Fig. 7. HS-LEIS spectra for BiVO₄-HT-50% with different cocatalysts.

wt% does not significantly increase the product yields. It is noteworthy that the loading of MoO_x alone onto the BiVO₄-HT-50% did not significantly enhance the C₂ compound yield (Table 3). Therefore, there exist synergistic effects between MoO_x and Pt on the photocatalytic coupling of HCHO.

We performed characterizations for the catalysts with MoO_x cocatalysts. The SEM measurements showed that MoO_x particles were preferentially deposited on {010} facets irrespective of the presence of Pt (Fig. 5b and 5c). Since photogenerated electrons preferentially moved to {010} facets, 32 this suggests the reductive deposition of MoO_x species by photogenerated electrons. It is worth mentioning that the sizes of MoO_x particles change owing to the preloading of Pt nanoparticle on {010} facets. We evaluated the distributions of sizes of particles photodeposited on {010} facets by counting 200 particles. The results showed that the mean size of Pt particles on the 0.5 wt% Pt-BiVO₄-HT-50% was 29 nm (Fig. S8a, ESI⁺). The distribution of sizes of MoO_x particles loaded on BiVO₄ without Pt was quite wide, and the mean size of MoO_x particles were evaluated to be 240 nm (Fig. S8b, ESI⁺). However, the distribution of sizes of MoO_x particles deposited on {010} facets preloaded with Pt became significant narrower (Fig. S8c, ESI⁺). The mean size of MoO_x-Pt particles decreased to 36 nm, which was slightly larger than that

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Table 4. Effect of co-catalysts on performances of BiVO₄-HT-50% for photocatalytic conversion of HCHO^a

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Catalyst ^b	Product	concentration	Total Cavield ^e (%)			
Catalyst	EG	CH₃CHO	HOCH ₂ CHO	total C ₂	нсоон	
BiVO ₄ -HT	0.35	0.072	0.30	0.72	0.46	12
3% MnO _x -BiVO ₄ -HT	0.41	0.077	0.34	0.83	0.57	14
3% CoO _x -BiVO ₄ -HT	0.38	0.074	0.33	0.78	0.50	13
3% PbO _x -BiVO ₄ -HT	0.32	0.061	0.28	0.66	0.43	11
3% MoO _x -0.5 wt%Pt-BiVO ₄ -HT	0.52	0.13	0.39	1.0	0.70	17
3% MnO _x -3% MoO _x -0.5 wt% Pt-BiVO ₄ -HT	0.70	0.15	0.45	1.3	0.90	21

^a Reaction conditions: catalyst, 10 mg; reactant solution, HCHO 12.3 mol dm⁻³, 5.0 cm³; light source, Xe lamp (λ = 320-780 nm), 300 W; irradiation time, 12 h. ^b BiVO₄-HT-50% was used. ^cThe yield was calculated on a molar carbon basis.



Fig. 8. XPS spectra for 3% MoO_x-0.5% Pt-BiVO₄-H1-50% after light irradiatio (a) Pt 4f, (b) Mo 3d.

of Pt but remarkably smaller than that of MoO_x particles alone. These observations allow us to speculate that MoO_x species were preferentially deposited on Pt nanoparticles.

We performed further studies for the MoO_x -Pt particles by using the high-sensitivity low-energy ion-scattering (HS-LEIS) technique, from which the atomic composition of the outmost surface layer could be meaured.³³ The ²⁰Ne⁺ source that can provide better sensitivities for heavier elements than lighter elements has been employed in our experiments. Fig. 7 shows that Bi exists on the outmost surface of all the catalysts. The signals of vanadium and oxygen were not strong enough to be observed in Fig. 7 because of their lower sensitivities with ²⁰Ne⁺ source. The presence of Pt on the outmost surface was confirmed for the 0.5 wt% Pt-BiVO₄-HT-50% catalyst. Mo and Pt co-exist on the outmost surface when MoO_x was deposited onto the 0.5% Pt-BiVO₄-HT-50% with a content of 0.5 wt%. When the content of Mo increased to 3.0 wt%, Pt could not observed and only Mo was present on the outer surfaces (Fig. 7). Similarly, Pt could not be observed on the outmost surface of the 5.0% MoO_x-0.5% Pt-BiVO₄-HT-50% catalyst. These observations suggest that the MoO_x species cover the Pt nanoparticles on the {010} facets of BiVO₄ single crystals to form a core-shell structure when the content of Mo is \geq

3.0 wt% (Fig. 5f). We believe that this is probably because the MoO_x species are preferentially deposited on Pt particles, on which the photogenerated electrons are accumulated, during the photodeposition process. Similar phenomena were reported previously for the CrO_x-Rh/GaN:ZnO and CuO_x-Pt/TiO₂ catalysts, where the CrO_x or CuO_x species was selectively photodeposited on Rh or Pt nanoparticles to form core-shell structures.^{34,35}

Our transient photocurrent response measurements showed that the loading of 3.0 wt% MoO_x onto the 0.5 wt% Pt-BiVO₄-HT-50% decreased the current density to some extent (Fig. 6). This indicates that the presence of MoO_x shell did not accelerate the electron-hole separation. This is also confirmed by the photoluminescence spectroscopic result (Fig. S7, ESI⁺). Thus, it becomes clear that the enhancement in the activity for C2-compound formation (Table 3) should not arise from the facilitation of electron-hole separation. This allows us to speculate that the MoO_x species function as genuine active sites for the activation and coupling of HCHO. It is worth mentioning that the reductive coupling of CH₃CHO to butenes could occur on silica-supported Mo^{IV} dimmers via a diolate intermediate, although this reaction is not catalytic due to the oxidation of Mo^{IV} to Mo^{VI.36} In our previous study, we already pointed out that the generation of V^{IV} species on BiVO₄ surfaces could enhance C₂compound formation and the V^{IV} species may function as the active site catalysing the coupling of HCHO.⁷ To gain further information on the functioning mechanism of MoO_x species, we performed pseudo in situ X-ray photoelectron spectroscopy (XPS) measurements for the 3 wt% MoO_x-0.5 wt% Pt-BiVO₄-HT-50% catalyst after light irradiation. The catalyst after light irradiation was transferred into the detection chamber without exposure to air. The binding energy of Pt 4f_{7/2} was 70.9 eV (Fig. 8), confirming that Pt was in metallic state in this catalyst.³⁷ The binding energy of Mo 3d_{5/2} was 231.5 eV (Fig. 8), which could be attributed to Mo^{V.38} We speculate that the redox of Mo^V/Mo^{VI} may participate in the coupling of HCHO. The HCHO molecules adsorbed on catalyst surfaces may be reduced into •CH₂OH radicals by accepting electrons from Mo^V sites, and the oxidized Mo^{VI} can be reduced by the photogenerated electrons to complete the catalytic cycle.

We also investigated the effect of several oxidation cocatalysts including MnO_x , CoO_x , and PbO_x on the photocatalytic behaviours of

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Fig. 9. TEM micrograph and EDS analysis for the 3% MnO_x-3% MoO_x-0.5% Pt-BiVO₄-HT-50% catalyst. (a) Dark-field TEM micrograph, (b) line-scan EDS analysis across the particle displayed in (a) (yellow line on the TEM micrograph).



Fig. 10. Performances of the MnO_x-3% MoO_x-0.5% Pt-BiVO₄-HT-50% catalyst under visible-light irradiation. Reaction conditions: catalyst, 10 mg; reactant solution, HCHO 12.3 mol dm⁻³, 5.0 cm³; light source, Xe lamp with λ = 420-780 nm, 300 W.

the BiVO₄-HT-50%. The low-valent metal cations were employed as the precursors of these cocatalysts. These cocatalysts were expected to be deposited onto BiVO₄ through an oxidative process via accepting photogenerated holes and thus may be located on the {110} facets. Our catalytic studies clarified that MnO_x exhibited the highest activity for C₂-compound formation among these cocatalysts, although the enhancement was not remarkable (Table 4). Thus, we performed characterizations for the 3 wt% MnO_x-BiVO₄-HT-50%. The SEM measurements confirmed our speculation that the MnO_x particles were predominantly deposited on the {110} facets of the BiVO₄-HT-50% (Fig. 5d). The transient photocurrent response measurements indicated that the loading of MnO_x increased the current density and thus facilitated the electron-hole separation. We speculate that the presence of MnO_x on the {110} facets may be beneficial to attracting holes. We further photodeposited MnO_x onto the 3 wt% MoO_x-0<u>e</u>-5-wt% Pt-BiVO₄-HT-50% catalyst. The SEM measurements (Fig. 5-6) and fine scan energy-dispersive X-ray spectroscopy (EDS) analyses (Fig. 9) suggested that MnO_x was deposited on the {110} facets, whereas Pt and Mo elements were located on the {010} facets of BiVO₄. The XPS studies suggested that Mn existed as MnO_x (1.5 < x < 2) species (Fig. S9, ESI⁺). The transient photocurrent response measurements suggested that the loading of MnO_x on the {110} facets of the 3 wt% MoO_x-0.5 wt% Pt-BiVO₄-HT-50% could also accelerate the electronhole separation. Our photocatalytic studies showed that the deposition of MnO_x onto the 3 wt% MoO_x-0.5 wt% Pt-BiVO₄-HT-50% enhanced the C₂ compound formation. The yields of EG and C₂ compounds reached 11% and 21%, respectively, under an irradiation with UV-vis light for 12 h (Table 4).

Therefore, we developed an efficient catalyst, i.e., 3 wt% MnO_x-3 wt% MoO_x-0.5 wt% Pt-BiVO₄-HT-50%, through careful catalyst design. The structural model of this catalyst is displayed in Fig. 5f. We propose that the photogenerated electrons and holes move separately onto {010} and {110} facets, and the ratio of the two facets is a key parameter for the electron-hole separation. The presence of Pt on $\{010\}$ and MoO_x on $\{110\}$ can further facilitate the separation of electron-hole pairs. The MoO_x shell formed on Pt core would provide active sites for catalysing the coupling of HCHO. We further measured the catalytic behaviour of the 3 wt% MnOx-3 wt% MoOx-0.5 wt% Pt-BiVO₄-HT-50% catalyst under visible-light irradiation. Fig. 10 shows that the concentrations of C-C coupling products increased with time almost linearly in 100 h. The recovered catalyst could be used repeatedly without significant deactivation. The apparent quantum yields were further measured under both UV- and visiblelight irradiation for this catalyst. The quantum yields for EG and total C_2 compounds were 6.5% and 11% under UV (λ = 350 nm) irradiation, and were 3.2% and 4.8% under visible-light (λ = 450 nm) irradiation, respectively.

4. Conclusions

We successfully synthesized BiVO₄ single crystals with uniform truncated tetragonal bipyramidal morphology and tunable ratios of exposed {010} and {110} facets by a hydrothermal method using Cl⁻ anions as morphology-controlling agents. The fraction of {010} facets could be regulated from 23% to 75% by controlling the concentration of Cl⁻ anions. We found that the photocatalytic coupling of HCHO to C₂ compounds depended on the ratio of the two facets. The catalyst with an equal fraction of exposed {010} and {110} facets, toward which the photogenerated electrons and holes migrate respectively, exhibited the highest C2-compound yield. We demonstrated that the catalyst with an equal fraction of {010} and {110} facets was the most efficient for the separation of electron-hole pairs. The loading of Pt@MoO_x core-shell structured cocatalyst on the $\{010\}$ facets and MnO_x cocatalyst on the {110} facets significantly enhanced the C-C coupling. The yields of EG and C₂ compounds reached 11% and 21%, respectively, under an irradiation with UV-vis light for 12 h. Apparent quantum yields for C_2 compound formation were 11% and 4.8% under UV- and visible-light irradiation, respectively. It has been elucidated that the Pt nanoparticles and the MnO_x accelerate the electron-hole separation, while the MoO_x provides active sites for activation of HCHO. Our present work provides important clues for

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promoting the activity of photocatalytic coupling of C₁ compounds by engineering the crystal facets and cocatalysts of the semiconductor catalyst, and would contribute to green chemical synthesis via solar-driven photocatalysis using robust semiconductors.

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Bismuth vanadate single crystals with controllable facets and cocatalysts show excellent performances for photocatalytic coupling of formaldehyde into C_2 compounds.