

Supporting Information

Polarized liquid-liquid interface meets visible-light-driven catalytic water oxidation

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ESI-1 Synthesis of [Co(bpy)₃](PF₆)₂ and [Co(bpy)₃](PF₆)₃

The cobalt complex, [Co(bpy)₃](PF₆)₂, and its oxidized form [Co(bpy)₃](PF₆)₃ were prepared according to the reported procedure.^{1,2} A mixture of CoCl₂·6H₂O (1.0 g, 4.12 mmol, 98% Aldrich) and 2,2-bipyridyl (2.2 g, 13.94 mmol, >99% Aldrich) were dissolved in methanol (100 mL) and refluxed for 2 h. After the resulting solution was cooled to room temperature, ammonium hexafluorophosphate (3.4 g, 20.86 mmol, 99.99% Aldrich) was added to the reaction mixture. The precipitate was washed with methanol and ethanol and dried under vacuum to obtain [Co(bpy)₃](PF₆)₂ (3.1 g, 92% yield) as yellow solid. Additional oxidation of [Co(bpy)₃](PF₆)₂ (500 mg, 0.612 mmol) was carried out by using NOBF₄ (107 mg, 0.916 mmol, 95% Aldrich) in acetonitrile (15 mL) at room temperature for 0.5 h. After removal of the solvent under reduced pressure (using the rotatory evaporator), the residue was dissolved in acetonitrile (5 mL) and NH₄PF₆ (502 mg, 3.08 mmol, 99.99% Aldrich) was added to the solution. [Co(bpy)₃](PF₆)₃ (530 mg) was precipitated with diethyl ether, filtrated, dried under vacuum and used without further purification.

ESI-2 Electrochemical characterization of [Co(bpy)₃](PF₆)₂ and [Co(bpy)₃](PF₆)₃

The electrochemical characterizations of the synthesized [Co(bpy)₃](PF₆)₂ and [Co(bpy)₃](PF₆)₃ were performed by recording the steady state cyclic voltammograms using the monopotentiostat μ -P3 (M. Schramm, Heinrich Heine University, Düsseldorf, Germany) in a three-electrode setup comprised of an Au microelectrode (Au ME, radius $r_T = 12.5 \mu\text{m}$) working electrode, an Ag quasi reference electrode and a Pt wire counter electrode (Figure S1). [Co(bpy)₃]²⁺ and [Co(bpy)₃]³⁺ were oxidized and reduced clearly with a half-wave potential of ca. 0.45 V vs. Ag (in 0.05 M TBAPF₆).

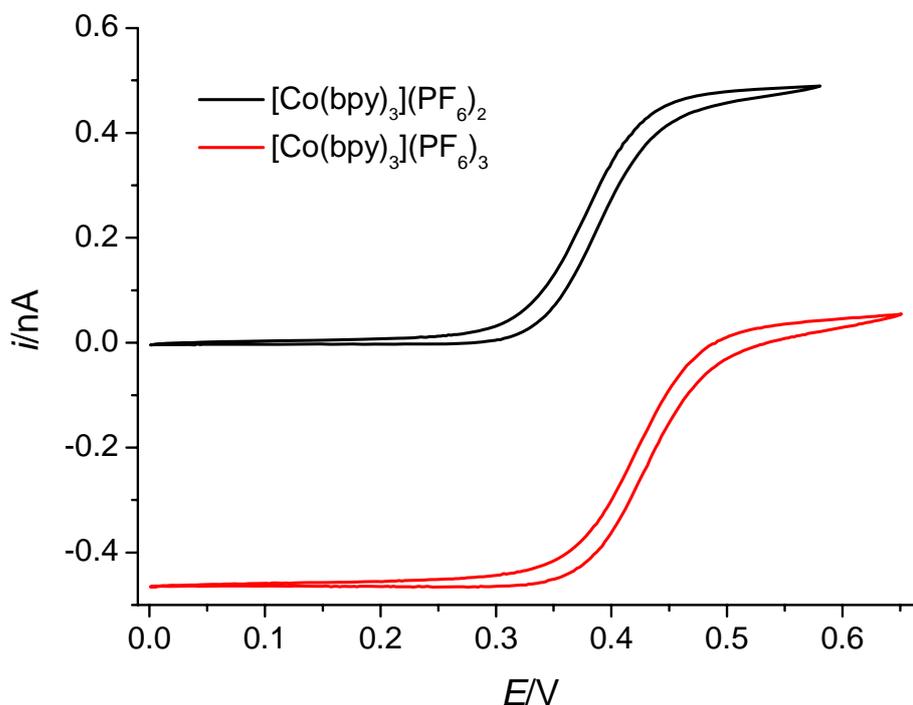


Figure S1. Cyclic voltammograms of [Co(bpy)₃]²⁺ oxidation (black solid line) and [Co(bpy)₃]³⁺ reduction (red solid line) in butyronitrile solution contained 0.5 mM the Co complexes and 0.05 M TBAPF₆ supporting electrolyte at a Au ME ($r_T = 12.5 \mu\text{m}$). Scan rates v was 10 mV s^{-1} .

ESI-3 Synthesis of nanocrystalline BiVO₄

BiVO₄ with a hyperbranched structure was synthesized by a hydrothermal procedure without the assistance of surfactants as published recently.^{3, 4} The benefits of this method are the relatively low temperature required, environmentally friendly reaction conditions, and controllable morphology and size distribution. In details, Bi(NO₃)₃ · 5 H₂O (1 mmol, 0.485 g) was dissolved in 20 mL of 1 M HNO₃ by stirring for 30 min at room temperature. An alkaline solution of NH₄VO₃ was prepared by dissolving 0.117g (1 mmol) of NH₄VO₃ in 20 mL of 0.5 M NaOH under stirring for 30 min at room temperature. The NH₄VO₄ solution was added dropwise to the Bi(NO₃)₃ solution with stirring to obtain a clear solution of pH 0.3-0.4. Subsequently, the pH was adjusted to 2 with 2 M NaOH to form the precursor. The resultant liquid was transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed and heated to 120 °C for 12 h under autogeneous pressure and allowed to cool to room temperature. The obtained samples were filtered, washed with deionized distilled water followed by absolute ethanol. Finally, the obtained solid samples were dried at 50 °C for 12 h in a hot air oven.

ESI-4 Structural characterization of nanocrystalline BiVO₄

The morphology of hyperbranched structure of the obtained BiVO₄ powders was obtained using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. SEM images of BiVO₄ powders samples (placed on a Cu grid) were measured using a Hitachi S-3200N scanning electron microscope with BSE (Robinson) detector equipped with EDX system (Oxford INCA system with PentaFET Precision INCA X-act). The TEM images were recorded by Joel 2100 F (Gatan Orius SC200D) equipped with Orius SC600 CCD cameras. To prepare the TEM grids, BiVO₄ nanocrystals were diluted in ethanol (by factor of 100) via sonication to form a homogeneous slurry. A drop of the slurry was then casted onto the carbon-coated copper TEM grid (hole or mesh) followed by solvent evaporation in air.

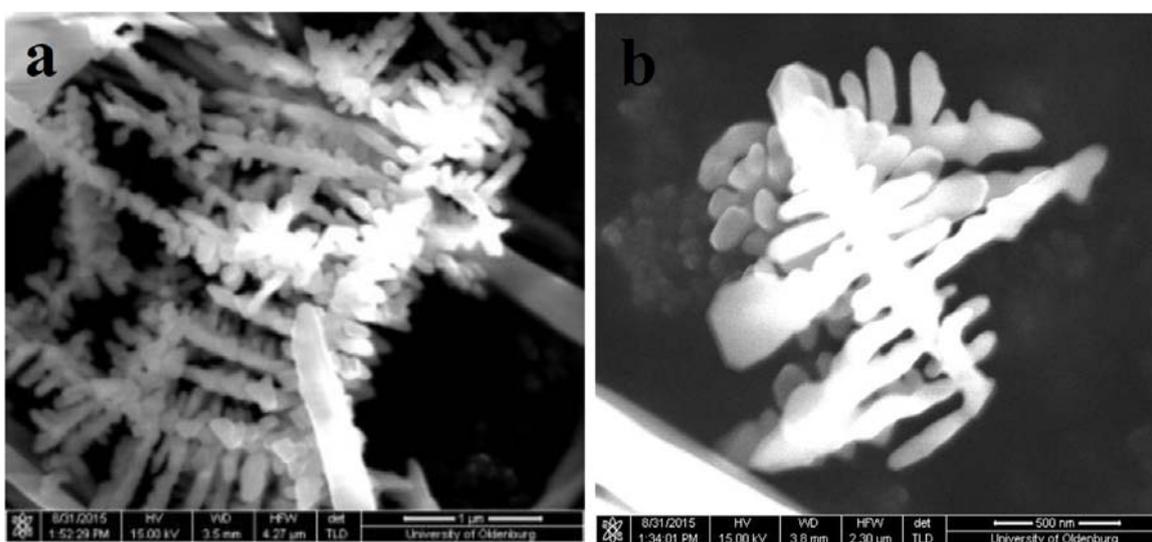


Figure S2. (a) A representative SEM image of the hyperbranched structure of BiVO₄. (b) A magnified SEM image that shows a trunk of an individual hyperbranch crystal of BiVO₄.

Figure S2 shows the SEM images of the synthesized BiVO₄. The SEM image of S2a reveals the hyperbranched morphology of BiVO₄. The images show the trunks of self-assembled nano-scaled branches which distributed symmetrically on opposite sides of the trunk (Figure S2b). The length of the trunks is 500 nm to 4 mm, whereas the length of the branches ranges from 50 to 500 nm. All of the branches have a similar structure and opposing directions of protrusion. It is also worth noting that there are some protuberances, rather than branches, that grow perpendicular to both the trunk and the branches. This hyperbranched structure exhibits excellent photoactivity, ascribed to its loosely packed building units because of firstly, the small crystal size which allows for more efficient transport of the electron-hole pairs generated inside the crystal and, secondly, the large surface area provides plentiful active sites to promote the reaction of adsorbed intermediates.

Also, the TEM images in Figures S3a and S3b confirm the hyperbranched structure of the synthesized BiVO₄ with different resolution. In addition, Figure S4 shows the EDX spectrum of BiVO₄. Only bismuth, vanadium, and oxygen signals were observed (copper and carbon signals arise from the TEM grid and Na is from NaOH solution used for synthesis of BiVO₄), which indicates the high purity of the product. The ratio of Bi:V atoms is approximately 1:1.11, which is consistent with the stoichiometric ratio of BiVO₄.^{3,4}

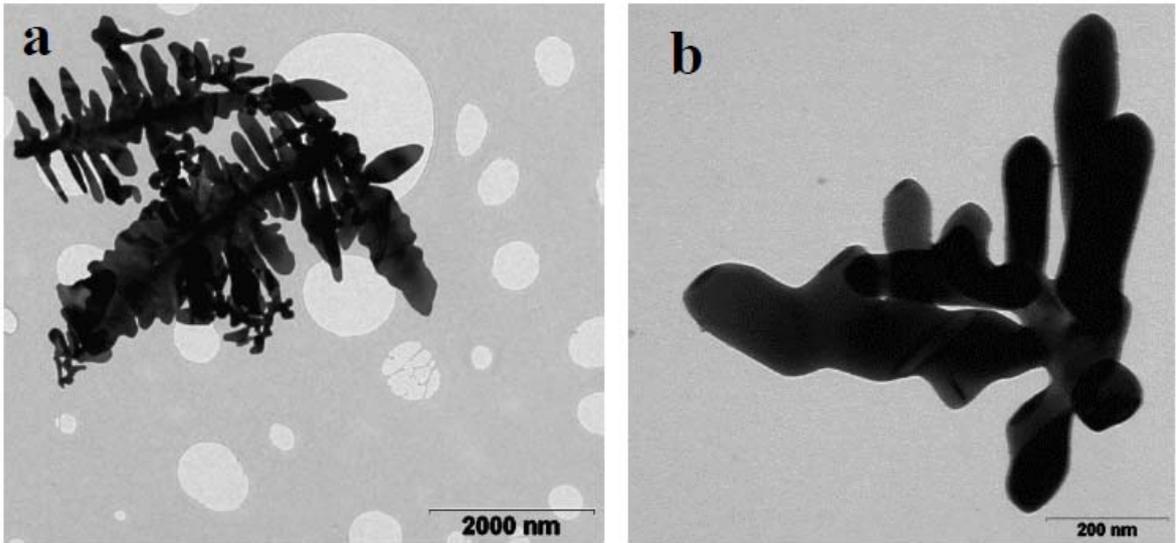


Figure S3. TEM images of the hyperbranch trunks of BiVO_4 with a) 2000 nm and b) 200 nm resolution.

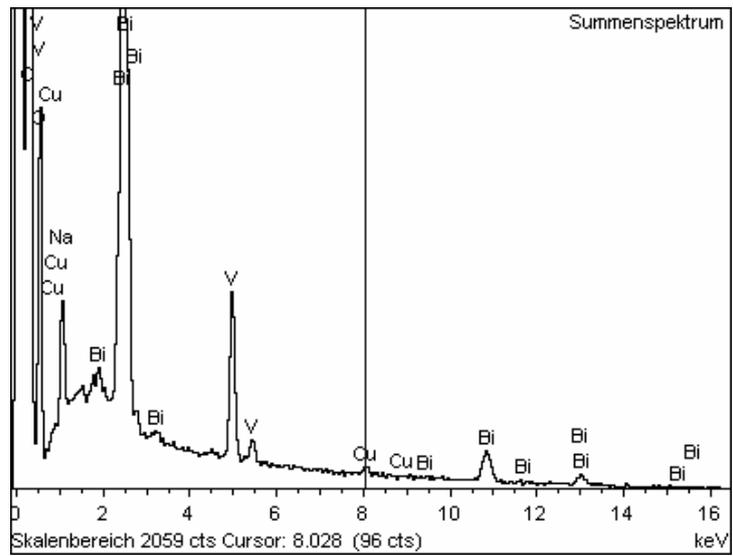


Figure S4. The EDX pattern of BiVO_4

ESI-5 Experimental details for recording the photocurrent transients

The photocurrent transients were obtained by scanning electrochemical microscopy (SECM) utilizing the home-built instrument⁵ operated under SECMx.⁶ A cell for the investigation of liquid-liquid interfaces was used (Figure S5). For all the SECM experiments, a monopotentiostat μ -P3 (M. Schramm, Heinrich Heine University, Düsseldorf, Germany) was used in the three-electrode configuration. An Ag quasi-reference electrode and a Pt wire counter electrode were positioned in the butyronitrile solution and the Au ME working electrode was placed closely to the interface in butyronitrile phase. Positioning was performed with an x - y - z stepper motor system (Scientific Precision Instruments, Oppenheim, Germany). Data were processed and analyzed with the in house software MIRA.⁷

An Au wire (diameter 25 μm , Goodfellow, Cambridge, UK) was sealed into a 1 cm Pyrex glass capillary under vacuum. The ME was polished and shaped conically by a wheel with 180-grid Carbimet paper disks and micropolishing cloths with 1.0 mm, 0.3 mm, and 0.05 mm alumina. The ME was sharpened to $\text{RG} \sim 10$, where RG is the ratio between the diameters of the glass sheath and the Au wire. Before each experiment, the ME was polished with 0.3 and 0.05 mm alumina powder and rinsed with water.

The density of the butyronitrile is $\rho = 0.795 \text{ g/cm}^3$ and of water is $\rho = 1 \text{ g cm}^{-3}$.

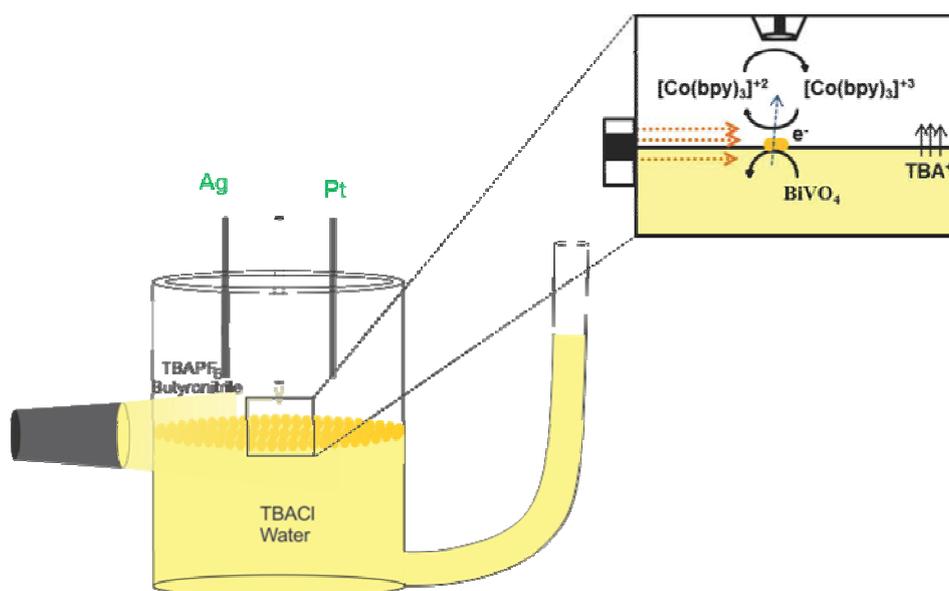


Figure S5. Schematic of the Cell used for the electrochemical experiments at liquid-liquid interface

ESI-6 Photocatalytic water oxidation

Photocatalytic water oxidation reactions were performed in a self-made quartz glass photoreactor with a total volume of 100 mL under irradiation of a 300 W Xe-arc lamp (LOT Oriol) in gas-tight circulation system.⁸⁻¹⁰ The photocatalysis setup with the applied flow through the photoreactor and GC system enables a continuous sampling during the photocatalytic process. Figure S6 shows a flow chart of the self-constructed photoreactor for photocatalytic O₂ production. The setup can be divided into three parts: 1) gas supply, including carrier gas line and calibration gas line, 2) photoreactor including irradiation source and 3) gas chromatograph (GC) as analyzer (Shimadzu GC-2014). The reaction temperature was maintained at 10 °C by a double-walled quartz jacket filled with a flow of cooling water from a thermostat (LAUDA) in order to prevent any thermal catalytic effect. High-purity argon (5.0) with a flow rate of 20 NmL min⁻¹ (controlled by a Bronkhorst mass flow controller) was used as carrier gas for the reaction products.

The GC-column (ShinCarbon ST 100/120, 2 m; Restek) is micro-packed with activated carbon and tempered at 35 °C. The produced gases are transported by the Ar carrier gas flow from the photoreactor gas outlet to the GC. The evolved gases were analyzed online using a multi-channel analyzer (Emerson) equipped with a thermal conductivity detector tempered at 125 °C with a bridge current of 50 mA.

In a typical run, 35 mg photocatalyst powder were dispersed in water (35 mL) with (or without) 0.01 M TBACl and 0.1 M NaCl as supporting electrolytes in the bottom of irradiation cell, whereas butyronitrile solution (35 mL) containing 0.05 M TBAPF₆ with (or without) [Co(bpy)₃](PF₆)₃ as an electron acceptor was added on the top of the aqueous phase. Prior to irradiation, the whole system including the photocatalysts was purged with Ar for 30 min to remove air completely. Afterwards, the photocatalyst settled at the water/butyronitrile interface. The liquid-liquid system was stirred by a magnetic stirrer in order to enlarge the liquid-liquid interface. The biphasic liquid reaction mixture with the photocatalyst at the liquid-liquid interface was irradiated by visible light from a 300-W Xe lamp after passage to a cutoff filter ($\lambda > 420$ nm).

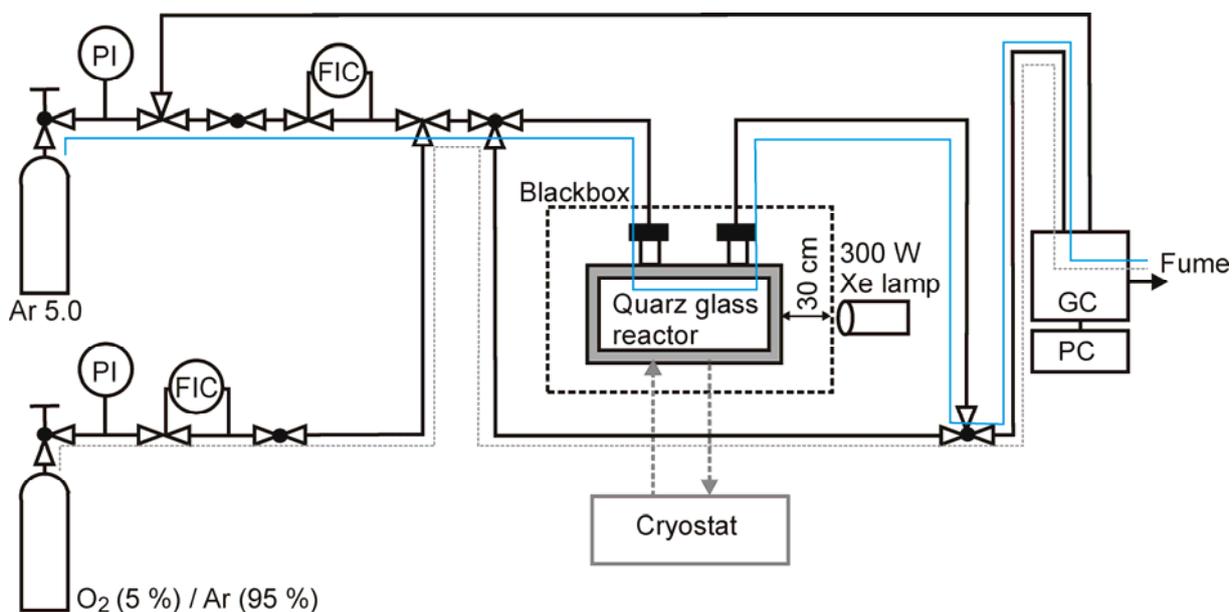


Figure S6: Flow chart of photocatalysis setup for standard performance tests (adapted from Merka¹¹) The blue line indicates the gas flow during the photoreaction. The grey dashed line indicates the flow during the calibration.

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