Electronic Supporting Information

## A Tandem Photoelectrochemical Water Splitting Cell Consisting of CuBi<sub>2</sub>O<sub>4</sub> and BiVO<sub>4</sub> Synthesized from a Single Bi<sub>4</sub>O<sub>5</sub>I<sub>2</sub> Nanosheet Template

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Figure S1. The UV-vis transmittance spectrum of Nafion 117<sup>TM</sup> membrane.



**Figure S2.** The SEM image (a) and (b)current density (*J*)–potential (*E*) curve of nanoBi<sub>4</sub>O<sub>5</sub>I<sub>2</sub>. The *J*-*E* curve was recorded in an aqueous 0.1 M B<sub>i</sub> buffer solution containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> (pH 9.2) under standardized and chopped solar-light illumination under N<sub>2</sub> atmosphere.



**Figure S3.** The *J*-*E* curves of the CuBi<sub>2</sub>O<sub>4</sub> converted from nanoBi<sub>4</sub>O<sub>5</sub>I<sub>2</sub> with  $D = 50 \ \mu L \ cm^{-2}$  and various *T*, recording in a 0.1 M B<sub>i</sub> buffer solution containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> (pH 9.2) under chopped solar-light illumination (100 mW cm<sup>-2</sup>, AM 1.5G) under N<sub>2</sub> atmosphere.



**Figure S4.** GI-XRD patterns of the CuBi<sub>2</sub>O<sub>4</sub> converted from nanoBi<sub>4</sub>O<sub>5</sub>I<sub>2</sub> with various *D* at  $T=550^{\circ}$ C. The second phase of Bi<sub>2</sub>O<sub>2.33</sub> and CuO exist if *D* is below and above 40 µL cm<sup>-2</sup>, respectively.



**Figure S5.** The *J*-*E* curve of microCuBi<sub>2</sub>O<sub>4</sub> recorded in an aqueous (i) 0.1 M B<sub>i</sub> buffer solution containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> (pH 9.2) and (ii) 1 M NaOH under chopped solar-light illumination (100 mW cm<sup>-2</sup>, AM 1.5G) under N<sub>2</sub> atmosphere.



**Figure S6.** The *J*-*E* curve of a microCuBi<sub>2</sub>O<sub>4</sub>|Co-B<sub>i</sub> recorded in an aqueous 0.1 M B<sub>i</sub> buffer solution containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> (pH 9.2) under N<sub>2</sub> atmosphere with standardized solar-light illumination (100 mW cm<sup>-2</sup>, AM 1.5G, red trace) and filtered by a nanoBiVO<sub>4</sub>|Co-B<sub>i</sub> electrode (black trace).



**Figure S7.** The *J-E* curve of BiVO<sub>4</sub> converted from nanoBi<sub>4</sub>O<sub>5</sub>I<sub>2</sub> with (i)  $D=50 \ \mu\text{L cm}^{-2}$ , (ii)  $D=67 \ \mu\text{L cm}^{-2}$ , (iii)  $D=33 \ \mu\text{L cm}^{-2}$ , and (iv)  $D=83 \ \mu\text{L cm}^{-2}$ , recording in an aqueous 0.1 M B<sub>i</sub> buffer solution containing 0.1 M Na<sub>2</sub>SO<sub>3</sub> (pH 9.2) under chopped solar-light illumination (100 mW cm<sup>-2</sup>, AM 1.5G) under N<sub>2</sub> atmosphere.



Figure S8. The UV-vis absorption spectra of nanoBiVO<sub>4</sub> and nanoBiVO<sub>4</sub>|Co-B<sub>i</sub>.



**Figure S9.** Overlaid |J|-*E* curves of nanoBiVO<sub>4</sub>|Co-B<sub>i</sub> (black solid) under chopped solar light irradiation (100 mW cm<sup>-2</sup>, AM 1.5G) and microCuBi<sub>2</sub>O<sub>4</sub>|Co-B<sub>i</sub> placed in the tandem cell position (illumination was filtered by nanoBiVO<sub>4</sub>|Co-B<sub>i</sub>, red solid). The measurements were performed in a three-electrode system in an aqueous 0.1 M Bi buffer solution containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> (pH 9.2). An Ag/AgCl/KCl<sub>sat</sub> electrode was used as the reference electrode, and a platinum foil as the counter electrode. A virtual curve (blue dash dot) shows a 0.2 V cathodic shift of the photocurrent curve of nanoBiVO<sub>4</sub>|Co-B<sub>i</sub>, and that an operating photocurrent of approximately 0.25 mA cm<sup>-2</sup> (red circle) should be obtained if an external bias of 0.2 V is applied to the BiVO<sub>4</sub>- CuBi<sub>2</sub>O<sub>4</sub> tandem cell. The nanoBiVO<sub>4</sub>|Co-B<sub>i</sub> and the microCuBi<sub>2</sub>O<sub>4</sub>|Co-B<sub>i</sub> electrodes have a same exposed geometrical surface area of 0.5 cm<sup>2</sup>.