

Electronic Supplementary Information for

**Photoelectrochemical dimethoxylation of furan *via* a bromide redox mediator using a  
BiVO<sub>4</sub>/WO<sub>3</sub> photoanode**

Hiroyuki Tateno, Yugo Miseki, Kazuhiro Sayama\*

*Advanced Functional Materials Team, Research Center for Photovoltaics (RCPV), National  
Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi,  
Tsukuba, Ibaraki 305-8565, Japan*

\*To whom the correspondence should be addressed.

E-mail: k. sayama@aist.go.jp

**This PDF file includes:**

Instrumentation

Materials

Experimental procedure

## 1. Instrumentation

Photoelectrochemical measurements were performed using a computer controlled bi-potentiostat (BAS. Inc., ALS Model 660E) and a solar simulator (SAN-EI ELECTRIC CO., Model XES-40S1) calibrated to AM 1.5 (1 sun, 100 mW cm<sup>-2</sup>) using a spectroradiometer (SOMA Optics., Model S-2440).

## 2. Materials

Furan was purified by flash chromatography on silica gel prior to use. All other reagents were purchased from commercial suppliers and used without further purification. Tetraethylammonium tetrafluoroborate (Et<sub>4</sub>NBF<sub>4</sub>) and furan were purchased from Tokyo Chemical Industry. Tetraethylammonium bromide (Et<sub>4</sub>NBr) and silica gel 60 (spherical) were purchased from Kanto Chemical Co. Acetonitrile (super dehydrated) was purchased from Wako Pure Chemical Industries.

## 3. Preparation of Photoelectrodes

The BiVO<sub>4</sub>/WO<sub>3</sub><sup>1</sup>, WO<sub>3</sub><sup>2</sup> and TiO<sub>2</sub><sup>3</sup> photoelectrodes were prepared according to the literature.

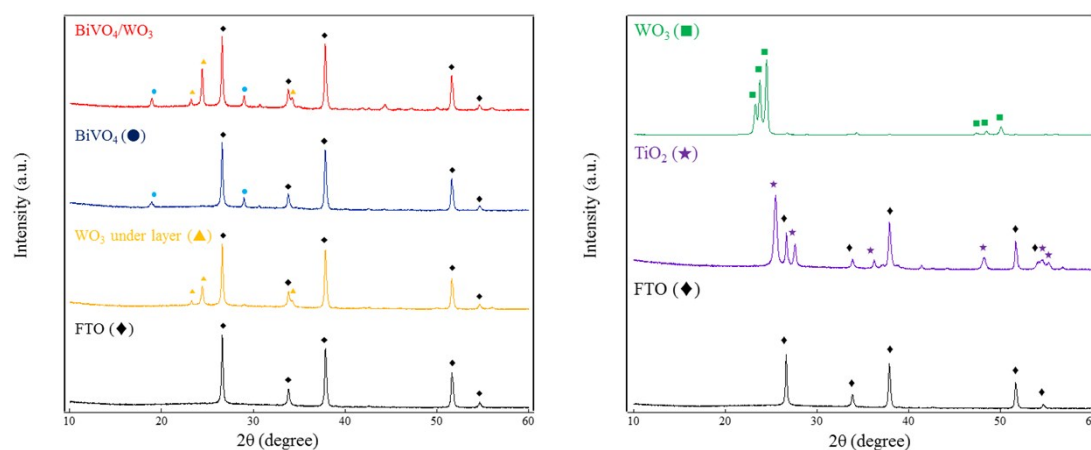
The BiVO<sub>4</sub>/WO<sub>3</sub> photoelectrode was prepared on a F-doped SnO<sub>2</sub> conductive glass (FTO) substrate (Nippon Sheet Glass Co., Ltd.). Tungsten hexachloride (WCl<sub>6</sub>) adjusted to 504 mM was coated onto the FTO by spin coating (1000 rpm, 15 s) before the film was calcined at 500°C for 30 min. The coating of a WO<sub>3</sub> layer was again performed using WCl<sub>6</sub> adjusting to 252 mM, resulting in the formation of a WO<sub>3</sub> underlayer possessing a rough porous surface. A mixed solution (Bi/V = 1:1) of bismuth oxide and vanadium oxide of EMOD (enhanced metal organic decomposition) materials (Synmetrix Co., USA) solved in butyl acetate containing ethylcellulose as a thickener, and an aggregation inhibition agent was coated onto the WO<sub>3</sub> underlayer by spin coating (500 rpm, 15 s). Then, the film was calcined at 550 °C for 30 min to form BiVO<sub>4</sub>/WO<sub>3</sub> photoelectrodes.

Porous WO<sub>3</sub> film was coated onto the FTO substrate by spin coating using an aqueous solution of H<sub>2</sub>WO<sub>4</sub>-containing PEG (average molecular weight = 300; PEG-300). Typically, as aqueous solution of H<sub>2</sub>WO<sub>4</sub>, prepared by passing an aqueous solution of Na<sub>2</sub>WO<sub>4</sub> (0.5 M) through a proton-exchange resin (Dowex 50WX2, 100-200 mesh), was dropped into ethanol (20 mL) to give a neutral pH in the dropped liquid. After PEG-300 (12.5 mL) was added to the aqueous solution, the mixture was evaporated at 65°C until the volume of the mixture was

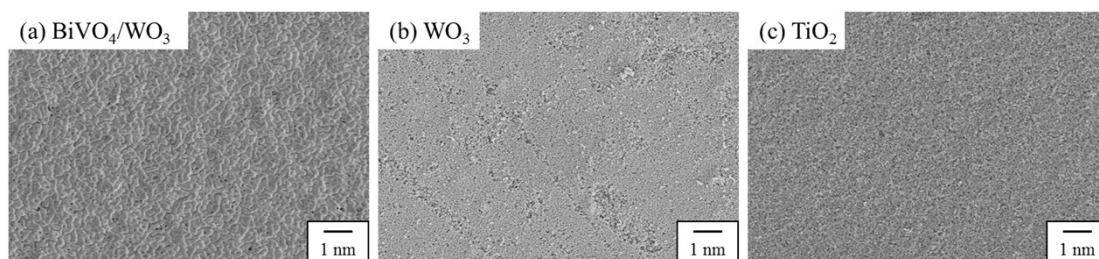
reduced to approximately 13 mL. The solution of  $\text{H}_2\text{WO}_4$ -containing PEG was coated onto the FTO by spin coating (2000 rpm, 15 s) before the film was calcined at  $550^\circ\text{C}$  for 30 min. The coating of a  $\text{WO}_3$  layer was repeated a dozen times, which resulted in the formation of a porous  $\text{WO}_3$  photoelectrode with high photoelectrochemical properties.

A  $\text{TiO}_2$  photoelectrode was prepared by pasting a viscous slurry onto the FTO. A mixture of  $\text{TiO}_2$  powder (P25, 0.3 g), acetylacetone (10  $\mu\text{l}$ ), Triton X (10  $\mu\text{l}$ ) and distilled water (600  $\mu\text{l}$ ) was ground in an agate mortar to prepared the viscous slurry. The slurry was then pasted onto the FTO substrate and calcined at  $500^\circ\text{C}$  for 30 min.

The photoelectrodes were characterized using x-ray fluorescence spectroscopy (XRF, Rigaku, ZSXmini), X-ray diffraction spectroscopy (XRD, PANalytical, Empyrean) and scanning electron microscopy (SEM, Hitachi, Ltd., S-4800). In Figure S1 the XRD spectra of prepared photoelectrodes were confirmed to  $\text{BiVO}_4$  (monoclinic, PDF number: 01-083-1699),  $\text{WO}_3$  (monoclinic, PDF number: 01-083-0950) and  $\text{TiO}_2$  (anatase, PDF number: 01-070-6826; rutile, PDF number: 01-071-4809).



**Figure S1.** The XRD spectra of the (left)  $\text{BiVO}_4/\text{WO}_3$ ,  $\text{BiVO}_4$ ,  $\text{WO}_3$  under layer photoelectrodes and FTO substrate and the (right)  $\text{WO}_3$ ,  $\text{TiO}_2$  photoelectrodes and FTO substrate.



**Figure S2.** The SEM images of the (a) BiVO<sub>4</sub>/WO<sub>3</sub>, (b) WO<sub>3</sub> and (c) TiO<sub>2</sub> photoelectrode

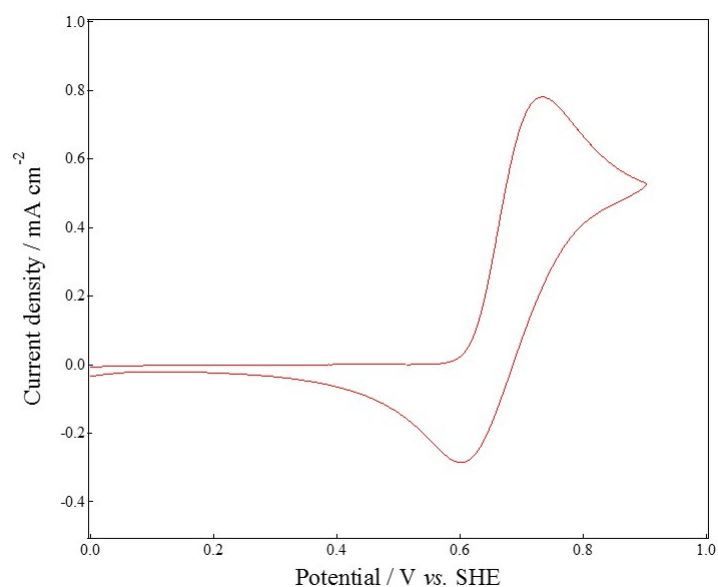
**Table S1.** The XRF analysis on the BiVO<sub>4</sub>/WO<sub>3</sub>, WO<sub>3</sub> and TiO<sub>2</sub> photoelectrodes

|                                    | / $\mu\text{mol cm}^{-2}$ |       |      |    |      |
|------------------------------------|---------------------------|-------|------|----|------|
|                                    | Bi                        | V     | W    | Ti | Sn   |
| BiVO <sub>4</sub> /WO <sub>3</sub> | 0.043                     | 0.051 | 0.41 |    | 2.5  |
| WO <sub>3</sub>                    |                           |       | 4.4  |    | 0.34 |
| TiO <sub>2</sub>                   |                           |       |      | 14 | 2.2  |

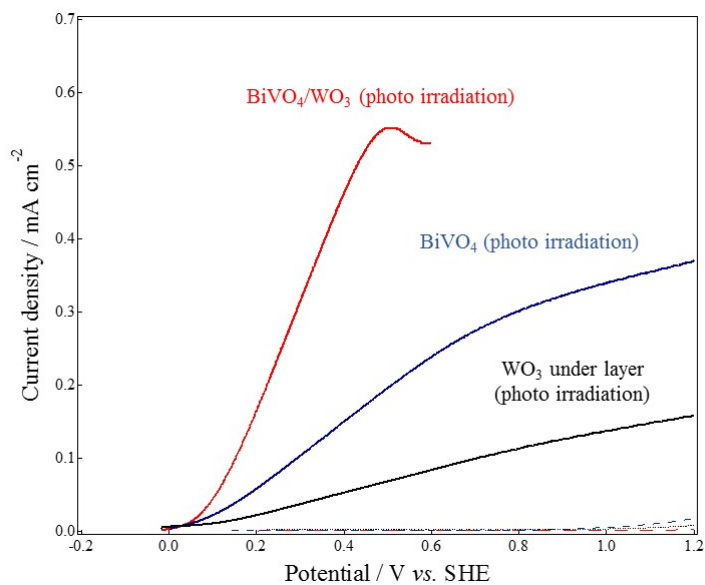
#### 4. Electrochemical Measurement

Linear sweep voltammograms were measured with a three-electrode system using a BiVO<sub>4</sub>/WO<sub>3</sub> photoelectrode (working electrode,  $2 \times 2.5 \text{ cm}^2$ ), FTO plate ( $2 \times 2.5 \text{ cm}^2$ ), Pt disk electrode ( $\varphi = 1.6 \text{ mm}$ ), a Pt wire (counter electrode) and a Ag wire (quasi-reference electrode). The ferrocene/ferrocenium couple (Fc/Fc<sup>+</sup>) was used as an internal reference standard for all electrochemical studies and the potential are reported with respect to the redox potential of Fc/Fc<sup>+</sup>.

The cyclic voltammograms of 10 mM Et<sub>4</sub>NBr and 90 mM Et<sub>4</sub>NBF<sub>4</sub> in MeCN (15 mL) was measured with a Pt disk electrode ( $\varphi = 1.6 \text{ mm}$ ), Pt wire (counter electrode), and Ag wire (quasi-reference electrode) to determine the redox potential of Br<sup>+</sup>/Br<sup>-</sup>. The redox potential of Br<sup>+</sup>/Br<sup>-</sup> was estimated +0.7 eV vs. SHE from Figure S3.



**Figure S3.** Linear sweep voltammogram of 10 mM Et<sub>4</sub>NBr and 90 mM Et<sub>4</sub>NBF<sub>4</sub> in MeCN (15 mL) using a Pt disk electrode.



**Figure S4.** Linear sweep voltammograms of 10 mM Et<sub>4</sub>NBr and 90 mM Et<sub>4</sub>NBF<sub>4</sub> in MeCN (15 mL) using the (red) BiVO<sub>4</sub>/WO<sub>3</sub>, (blue) BiVO<sub>4</sub> and (black) WO<sub>3</sub> under layer photoelectrodes in the (dashed line) dark and (solid line) photo irradiation.

## 5. General Procedure for Photoelectrochemical Dimethoxylation of Furan Using Photoelectrodes

Constant potential photoelectrolysis was conducted using a bi-potentiostat (BAS. Inc., ALS Model 660E). Photoelectrochemical dimethoxylation of furan (11 mmol, 0.7 M) to 2,5-dimethoxytetrahydrofuran was performed at the BiVO<sub>4</sub>/WO<sub>3</sub>, WO<sub>3</sub> and TiO<sub>2</sub> photoanodes (working electrode, 2 × 2.5 cm<sup>2</sup>), Pt wire cathode (counter electrode) and Ag wire (quasi-reference electrode) in 90 mM Et<sub>4</sub>NBF<sub>4</sub> and 10 mM Et<sub>4</sub>NBr electrolyte solution (MeOH/MeCN = 1/9, 15 mL). Photoelectrolysis was conducted in constant potential mode (0.1 or 0.5 V *vs.* SHE) under mechanical stirring with a rotating magnet bar. After the photoelectrolysis, the reaction mixture (200 µl) was poured into H<sub>2</sub>O (1 mL) and then extracted with diethyl ether (2 mL). The organic phase was analysed by gas chromatography (Shimazu, GC-2014) using biphenyl as an internal standard to determine the current efficiency of the methoxylated product.

The turn over number was defined moles of methoxylated product per moles of BiVO<sub>4</sub>.

## 6. General Procedure for Photoelectrochemical Dimethoxylation of Furan in Various Concentration of Et<sub>4</sub>NBr Electrolyte Solutions

Photoelectrochemical dimethoxylation was conducted in constant potential mode (0.1 or 0.5 V *vs.* SHE) using a one-compartment cell with a BiVO<sub>4</sub>/WO<sub>3</sub> photoanode (working electrode, 2.5 × 2 cm<sup>2</sup>), Pt wire (counter electrode), and Ag wire (quasi-reference electrode). The electrolyte was consisted of furan (11 mmol, 0.7 M) Et<sub>4</sub>NBr and Et<sub>4</sub>NBF<sub>4</sub> (total concentration of supporting electrolyte was 100 mM) in MeCN/MeOH (1/9, 15 mL). The workup procedure and analysis of the product were the same as described above. Table S2 shows that the photoelectrochemical dimethoxylation of furan in the Et<sub>4</sub>NBr concentration range of 1-100 mM at 0.1 V *vs.* SHE. Similar trend of the result of the dimethoxylation reaction at 0.5 V *vs.* SHE was obtained. These results suggest that the effect of the supporting electrolytes was not depended on the applied bias.

**Table S2.** Photoelectrochemical dimethoxylation of furan in the Et<sub>4</sub>NBr concentration range of 1-100 mM at 0.1 V vs. SHE<sup>a</sup>

$$\text{Furan} \xrightarrow[-4\text{H}^+]{-2\text{e}, 2\text{MeOH}} \text{2,5-dimethoxyfuran}$$

| Entry | Ratio of Et <sub>4</sub> NBr/Et <sub>4</sub> NBF <sub>4</sub> | Faradaic efficiency <sup>b</sup> (%) |
|-------|---|--------------------------------------|
| 1     | 0/100   | < 1                                  |
| 2     | 10/90   | > 99                                 |
| 3     | 50/50   | 70                                   |
| 4     | 100/0   | 56                                   |

Substrate concentration: 0.7 M (11 mmol); volume of MeCN: 15 ml; supporting electrolyte: Et<sub>4</sub>NBr + Et<sub>4</sub>NBF<sub>4</sub> (total concentration of supporting electrolyte was 100 mM); working electrode: BiVO<sub>4</sub>/WO<sub>3</sub> photoanodes; counter electrode: Pt wire; quasi-reference electrode: Ag wire; cell type: one-compartment cell; light source: solar simulator (calibrated to AM 1.5, 100 mW cm<sup>-2</sup>).

<sup>a</sup> Constant potential electrolysis, electricity: 5 C.

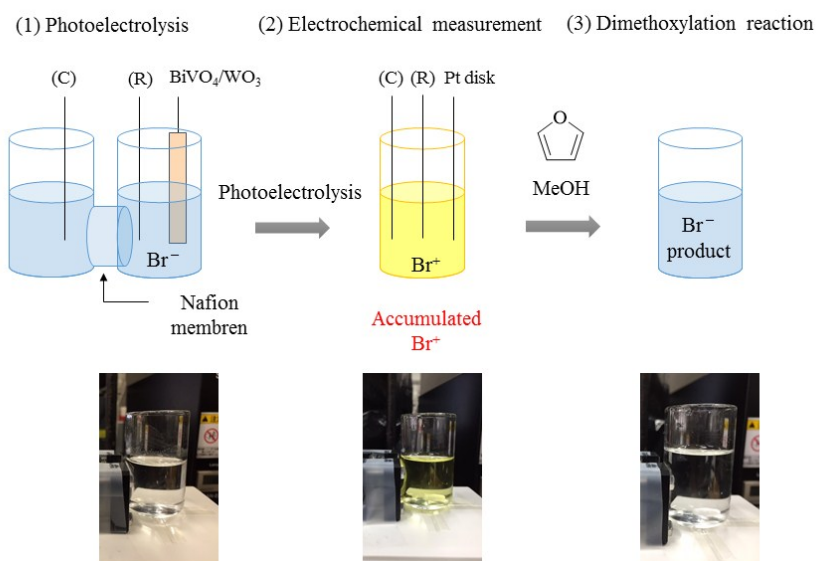
<sup>b</sup> Determined by GC using biphenyl as an internal standard.

## 7. General Procedure for Accumulation of Br<sup>+</sup> species

As shown in Figure S5, photoelectrolysis was conducted in constant potential mode (0.5 V vs. SHE) using a divided two-compartment cell with a BiVO<sub>4</sub>/WO<sub>3</sub> photoanode (working electrode, 2.5 × 2 cm<sup>2</sup>), Pt wire (counter electrode), and Ag wire (quasi-reference electrode). The anolyte and catholyte each consisted of 90 mM Et<sub>4</sub>NBF<sub>4</sub> and 10 mM Et<sub>4</sub>NBr/MeCN (15 mL). The anode and cathode compartments were separated by Nafion membrane (Aldrich, Nafion NRE-212). After charge was passed (5 C), the anolyte changed from colorless to yellow and linear sweep voltammogram of anolyte was measured to detect the generated Br<sup>+</sup> with a Pt disk electrode ( $\varphi$  = 1.6 mm), Pt wire (counter electrode), and Ag wire (quasi-reference electrode). The anolyte was then returned from colorless to yellow by the additional of furan (0.8 mL) and MeOH (2.2 mL). The workup procedure and analysis of the product were the same as described above.

## 8. General Procedure for Preparative Scale of Photoelectrochemical Dimethoxylation of Furan Using Photoelectrodes

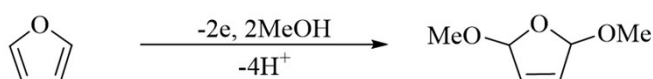
Photoelectrolysis was conducted in constant potential mode (0.5 V vs. SHE) using a divided two-compartment cell (Figure S5) with a BiVO<sub>4</sub>/WO<sub>3</sub>, WO<sub>3</sub>, TiO<sub>2</sub> photoanodes (working electrode, 2.5 × 2 cm<sup>2</sup>), Pt wire (counter electrode), and Ag wire (quasi-reference electrode). The anolyte and catholyte each consisted of 90 mM Et<sub>4</sub>NBF<sub>4</sub> and 10 mM Et<sub>4</sub>NBr/MeCN (15 mL). The anode and cathode compartments were separated by Nafion membrane (Aldrich, Nafion NRE-212). After charge was passed (5 C), the accumulated Br<sup>+</sup> was detected by cyclic voltammetry using Pt disk electrode and 16 mM furan/MeOH (1 mL) was added to anolyte. The workup procedure and analysis of the product were the same as described above. The faradaic efficiencies for dimethoxylation reaction of furan using various photoelectrode in two-step procedure were shown in Table S3.



**Figure S5.** Photoelectrochemical accumulation of Br<sup>+</sup> and its reaction with furan and MeOH.



**Table S3.** Photoelectrochemical accumulation of Br<sup>+</sup> and its reaction with furan and MeOH using various photoelectrodes in a two-step procedure



| Entry | Photoelectrode                     | Faradaic efficiency <sup>b</sup> (%) |
|-------|------------------------------------|--------------------------------------|
| 1     | BiVO <sub>4</sub> /WO <sub>3</sub> | 84                                   |
| 2     | WO <sub>3</sub>                    | 43                                   |
| 3     | TiO <sub>2</sub>                   | 16                                   |

Volume of MeCN: 15 ml; supporting electrolyte: 10 mM Et<sub>4</sub>NBr and 90 mM Et<sub>4</sub>NBF<sub>4</sub>; working electrode: BiVO<sub>4</sub>/WO<sub>3</sub>, WO<sub>3</sub> and TiO<sub>2</sub> photoanodes; counter electrode: Pt wire; quasi-reference electrode: Ag wire; cell type: two-compartment divided cell; light source: solar simulator (calibrated to AM 1.5, 100 mW cm<sup>-2</sup>).

<sup>a</sup> Constant potential electrolysis, electricity: 5 C.

<sup>b</sup> Determined by GC using biphenyl as an internal standard.

## 9. Reference

1. K. Fuku and K. Sayama, *Chem. Commun.*, 2016, **52**, 5406-5409.
2. B. D. Alexander, P. J. Kulesza, I. Rutkowska, R. Solarska and J. Augustynski, *J. Mater. Chem.*, 2008, **18**, 2298-2303.
3. K. Maeda, *Chem. Lett.*, 2015, **44**, 934-936.