Supporting Information:

Fabrication of porous Cu-doped $BiVO_4$ nanotubes as efficient oxygen-evolving photocatalysts

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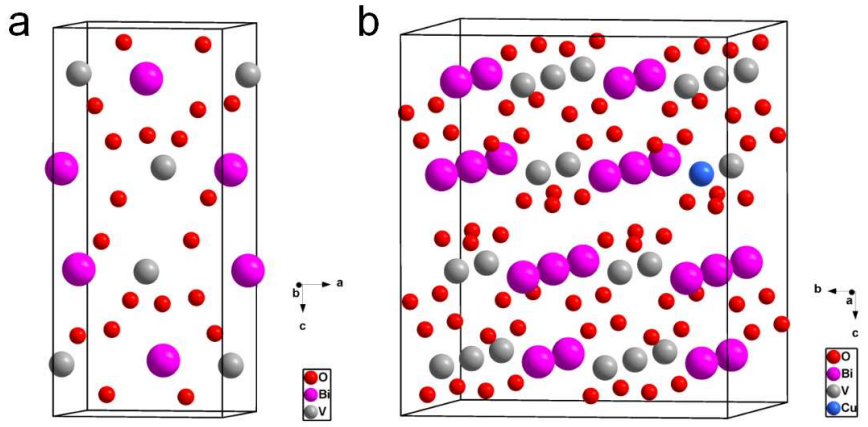

Figure S1. (a) The conventional cell of BVO and (b) Supercell model of Cu-BVO-5.0% considered in this work.

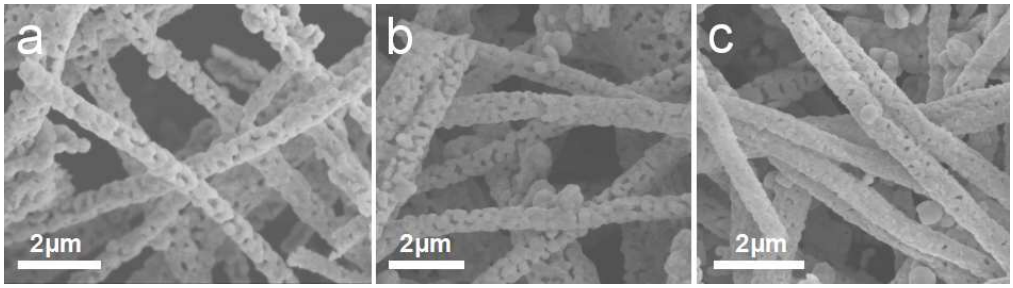

Figure S2. SEM images of the as-prepared (a) BVO, (b) Cu-BVO-3.0%, and Cu-BVO-10.0% samples.

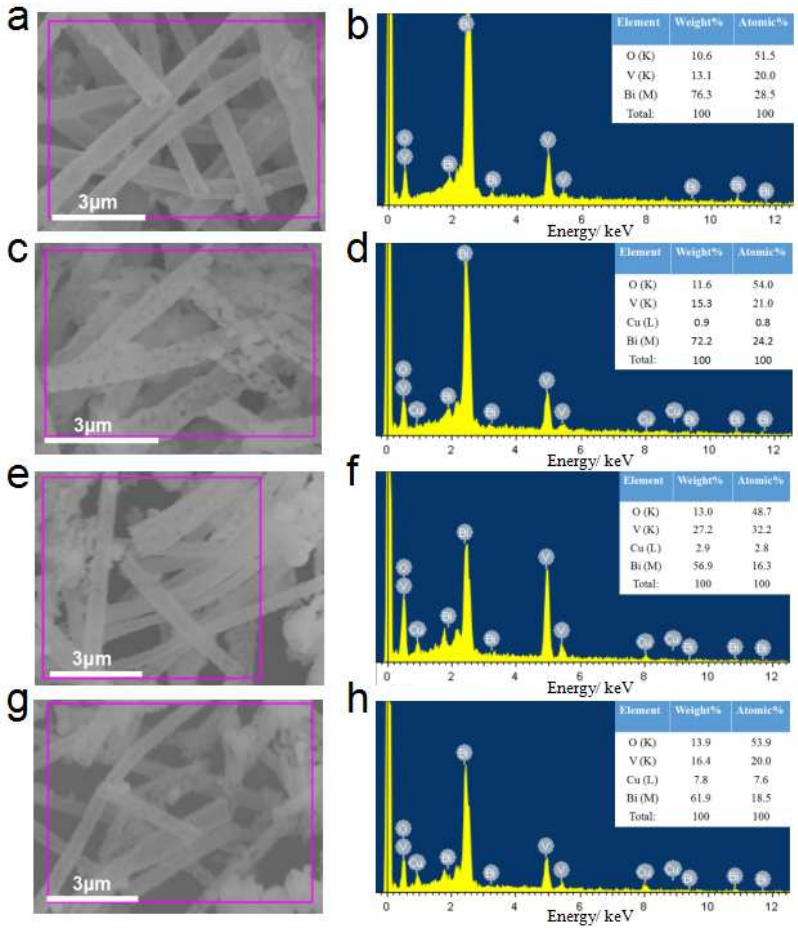

Figure S3. SEM images and the corresponding EDS patterns of the as-prepared samples: (a, b) BVO, (c, d) Cu-BVO-3.0%, (e, f) Cu-BVO-5.0% and (g, h) Cu-BVO-10.0%, element contents (inset).

Table S1. Elemental composition (atomic percentage) of the as-prepared different photocatalysts.

Photocatalysts	O (at%)	V (at%)	Cu (at%)	Bi (at%)
BVO	51.5	20.0	0	28.5
Cu-BVO-3.0%	54.0	21.0	0.8	24.2
Cu-BVO-5.0%	48.7	32.2	2.8	16.3
Cu-BVO-10.0%	53.9	20.0	7.6	18.5

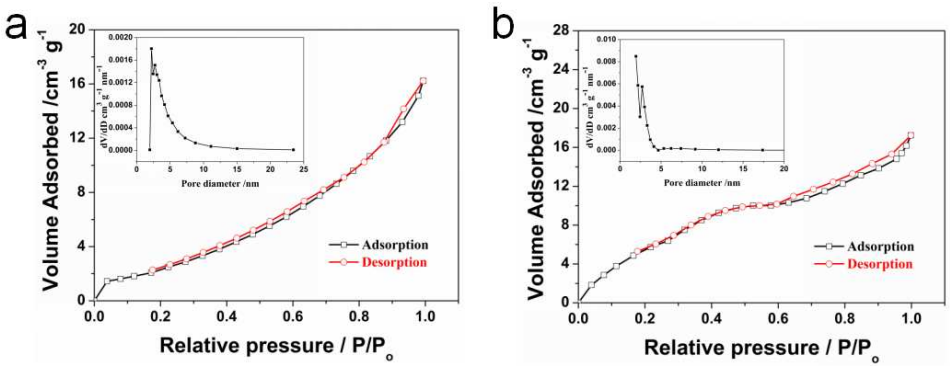

Figure S4. N_2 adsorption-desorption isotherms and pore size distribution of the as-prepared: (a) pure BVO, (b) Cu-BVO-5.0% samples.

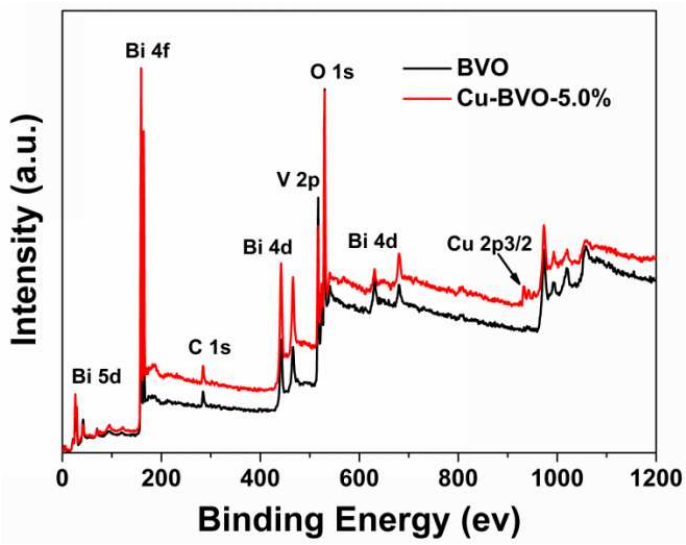

Figure S5. XPS survey spectra of pristine BVO and Cu-BVO-5.0% samples.

Table S2. Relative VB and CB of all the photocatalysts.

Photocatalysts	Band-gap(eV)	Mott-Schottky	
		VB(eV)	CB(eV)
BVO	2.30	2.11	-0.19
Cu-BVO-3.0%	2.12	2.48	0.36
Cu-BVO-5.0%	2.07	2.4	0.33
Cu-BVO-10.0%	2.02	2.44	0.42

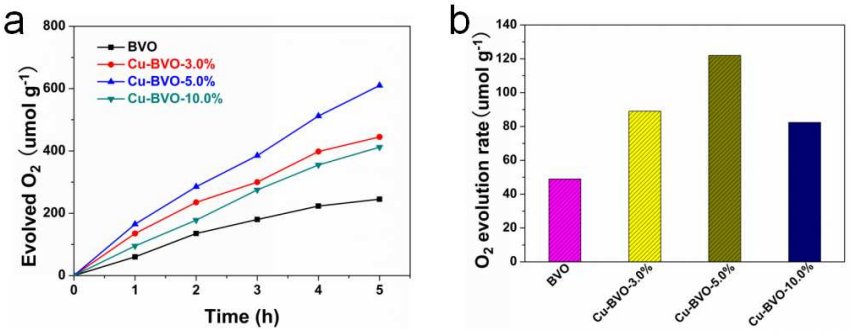

Figure S6. (a) Time course photocatalytic O_2 evolution and (b) O_2 evolution rate for different concentrations of Cu^{2+} doping samples without the co-catalyst under visible-light irradiation ($\lambda >$ 420 nm).

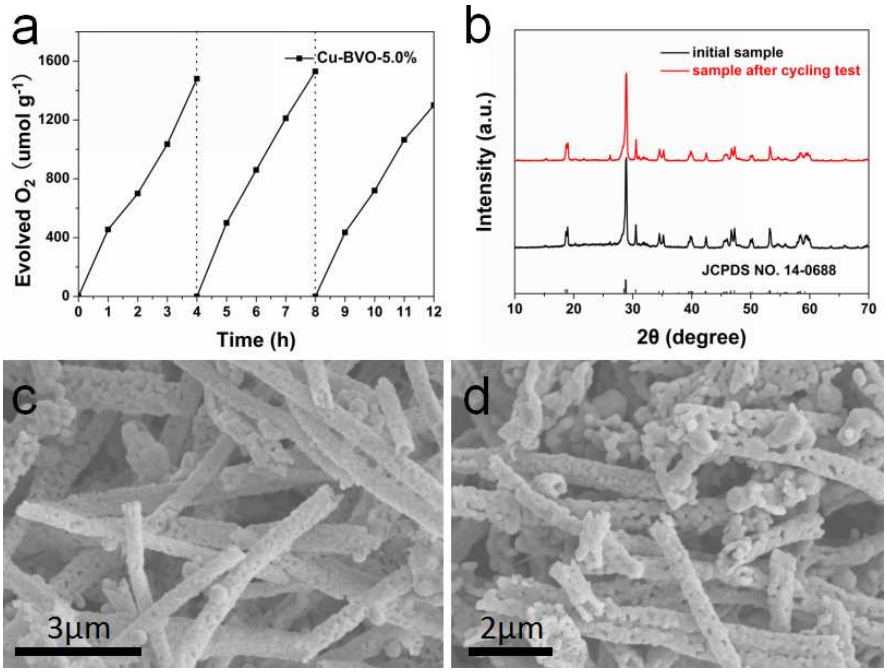

Figure S7. (a) The O_2 evolution performance of Cu-BVO-5.0% in the three cycling test. (b) XRD patterns and (c, d) SEM images of Cu-BVO-5.0% before and after cycling test.

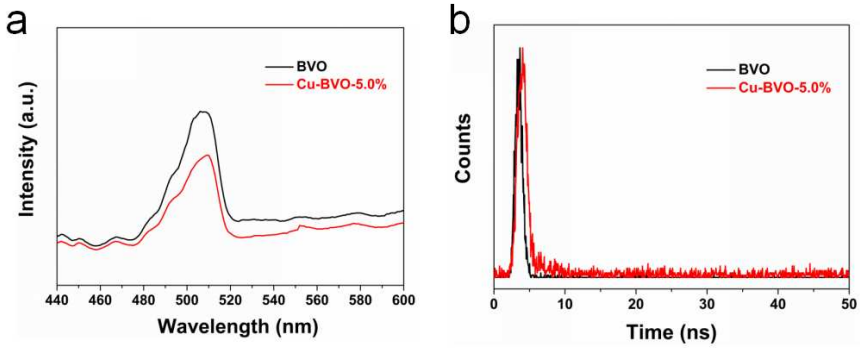

Figure S8. (a) PL spectra and (b) PL decay spectra of the as-prepared pristine BVO and Cu-BVO-5.0% samples.

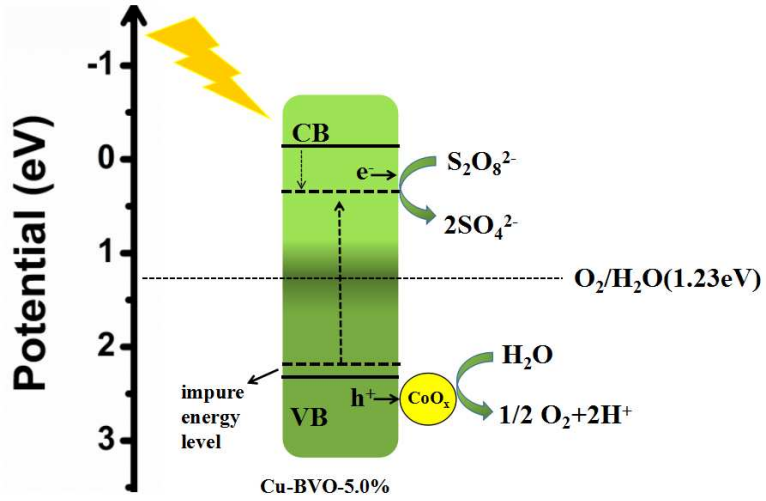

Figure S9. Schematic diagram representing the charge-transfer process in the Cu-BVO-5.0% sample for water oxidation reaction under UV-visible light irradiation (λ> 420 nm).

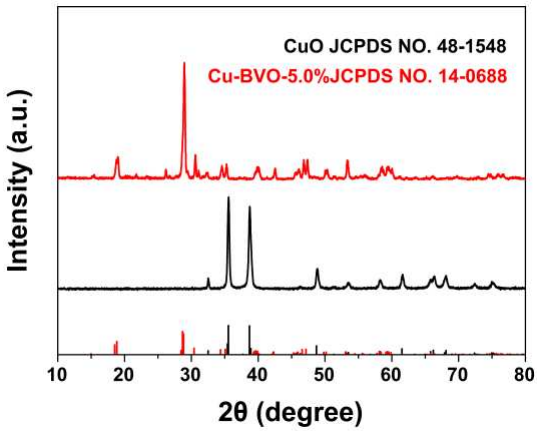

Figure S10. XRD patterns of bare CuO and Cu-BVO-5.0% samples.

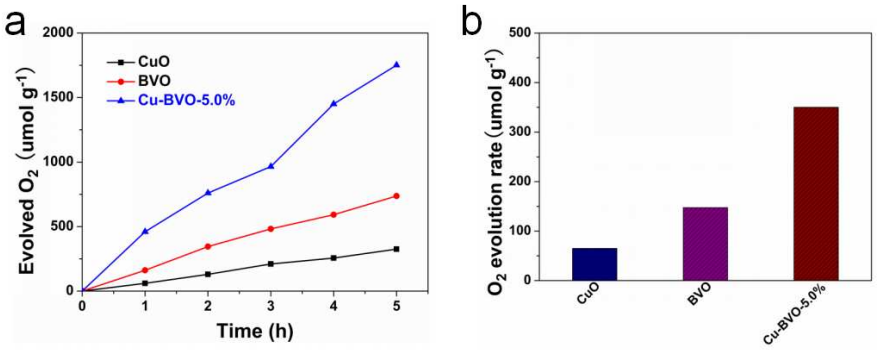

Figure S11. (a) Time course photocatalytic O_2 evolution and (b) O_2 evolution rate for BVO, CuO, Cu-BVO-5.0% samples under visible-light irradiation ($\lambda > 420$ nm).

Table S3 A comparison study of the photocatalysts in this work and previous reported $BiVO_4$-based photocatalysts for water oxidation reaction.

Photocatalysts	Morphology	Light source	Wavelength	Sacrificial agents	O_2 evolution rate ($\mu mol\ g^{-1}\ h^{-1}$)	References
$BiVO_4$	Rod-like nanostructure	300 W Xe	>300 nm	$AgNO_3$	82.8	1
$BiVO_4$	Nanoparticle	300 W Xe	>420 nm	$AgNO_3$	60.9	2
$BiVO_4$	Nanoparticle	300 W Xe	>420 nm	$FeCl_3$	108	3
SiC/$BiVO_4$	Nanoparticle	300 W Xe	≥420 nm	FeCl3	658	4
Fe/Mo-BVO/CoO_x	Shuttle-like nanostructure	300 W Xe	≥420 nm	$NaOH/Na_2S_2O_8$	191.5	5
BVO	Nanotube	300 W Xe	>420 nm	$NaOH/Na_2S_2O_8$	94	This work
BVO/CoO_x	Nanotube	300 W Xe	>420 nm	$NaOH/Na_2S_2O_8$	146.1	This work
Cu-BVO-5.0%	Nanotube	300 W Xe	>420 nm	$NaOH/Na_2S_2O_8$	122	This work
Cu-BVO-5.0%/CoO_x	Nanotube	300 W Xe	>420 nm	$NaOH/Na_2S_2O_8$	350.2	This work

References:

(1) Thalluri, S. M.; Suarez, C. M.; Hernández, S.; Bensaid, S.; Saracco, G.; Russo, N. Elucidation of Important Parameters of $BiVO_4$ Responsible for Photocatalytic O_2 Evolution and Insights About the Rate of the Catalytic Process. *Chem Eng J.* **2014**, *245*, 124-132.

(2) Thalluri, S. M.; Suarez, C. M.; Hussain, M.; Hernandez, M.; Virga, A.; Saracco, G.; Russo, N. Evaluation of the Parameters Affecting the Visible-Light-Induced Photocatalytic Activity of Monoclinic $BiVO_4$ for Water Oxidation. *Ind. Eng. Chem. Res.* **2013**, *52*, 17414-17418.

(3) Iwase, A.; Kudo, A. Photoelectrochemical Water Splitting using Visible-Light-Responsive $BiVO_4$ Fine Particles Prepared in an Aqueousacetic Acid Solution. *J. Mater. Chem.* **2010**, *20*, 7536-7542.

(4) Wang, D.; Guo, Z. N.; Peng, Y.; Yuan, W. X. A Simple Route to Significant Enhancement of Photocatalytic Water Oxidation on $BiVO_4$ by Heterojunction with SiC. *Chem Eng J.* **2015**, *281*, 102-108.

(5) Liu, R.; Ren, J. B.; Zhao, D.; Ning, J. Q.; Zhang, Z. Y.; Wang, Y. J.; Zhong, Y. J.; Zheng, C. C.;

Hu. Y. Band Gap Engineering of Porous $BiVO_4$ Nanoshuttles by Fe and Mo Co-Doping for Efficient Photocatalytic Water Oxidation. *Inorg. Chem. Front*. **2017**, *4*, 2045-2054.