Supporting Information

Non-noble-metal bismuth nanoparticle-decorated bismuth vanadate nanoarray photoanode for efficient water splitting

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Photoelectrochemical measurement

All electrochemical and photoelectrochemical tests were performed on a typical three-electrode system in 0.5 M sodium sulfate (Na₂SO₄) solution (pH = 6.8) with or without 0.5 M sodium sulfite (Na₂SO₃) as a hole scavenger on a CHI760E electrochemical workstation. The simulated solar illumination was obtained by passing light from a 300 W Xenon arc lamp through an AM 1.5G filter and the light intensity at the surface of the electrode was 100 mW cm⁻². All measurements were carried out using a reference electrode of Ag/AgCl (saturated KCl), a Pt wire counter electrode and the working electrodes of as-obtained samples, all potentials in this work were converted to reversible hydrogen electrode (RHE) for the convenience of comparison with H₂ and O₂ redox levels. The conversion between potential versus Ag/AgCl and *vs*. RHE is obtained using the following equations (S1-2).

$$E(vs. RHE) = E(vs. Ag/AgCl) + E_{Ag/AgCl}(reference) + 0.0591 V \times pH \dots (S1)$$

$$(E_{Ag/AgCl} (reference) = 0.1976 V vs. NHE at 25 °C) \dots (S2)$$

In this work, incident photon-to-current efficiency (IPCE) at each wavelength was determined using illumination from a 300 W Xe arc lamp passed through an AM 1.5G filter to approximate the output of the sun. Monochromatic light was produced using an Omni-X 3007 monochromator and the output was measured with research irradiatometer. IPCE was measured at 1.23 V *vs*. RHE in 0.5 M Na₂SO₄ with the same three-electrode setup described above for photocurrent measurements, where J is the photocurrent density under the irradiation of single wavelength, P_{in} and λ were the incident illumination power density and the wavelength of light, respectively. APCE was obtained by dividing the IPCE by the light harvesting efficiency (LHE) at each

wavelength. The IPCE, APCE and LHE were calculated by using the following equations (S3-5).

$$IPCE(\%) = \frac{1240 \times J(mA \text{ cm}^{-2})}{P_{in}(mW \text{ cm}^{-2}) \times \lambda(nm)} \times 100 \dots (S3)$$

$$APCE(\%) = IPCE(\%) / LHE \dots (S4)$$

LHE =
$$1 - 10^{-A_{(\lambda)}}$$
 (A_(λ): absorbance at wavelength λ)(S5)

The applied bias photon-to-current efficiency (ABPE) was calculated from the J-V curves assuming 100% Faradaic efficiency using the following equation, where J is the photocurrent density, V_{bias} (V *vs.* RHE) is the applied bias between working electrode and counter electrode and P_{in} is the incident illumination power density (AM 1.5G, 100 mW cm⁻²). The calculating method is presented as following equation (S6):

ABPE(%) =
$$\left[\frac{J(mA \text{ cm}^{-2}) \times (1.23 \text{ -} V_{\text{bias}})(V)}{P_{\text{in}}(mW \text{ cm}^{-2})}\right]_{AM \, 1.5G} \times 100 \dots (S6)$$

The photocurrent measurements were performed at an applied potential of 50 mV versus Ag/AgCl (*vs.* Ag/AgCl) under visible light irradiation. The Mott-Schottky (M-S) curves were taken with a voltage of 5 mV at a frequency of 1000 Hz in light. The electrochemical impedance spectroscopy (EIS) was determined over the frequency range from 100000 to 0.01 Hz with an alternating current (AC) amplitude of 10 mV at the open circuit voltage under AM 1.5G illumination. The amperometric i-t curve was performed at 1.23 V *vs.* RHE under AM 1.5G illumination.

The charge injection yield (P_{inj}) was calculated using the following equation, where $J_{photocurrent}^{H2O}$ is the measured photocurrent density by water oxidation, J_{abs} is the photo absorption rate expressed as current density, the P_{sep} is the yield of the photogenerated electron-hole separation, and P_{inj} is the yield of the surface holes that are injected into

the solution and participate in water oxidation reaction subsequently. As the sulfite oxidation with extremely fast oxidation kinetics, surface recombination is negligible and P_{inj} is 1. In addition, the sodium sulfite with high concentration was used as the hole scavenger to determine the yield of photogenerated holes of the catalysts. The photocurrent derived from sulfite oxidation can be expressed as the following equations (S7-8).

$$J_{photocurrent}^{H_2O} = J_{abs} \times P_{sep} \times P_{inj} \dots (S7)$$

And thus, the charge injection yield can be expressed by the following equation (S9):

$$P_{inj} = J_{photocurrent}^{H_2O} / J_{photocurrent}^{Na_2SO_3}$$
(S9)



Fig. S1 The transient photocurrent of (a) $BiVO_4$ and (b) $0.1Bi/BiVO_4$ at different potential in 0.5 M Na_2SO_4 electrolyte. The dashed area is the accumulated charge.



Fig. S2 The stability test of 0.1Bi/BiVO₄ photoanode at 1.23 V vs. RHE under AM 1.5G illumination.



Fig. S3 (a) The light harvest efficiency (LHE) of $BiVO_4$ and $0.1Bi/BiVO_4$. The energy density flux (blue) of the simulated AM 1.5G sunlight (100 mW cm⁻²) is also presented. (b) The calculated current density flux 100% IPCE for the absorbed photons and the integrated current of the $BiVO_4$ and $0.1Bi/BiVO_4$ electrodes.



Fig. S4 J-V curves of $BiVO_4$ and $0.1Bi/BiVO_4$ photoanodes in electrolytes of 0.5 M Na_2SO_4 and $0.5 \text{ M Na}_2SO_4+0.5 \text{ M Na}_2SO_3$, respectively.