Electronic Supplementary Material (ESI) for ChemComm.

Visible-light-induced water oxidation by a hybrid photocatalyst consisting of bismuth vanadate and copper(II) meso-tetra(4-carboxyphenyl)porphyrin

Shu Nakashima, Ryo Negishi, and Hiroaki Tada *

Department of Applied Chemistry, School of Science and Engineering, Kinki University, 3-4-1, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

* To whom correspondence should be addressed: TEL: +81-6-6721-2332, FAX: +81-6-6727-2024,

E-mail: h-tada@apch.kindai.ac.jp.

Experimental details

Synthesis of monoclinic sheelite $BiVO_4$ particles

$Bi(NO_3)_3 \cdot 5H_2O$ (0.1 mol) was dissolved into an aqueous solution of HNO_3 (13.1M HNO_3 100 mL + distilled water 400 mL) by stirring in an egg-plant flask. To the solution, NH_4VO_3 (0.1 mol) was added with stirring, and then, urea was added with stirring continued for 5 min. The resulting solution was heated at 80°C for 8 h. After the reaction, the solids were separated by centrifugation, and sufficiently washed with distilled water and dried in a vacuum desiccator. Further, the solids were heated in the air at 400°C for 1 h.

Preparation of the $BiVO_4$-based photoanodes

$BiVO_4$ photoanode. $Bi(NO_3)_3 \cdot 5H_2O$ (1 mmol) and NH_4VO_3 (1 mmol) were added to two mL of 13.1 mol dm^{-3} HNO_3 placed in an agate mortar, and mixed. To the solution, polyethylene glycol (Mw = 20000, 4 g) was added step by step. After mixing sufficiently, one drop of Triton-X was added. The resulting paste was coated on FTO electrode by the doctor blade technique, and then, the sample was heated at 400°C for 4 h.

$Cu^{2+}/BiVO_4$ photoanode. $Cu(OAc)_2 \cdot H_2O$(2.5 mg, 0.0125 mmol) was dissolved into DMF to yield a 50 mL of 0.25 m ol dm^{-3} solution. The $BiVO_4$–film coated FTO substrate was immersed into the solution, being allowed to stand for 24 h at 25°C h in the dark. The sample was washed with DMF, and then dried in a vacuum desiccator for 24 h ($Cu^{2+}/BiVO_4$).

TCPP/$BiVO_4$ and CuTCPP/$BiVO_4$ photoanodes. TCPP(9.885 mg, 0.0125 mmol) was dissolved in DMF, and 50 mL of 0.25 mmol dm^{-3} TCPP solution was prepared. The $BiVO_4$–film coated FTO substrate was immersed into the solution, being allowed to stand for 24 h at 25°C h in the dark. The sample was washed with DMF, and then dried in a vacuum desiccator for 24 h (TCPP/$BiVO_4$). $Cu(OAc)_2 \cdot H_2O$(2.5 mg, 0.0125 mmol) was dissolved into DMF to yield a 50 mL of 0.25 m ol dm^{-3} solution. The TCPP/$BiVO_4$ was immersed into the solution, being allowed to stand for 24 h at 25°C in the dark. Then, sample was washed with DMF, and then dried in a vacuum desiccator for 24 h (CuTCPP/$BiVO_4$).

Adsorption experiments

$BiVO_4$ particles (0.5 g) was added to 10 mL of DMF solutions of TCPP with varying concentrations (0.0125 ~ 0.125 mmol dm^{-3}), and allowed to stand for 24 h at 25°C in the dark. The solutions before and after adsorption was 100 times diluted with DMF, and the UV-visible absorption spectra were measured by a Hitachi U-1800 spectrometer. The adsorption amount of TCPP was calculated from the difference in the absorbance at 418 nm.

Characterization

Powder X-Ray diffraction (XRD) measurements for $BiVO_4$ particles and $BiVO_4$ film coated on FTO were performed using Rigaku SmartLab9KW with the CuKa X-ray

radiation (0.15418 nm). To identify the synthesized solids, X-ray diffraction (XRD) measurements were carried out (Fig. S1 in ESI). In the XRD pattern, sharp peaks are present at 2θ = 18.7º, 29.0º, and 31.0º, which are assignable to the diffraction from the (110), (112), and (200) crystal planes of monoclinic sheelite (*ms*)-$BiVO_4$ (ICDD No. 00-014-0688), respectively.

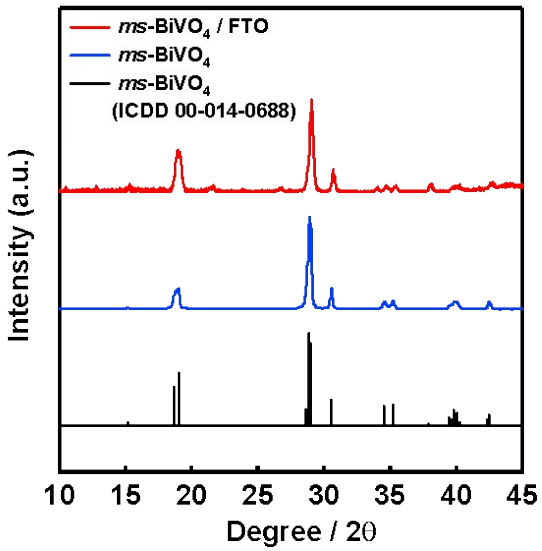

Fig. S1. XRD patterns of the samples (red and blue) and $BiVO_4$ for comparison (black).

The specific surface area was determined by nitrogen adsorption-desorption isotherms at 77 K with a micromeritics automatic surface area and porosimetry analyzer (TriStar 3000, Shimadzu). Prior to the nitrogen adsorption, all samples were degassed at 423 K for 1 h under vacuum.

Diffuse reflectance UV-visible spectra for $BiVO_4$, TCPP/$BiVO_4$, and CuTCPP/$BiVO_4$ were recorded on a Hitachi U-4000 spectrometer mounted with an integrating sphere at room temperature. The reflectance (R_∞) was recorded with respect to a reference of $BaSO_4$, and the Kubelka-Munk function ($F(R_\infty)$) expressing the relative absorption coefficient was calculated by the equation of $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$.

Diffuse reflectance Fourier transform infrared (DRIFT) spectra for $BiVO_4$, TCPP/$BiVO_4$, and CuTCPP/$BiVO_4$ were measured in the range from 4000 to 400 cm^{-1} using a FT/IR-4100 (JASCO) with an integrating sphere attached (resolution = 4 cm^{-1}, scan number = 512). Spectroscopic grade KBr (Wako) was used as a reference.

X-ray photoelectron spectroscopic (XPS) measurements were performed using a Kratos Axis Nova X-ray photoelectron spectrometer with a monochromated Al K_α X-ray source ($h\nu$ = 1486.6 eV) operated at 15 kV and 10 mA. The take-off angle was 90º, and spectra were obtained for Cu_{2p} photopeaks. All the binding energies were referenced with respect to the C_{1s} at 284.6 eV.

Photoelectrochemical water oxidation

$BiVO_4$, $Cu^{2+}/BiVO_4$, TCPP/$BiVO_4$, and CuTCPP/$BiVO_4$ were used as the photoanodes for PEC cells. Three electrode PEC cells with a structure of the photoanode | 0.1 mol dm^{-3} $NaClO_4$ aqueous solution | Ag/AgCl (reference electrode) | glassy carbon (cathode) were fabricated. The apparent active area of the photoanode was 2.0 × 2.0 cm^2. Prior to the measurements, the dissolved O_2 was removed by argon bubbling for 1 h. Under illumination at one sun (AM 1.5, 100 mW cm^{-2}) by a solar simulator (PEC-L10, Peccell technologies, Inc.) with a cut off filter Y-45 (λ > 430 nm, AGC TECHNO GLASS), the current density J (μA cm^{-2}) was measured under deaerated conditions at the dark rest potential by using a galvanostat/potentiostat (HZ-5000, Hokuto Denko). The incident photon-to-current efficiency (IPCE) was calculated by the following equation as the function of light wavelength (λ): IPCE(%) = ($JN_Ahc/IF\lambda$) × 100, where I is the light intensity at λ (W cm^{-2}), F is the Faraday constant, and c is the speed of light.

The concentration of oxygen (O_2) in the water phase during the irradiation was measured by a dissolved O_2 meter (SG-6, Mettler Toledo) in the system.

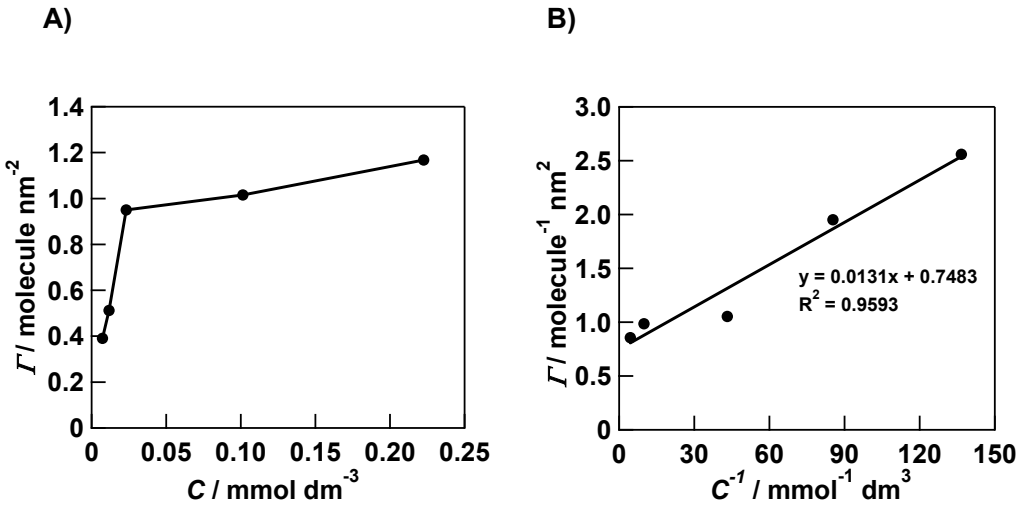

Fig. S2. (A) Adsorption isotherm of TCPP on $BiVO_4$ at 298 K. (B) Langmuir plot for the adsorption of TCPP on $BiVO_4$.

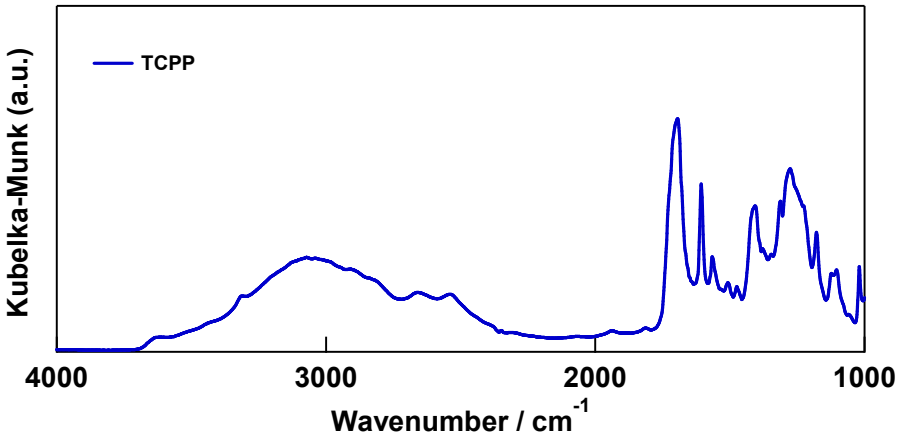

Fig. S3. FT-IR spectrum of TCPP.

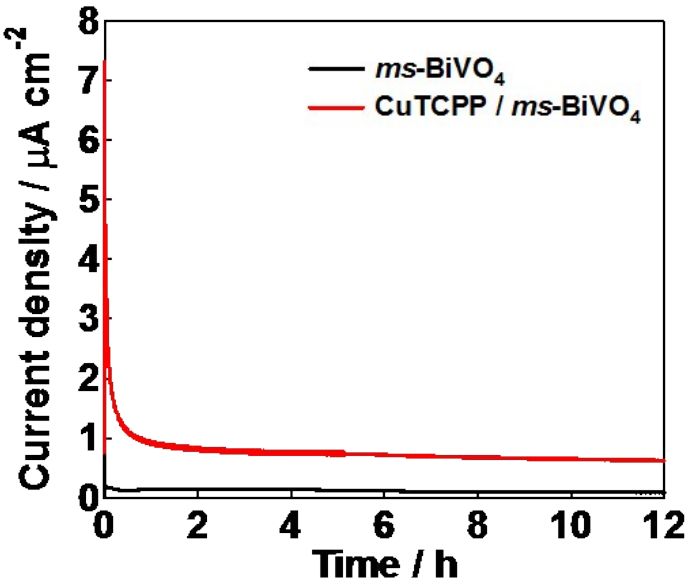

Fig. S4. Time courses for the photocurrents for the $BiVO_4$ and CuTCPP/$BiVO_4$ electrodes.

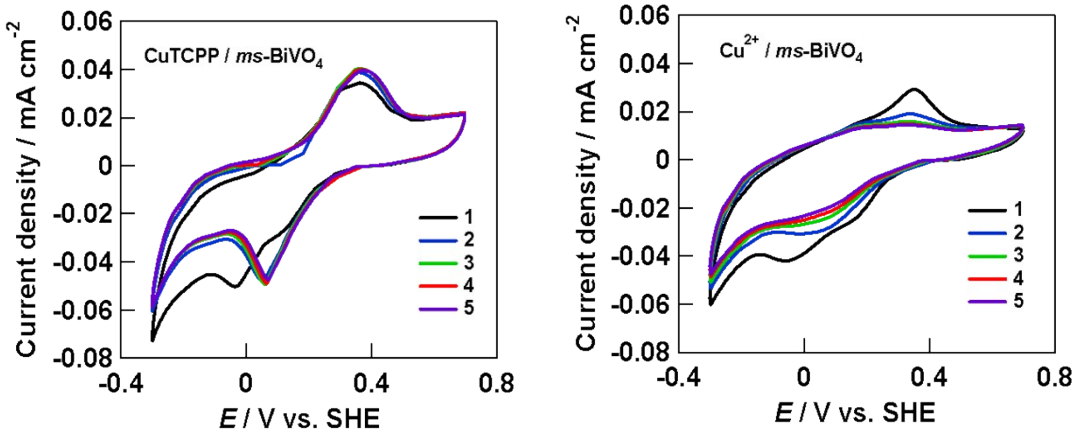

Fig. S5. CV cycles for the CuTCPP/$BiVO_4$ electrode (left) and the Cu^{2+}/$BiVO_4$ electrode (right).