Electronic Supplementary Information (ESI)

Direct conversion of formaldehyde to ethylene glycol via photocatalytic carbon-carbon coupling over bismuth vanadate

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Detailed experimental procedures

Materials and photocatalyst preparation. $BiVO_4$ was prepared by a precipitation method using NH_4VO_3 and $Bi(NO_3)_3 \cdot 5H_2O$ in aqueous solution as precursors. The precipitate was dried at 353 K for 12 h. Then, the obtained powdery sample was typically calcined at 773 K in air for 6 h to obtain $BiVO_4$. To investigate the effect of pretreatment conditions on catalytic behaviours, we treated the dried powdery sample under both air and N_2 atmospheres at different temperatures for 6 h. The samples treated under air at 773 and 973 K were denoted as $BiVO_4$-773A (or $BiVO_4$) and $BiVO_4$-973A. The samples treated under N_2 at 773, 873, 923, 973 and 1073 K were denoted as $BiVO_4$-773N, $BiVO_4$-873N, $BiVO_4$-923N, $BiVO_4$-973N and $BiVO_4$-1073N, respectively.

TiO_2 (P25), which contained 20% rutile and 80% anatase, was purchased from Degussa. WO_3 was purchased from Alfa Aesar Reagent Co. Ltd. Pt-modified TiO_2 (Pt-TiO_2) was prepared by a photodeposition method. TiO_2 was suspended an aqueous solution of hexachloroplatinic acid (H_2PtCl_6) with a concentration of 0.020 M. The suspension was irradiated with a 300 W Hg lamp for 1 h. The obtained sample was recovered by filtration, followed by washing repeatedly with deionized water and drying overnight in vacuum. The loading of Pt was 0.5 wt%. ZnS was prepared by a precipitation method.[1] In brief, aqueous solutions of $ZnSO_4$ and Na_2S with concentrations of 0.1 M were mixed together, resulting precipitation. The precipitate was recovered by filtration, followed by washing with distilled water and drying at 333 K for 12 h. CdS was prepared by a hydrothermal method.[2] A mixed aqueous solution containing $CdSO_4$ (24 mmol), thioacetamide (48 mmol) and ethylenediamine (48 mmol) was transferred into an autoclave and was subjected to hydrothermal treatment at 423 K for 8 h. The obtained solid product was recovered by filtration, followed by washing with distilled water and ethanol, and then drying in vacuum at 333 K for 8 h.

Cu_2O was synthesized by a hydrolysis method.[3] CuCl was hydrolysed by adding an aqueous solution of Na_3PO_4 (1.0 M, 40 mL) into a NaCl aqueous solution (5.0 M, 400 mL) containing CuCl (0.04 mol) under vigorous stirring and an argon flow. The obtained powder was washed with distilled water, followed by drying in vacuum. Cu_2O powder was obtained by heating at 673 K for 24 h in vacuum.

Bi_2WO_6 was synthesized by a solid-state reaction method.[4] Bi_2O_3 and WO_3 with a molar ratio of 1:1 were mixed in ethanol. The mixture was dried at 353 K for 5 h, and then calcined at 1173 K for 12 h in air.

Characterizations. X-ray diffraction (XRD) patterns were recorded on a Panalytical X'pert Pro diffractometer using Cu K_α radiation (40 kV, 30 mA). N_2 physisorption was carried out with a Micromeritics Tristar 3020 surface area and porosimetry analyzer. Diffuse-reflectance UV-visible (UV-vis) spectra were recorded on a Varian-Cary 5000 spectrometer equipped with a diffuse-reflectance accessory. The spectra were collected with $BaSO_4$ as a reference. The photoluminescence (PL) spectroscopic measurements were performed with Hitachi F-7000 fluorescence spectrophotometer. Scanning electron microscopy (SEM) was carried out using ZEISS SIGMA scanning electron microscope with 20 kV accelerating voltage.

Electron spin resonance (ESR) spectroscopic measurements were performed at room temperature using a Bruker EMX-10/12 ESR spectrometer operated at X-band frequency. The parameters for ESR measurements were as follows: microwave frequency 9.8 GZ, microwave power 20 mW, modulation frequency 100 kHz, attenuator 10 dB. For in situ ESR measurements, $BiVO_4$ powders were dispersed in a mixed aqueous solution of DMPO (0.080 M), which was used as a spin-trapping agent, and HCHO (12.3 M) by ultrasonic treatment. Then, the suspension was injected into a glass capillary and the glass capillary was placed in a sealed glass tube under N_2 atmosphere. The sealed glass tube was placed in the microwave cavity of ESR spectrometer and was irradiated with Xe lamp (λ = 320-780 nm) during ESR measurements at room temperature. For quantitative ESR measurements, 100 mg $BiVO_4$ powders were placed in a sealed glass tube under N_2 atmosphere, and then the sealed glass tube was placed in the microwave cavity for ESR measurements at room temperature. The weight of each sample was fixed. The concentration of V^{4+} was estimated by using an external standard, i.e., $CuSO_4 \cdot 5H_2O$. The number of spins of V^{4+} participating in resonance was evaluated with the reference ($CuSO_4 \cdot 5H_2O$) by using the following equation.[5]

$$S_x = S_{std}A_xG_{std}(g_{std})^2/A_{std}G_x(g_x)^2$$

where S is the number of spins, and A is the area under the absorption curve, which can be obtained by double integrating the first derivative absorption curve. G is the gain. g is the spectroscopic splitting factor. The subscript *std* denotes $CuSO_4 \cdot 5H_2O$, while x denotes the sample to be measured.

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 NaH_2PO_4 and 0.5 M Na_2SO_3 was used as the electrolyte. The working electrodes were prepared by electrophoretic deposition on cleaning F-doped SnO_2-coated glasses (FTO glass, 1 cm × 2 cm). The electrophoretic deposition was carried out in an acetone solution (100 cm^3) containing iodine (30 mg) and $BiVO_4$ 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 $BiVO_4$-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}.

Photocatalytic reactions. Photocatalytic reactions were carried out in a sealed quartz-tube reactor (volume, 20 cm^3; inner diameter, 16 mm). Typically, the height of the reaction solution was 19 mm. The light source was a 300 W Xe lamp. The light intensity was adjusted to 800 mW/cm^2 and the irradiation area was 3.0 cm^2. Typically, 10 mg of solid catalyst was ultrasonically dispersed in 5.0 cm^3 aqueous solution containing HCHO. Then the reactor was evacuated and filled with nitrogen. The photocatalytic reaction was performed at room temperature typically for 12 h. After the reaction, the liquid products were analysed by high-performance liquid chromatography (HPLC, Shimazu LC-20A) with refractive index (RI) and UV detectors together with a Shodex SUGARSH-1011 column (8 mm × 300 mm) using a dilute H_2SO_4 aqueous solution as the mobile phase. H_2, CO and CO_2 were analysed by an Agilent Micro GC3000 equipped with a molecular sieve 5A column and a high-sensitivity thermal conductivity detector. The photocatalytic reaction for each catalyst under each condition was performed at least for 3 times and the relative error was typically within 5%. The turnover number (TON) was estimated by using the following equation: TON = (mole of HCHO reacted)/(moles of photocatalyst).[6]

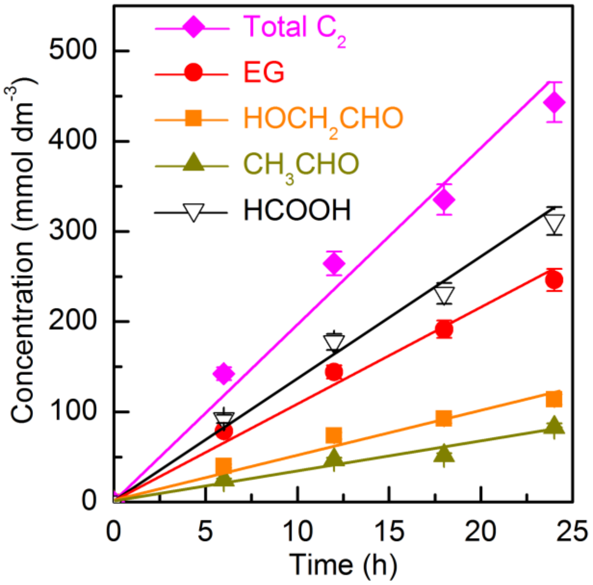

Fig. S1 Dependences of product concentrations on reaction time in photocatalytic conversion of HCHO over $BiVO_4$ catalyst. Reaction conditions: catalyst, 10 mg; reactant solution, HCHO 6.7 mol dm^{-3}, 5.0 cm^3; light source, Xe lamp (λ = 320-780 nm), 300 W.

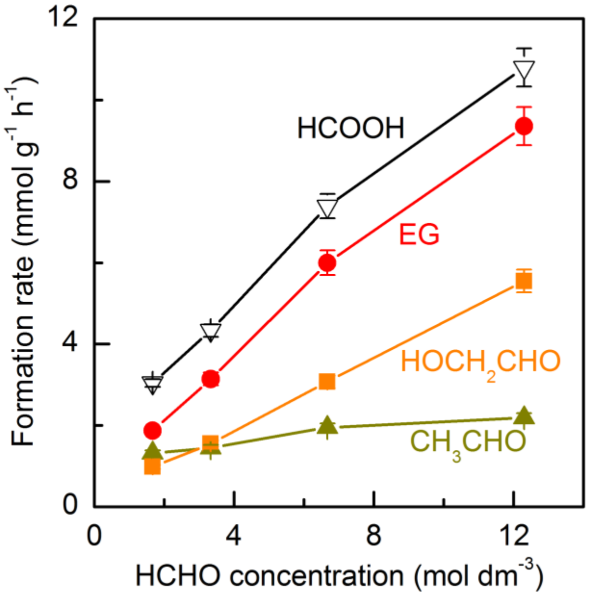

Fig. S2 Dependences of product concentrations on HCHO concentration in photocatalytic conversion of HCHO over $BiVO_4$ catalyst. Reaction conditions: catalyst, 10 mg; reactant solution, 5.0 cm^3; light source, Xe lamp (λ = 320-780 nm), 300 W; irradiation time, 12 h.

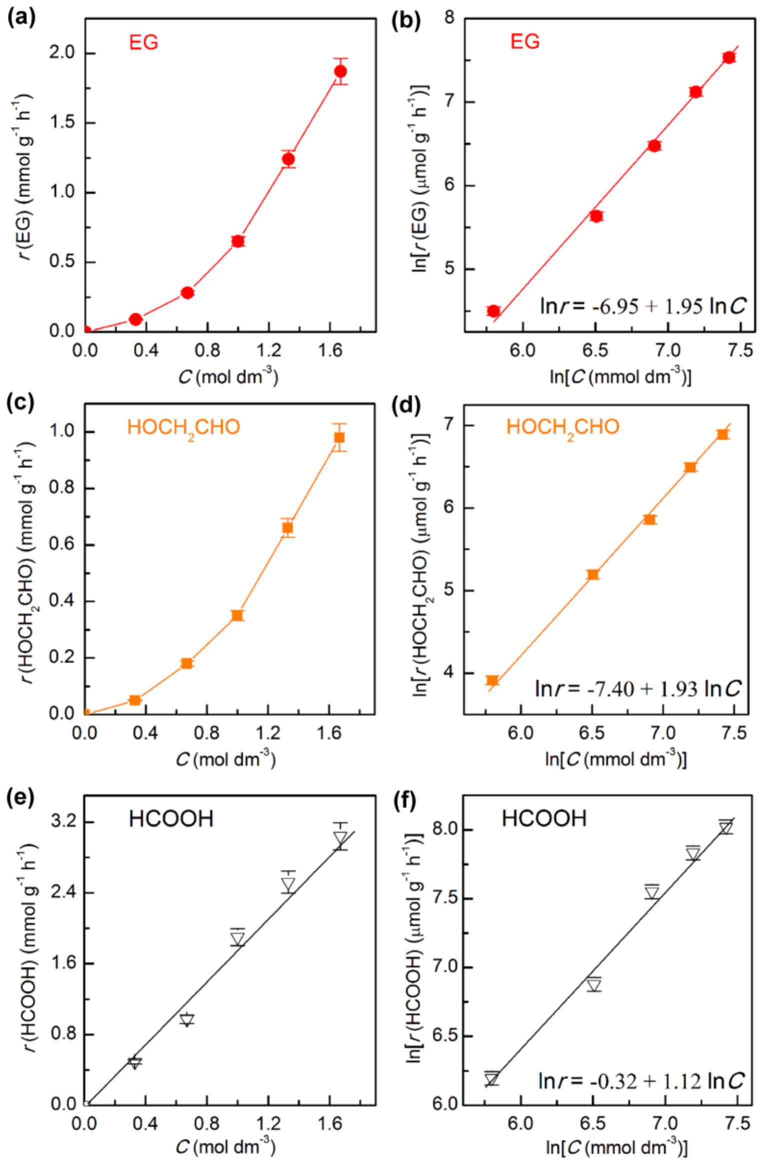

Fig. S3 Product formation rates versus HCHO concentration in photocatalytic conversion of HCHO over $BiVO_4$ catalyst. (a), (b), EG. (c), (d), glycoaldehyde. (e), (f), HCOOH. (a), (c), (e), rate versus HCHO concentration. (b), (d), (f), logarithm of rates versus logarithm of HCHO concentration. Reaction conditions: catalyst, 10 mg; reactant solution, 5.0 cm^3; light source, Xe lamp (λ = 320-780 nm), 300 W; irradiation time, 12 h. The concentration of HCHO was controlled at < 2 mol dm^{-3}.

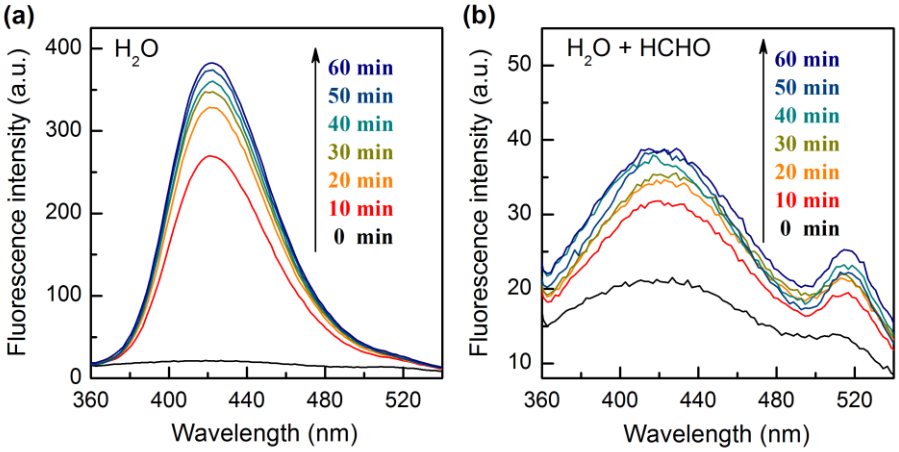

Fig. S4 Photoluminescence spectra for •OH radical detection. (a) In the absence of HCHO. (b) In the presence of 3% HCHO.

For the experiment, 0.10 g $BiVO_4$ was dispersed in a mixed aqueous solution of 0.5 mM terephthalic acid (TA) and 2 mM NaOH. The detailed experimental procedures were similar to those for the photocatalytic activity measurements except that the aqueous HCHO solution was replaced by the aqueous basic terephthalic acid (TA) solution. The fluorescence spectra were recorded on a fluorescence spectrophotometer (Hitachi F-7000, Japan). TA can react with the formed •OH to produce 2-hydroxy-terephthalic acid (TA-OH), which fluoresces at ~425 nm on 315 nm light excitation.[7] Thus, the increase in the fluorescence at ~425 nm with time in Fig. S4a indicates the formation of •OH. The decrease in the intensity of the fluorescence at ~425 nm after the addition of HCHO suggests the consumption of •OH by HCHO through reaction.

Table S1 Photocatalytic performance of $BiVO_4$ catalysts pretreated under different conditions for the conversion of HCHO.[a]

Catalyst[b]	Product concentration (mmol dm^{-3})					Product yield (%)[c]		e^-/h^+
	EG	CH_3CHO	$HOCH_2CHO$	Total C_2	HCOOH	EG	Total C_2	
$BiVO_4$-773A	230	53	130	410	250	3.8	6.7	1.10
$BiVO_4$-973A	180	45	120	350	230	2.9	5.6	0.98
$BiVO_4$-773N	240	60	150	450	310	3.9	7.3	0.97
$BiVO_4$-873N	270	66	170	510	370	4.3	8.2	0.93
$BiVO_4$-923N	300	73	210	580	400	4.9	9.5	0.95
$BiVO_4$-973N	330	79	270	680	450	5.4	11	0.93
$BiVO_4$-1073N	140	30	94	260	180	2.3	4.2	0.94

[a] Reaction conditions: catalyst, 10 mg; reactant solution, HCHO 12.3 mol dm^{-3}, 5.0 cm^3; light source, Xe lamp (λ = 320-780 nm), 300 W; irradiation time, 12 h. The relative error was ±5%. [b] The number denotes the temperature (K), and A or N denotes air or N_2 for pretreatment. [c] The yield was calculated on a molar carbon basis.

Table S2 Specific surface areas, mean sizes and bandgap energies of $BiVO_4$ catalysts pretreated under different conditions.

Catalyst[a]	Surface area (m^2 g^{-1})	Mean size[b] (μm)	Bandgap energy[c] (eV)
$BiVO_4$-773A	1.3	1.8	2.2
$BiVO_4$-973A	0.68	2.5	2.2
$BiVO_4$-773N	1.6	1.7	2.2
$BiVO_4$-873N	1.2	1.9	2.2
$BiVO_4$-923N	0.88	2.2	2.2
$BiVO_4$-973N	0.74	2.4	2.2
$BiVO_4$-1073N	0.18	6.0	2.2

[a] The number denotes the temperature (K), and A or N denotes air or N_2 for pretreatment. [b] The mean size was calculated from SEM micrographs by counting 50-100 particles. [c] The bandgap energy was calculated from the diffuse-reflectance UV-vis spectra.

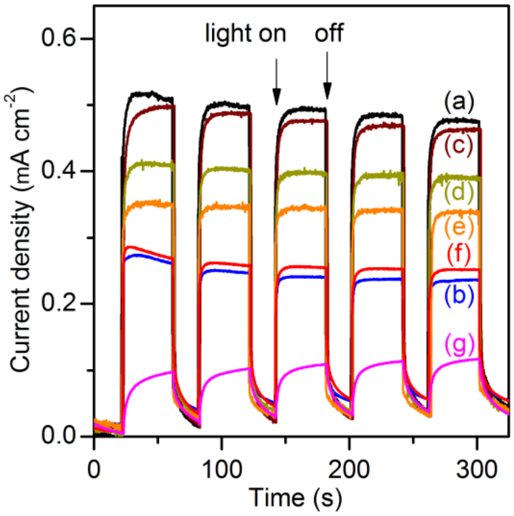

Fig. S5 Transient photocurrent responses for $BiVO_4$ catalysts pretreated under different conditions. (a) $BiVO_4$-773A. (b) $BiVO_4$-973A. (c) $BiVO_4$-773N. (d) $BiVO_4$-873N. (e) $BiVO_4$-923N. (f) $BiVO_4$-973N. (g) $BiVO_4$-1073N. In the sample name, the number denotes the temperature (K), and A or N denotes air or N_2 for pretreatment.

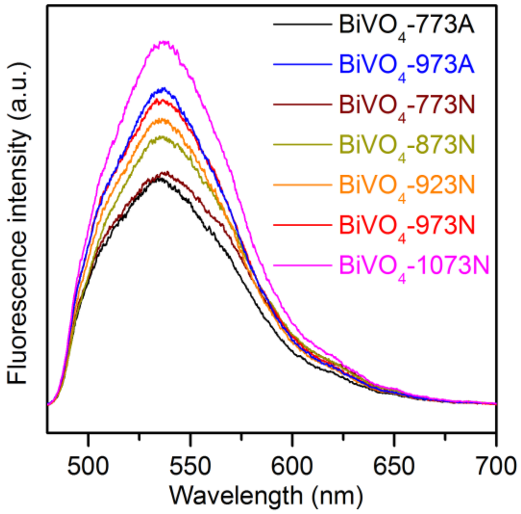

Fig. S6 Photoluminescence emission spectra under 325 nm excitation for $BiVO_4$ catalysts with different pretreatments. In the sample name, the number denotes the temperature (K), and A or N denotes air or N_2 for pretreatment.

The emission peak of the luminescence band was observed at ~535 nm, which was caused by the recombination of photogenerated electron-hole pairs. The intensity decreased in the order of $BiVO_4$-1073N > $BiVO_4$-973A > $BiVO_4$-973N > $BiVO_4$-923N > $BiVO_4$-873N > $BiVO_4$-773N > $BiVO_4$-773A. The higher intensity of the emission peak indicates the higher probability of recombination of the photogenerated electron-hole pairs. Thus, the result here agrees well with that from the transient photocurrent response measurements (Fig. S5).

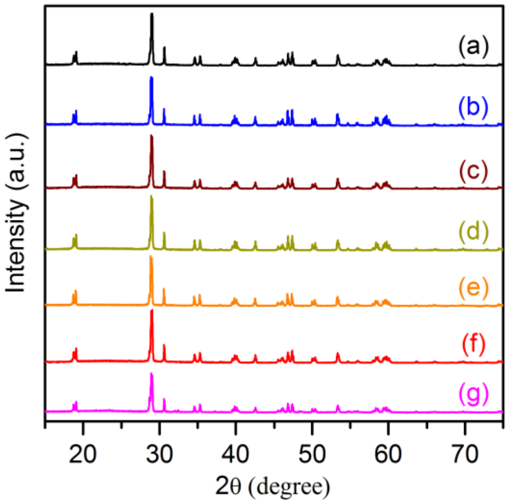

Fig. S7 XRD patterns of $BiVO_4$ samples synthesized under different calcination temperature and atmosphere. (a) $BiVO_4$-773A. (b) $BiVO_4$-973A. (c) $BiVO_4$-773N. (d) $BiVO_4$-873N. (e) $BiVO_4$-923N. (f) $BiVO_4$-973N. (g) $BiVO_4$-1073N. In the sample name, the number denotes the temperature (K), and A or N denotes air or N_2 for pretreatment.

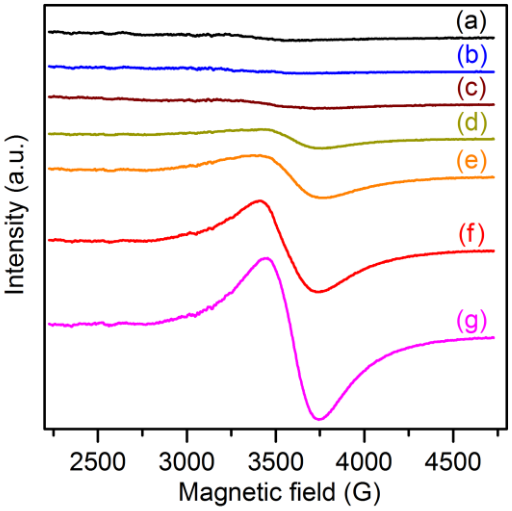

Fig. S8 ESR spectra for $BiVO_4$ samples synthesized under different calcination temperature and atmosphere. (a) $BiVO_4$-773A. (b) $BiVO_4$-973A. (c) $BiVO_4$-773N. (d) $BiVO_4$-873N. (e) $BiVO_4$-923N. (f) $BiVO_4$-973N. (g) $BiVO_4$-1073N. In the sample name, the number denotes the temperature (K), and A or N denotes air or N_2 for pretreatment.

ESR measurements were carried out at room temperature. It is known that V^{5+} in $BiVO_4$ with electronic configuration of $[Ar]3d^04s^0$ is ESR silent. Bi^{3+} ($[Xe]4f^{14}5d^86s^26p^0$) and O^{2-} ($1s^22s^22p^6$) are also ESR silent. The ESR signal observed at $g = 1.96$ can be ascribed to paramagnetic V^{4+}.[5]

Table S3 The number of spins and molar fraction of V^{4+} in $BiVO_4$ catalysts pretreated under different conditions.

Catalyst[a]	**V^{4+} (× 10^{18} spins g^{-1})**	**V^{4+} molar fraction (%)**
$BiVO_4$-773A	0.11	0.0059
$BiVO_4$-973A	0.12	0.0065
$BiVO_4$-773N	0.14	0.0076
$BiVO_4$-873N	1.7	0.090
$BiVO_4$-923N	5.2	0.28
$BiVO_4$-973N	11	0.59
$BiVO_4$-1073N	18	1.0

[a] The number denotes the temperature (K), and A or N denotes air or N_2 for pretreatment.

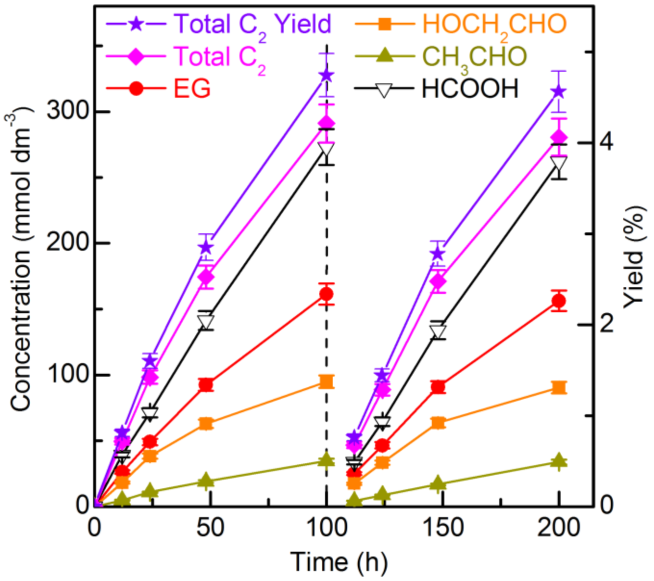

Fig. S9 Photocatalytic conversion of HCHO over the $BiVO_4$ catalyst pretreated at 973 K under N_2 under visible-light irradiation. Reaction conditions: catalyst, 10 mg; reactant solution, HCHO 12.3 mol dm^{-3}, 5.0 cm^3; light source, Xe lamp with λ = 420-780 nm, 300 W.

References

1 S. Yanagida, T. Azuma, H. Kawakami, H. Kizumoto and H. Sakurai, *J. Chem. Soc. Chem. Commun.*, 1984, 21-22.

2 Y. Li, Y. Hu, S. Peng, G. Lu and S. Li, *J. Phys. Chem. C*, 2009, **113**, 9352-9358.

3 M. Hara, T. Kondo, M. Komoda, S. Ikeda, K. Shinohara, A. Tanaka, J. N. Kondo and K. Domen, *Chem. Commun.*, 1998, 357-358.

4 J. Tang, Z. Zou and J. Ye, *Catal. Lett.*, 2004, **92**, 53-56.

5 S. Gupta, N. Khanijo and A. Mansingh, *J. Non-Cryst. Solids*, 1995, **181**, 58-63.

6 A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253-278.

7 T. Hirakawa and Y. Nosaka, *Langmuir*, 2002, **18**, 3247-3254.