

Supporting information

A brand-new 1D branched CuO nanowire arrays for efficient photoelectrochemical water reduction

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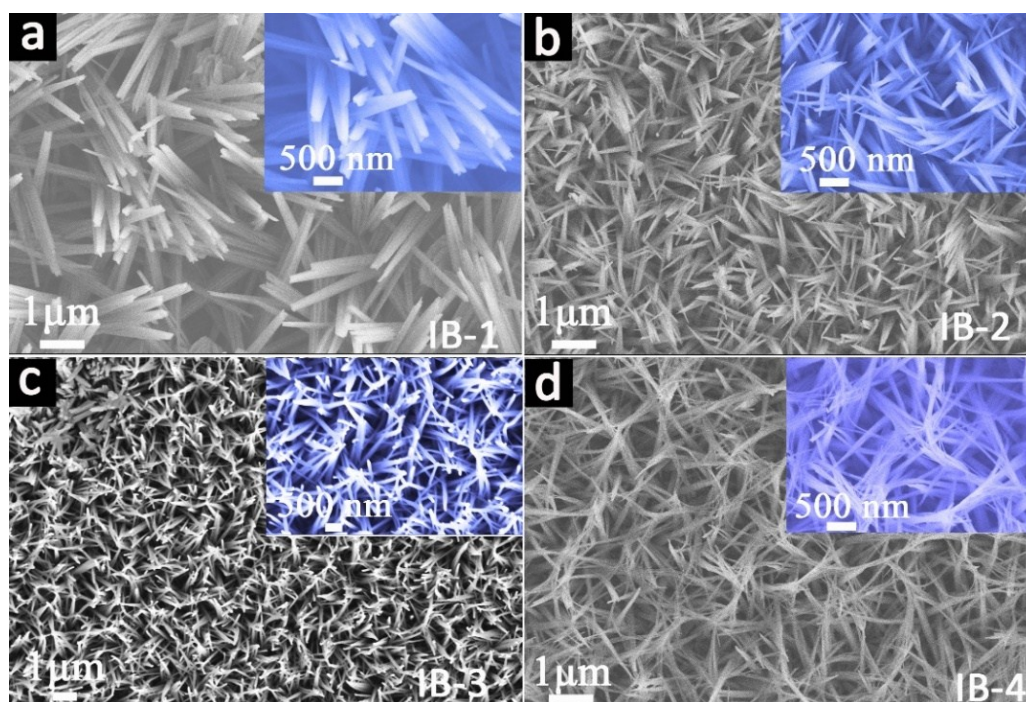


Fig. S1 SEM images of the sample prepared under ice bath (IB) condition, with the concentration of etching solution and reaction time of a) $\text{K}_2\text{S}_2\text{O}_8$ (0.05 M), NaOH (1.0 M), 50 min; b) $\text{K}_2\text{S}_2\text{O}_8$ (0.05 M), NaOH (1.0 M), 10 min; c) $\text{K}_2\text{S}_2\text{O}_8$ (0.01 M), NaOH (0.2 M), 50 min; d) (0.01 M), NaOH (0.2 M), 2 h.

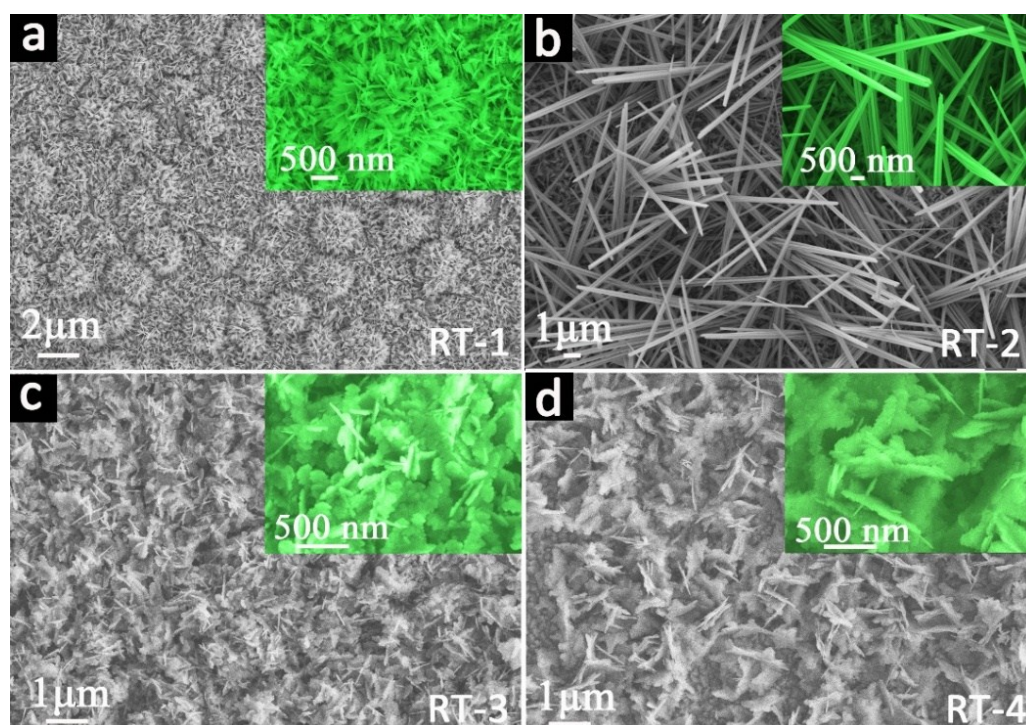


Fig. S2 SEM images of the sample prepared at room temperature (RT) condition, with the concentration of etching solution and reaction time of a) $\text{K}_2\text{S}_2\text{O}_8$ (0.01 M), NaOH (0.2 M), 6 h; b) $\text{K}_2\text{S}_2\text{O}_8$ (0.05 M), NaOH (1.0 M), 20 min; c) $\text{K}_2\text{S}_2\text{O}_8$ (0.05 M), NaOH (1.0 M), 1 h; d) (0.15 M), NaOH (3.0 M), 20 min.

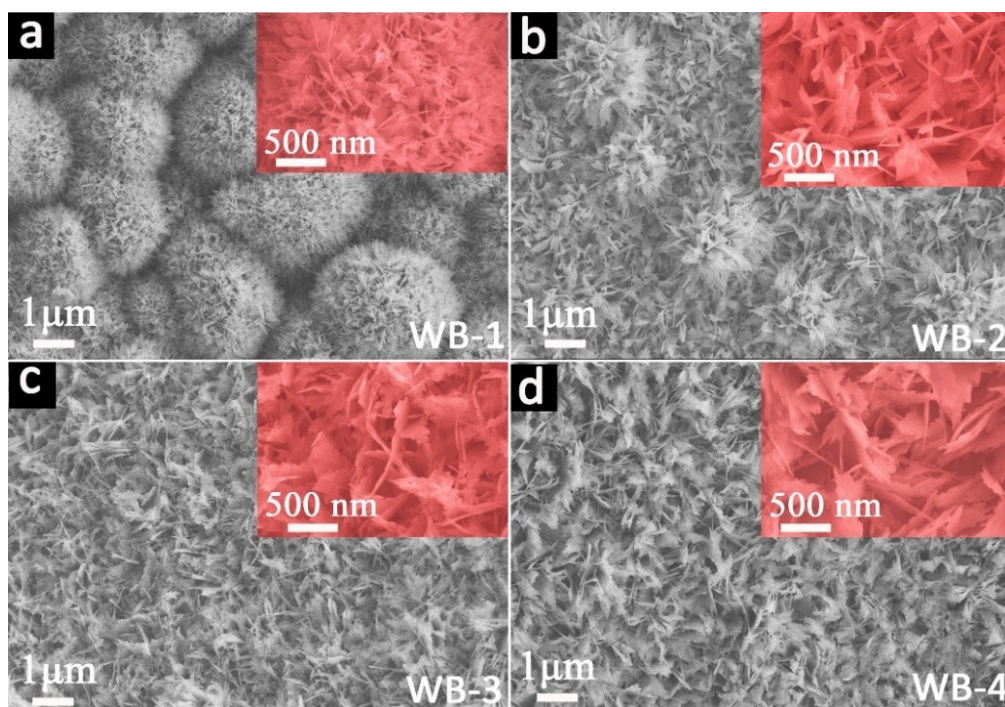


Fig. S3 SEM images of the sample prepared with different concentration of etching solution and temperature of water bath (WB) for 20 min, a) $\text{K}_2\text{S}_2\text{O}_8$ (0.01 M), NaOH (0.2 M), 50 °C; b) $\text{K}_2\text{S}_2\text{O}_8$ (0.01 M), NaOH (0.2 M), 80 °C; c) $\text{K}_2\text{S}_2\text{O}_8$ (0.05 M), NaOH (1.0 M), 50 °C; d) (0.05 M), NaOH (1.0 M), 80 °C.

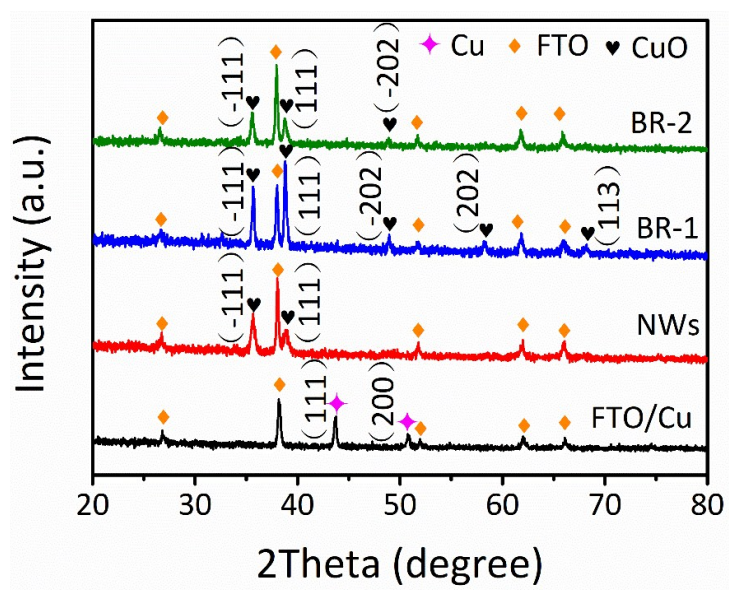


Fig. S4 XRD diffraction pattern of the samples.

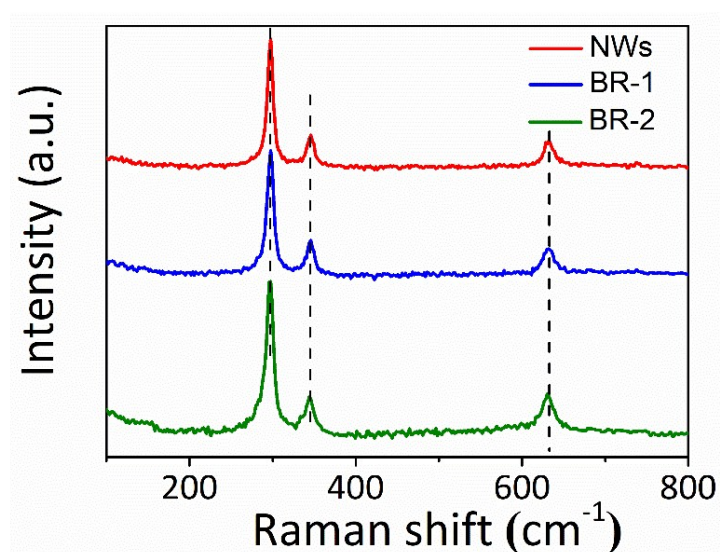


Fig. S5 Raman spectra of the samples.

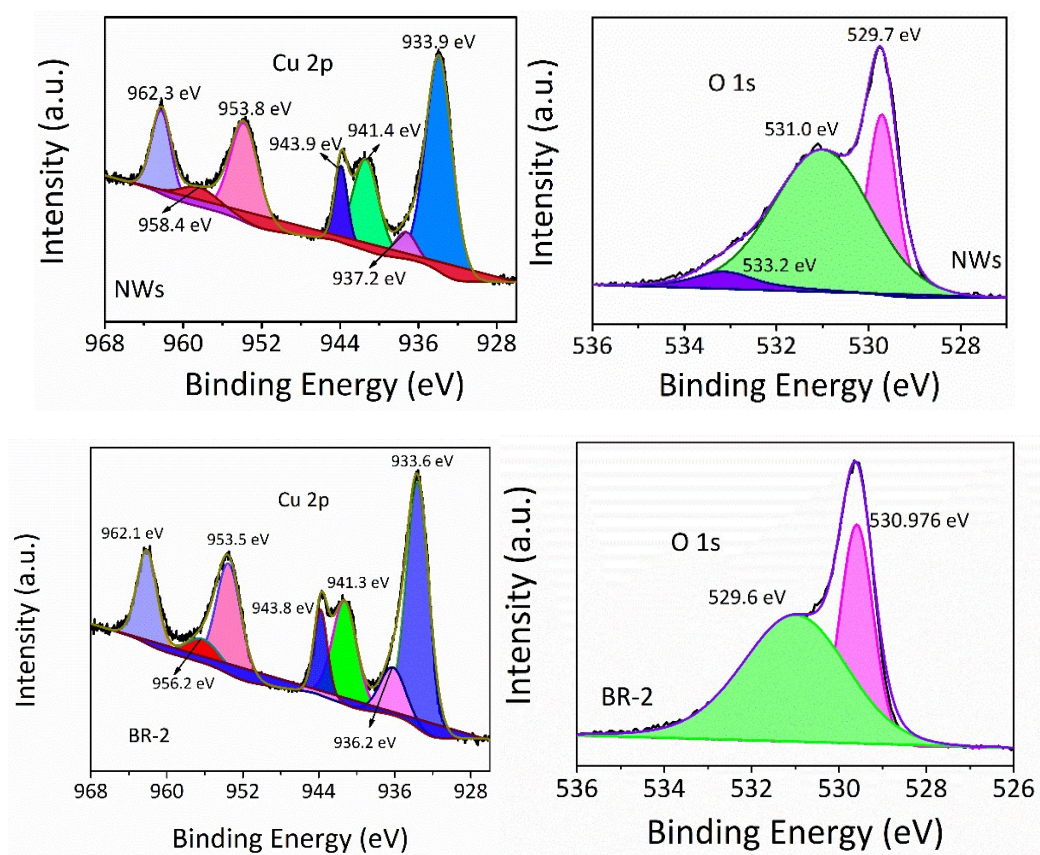


Fig. S6 High-resolution XPS Cu 2p and O 1s spectra of the samples.

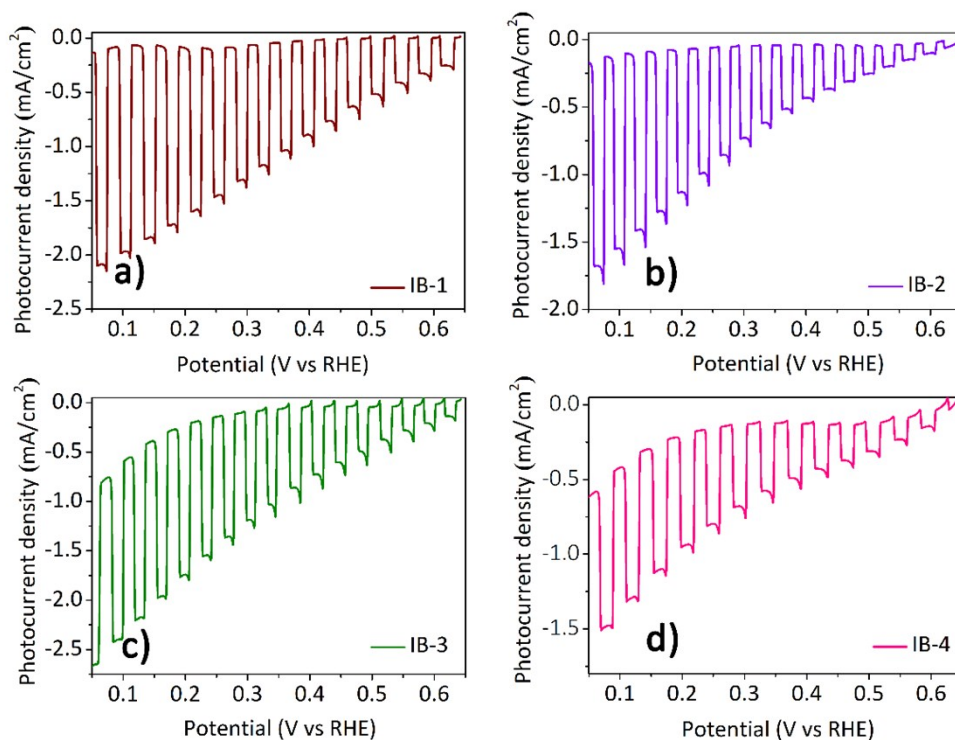


Fig. S7 Photocurrent response of the samples prepared in ice bath.

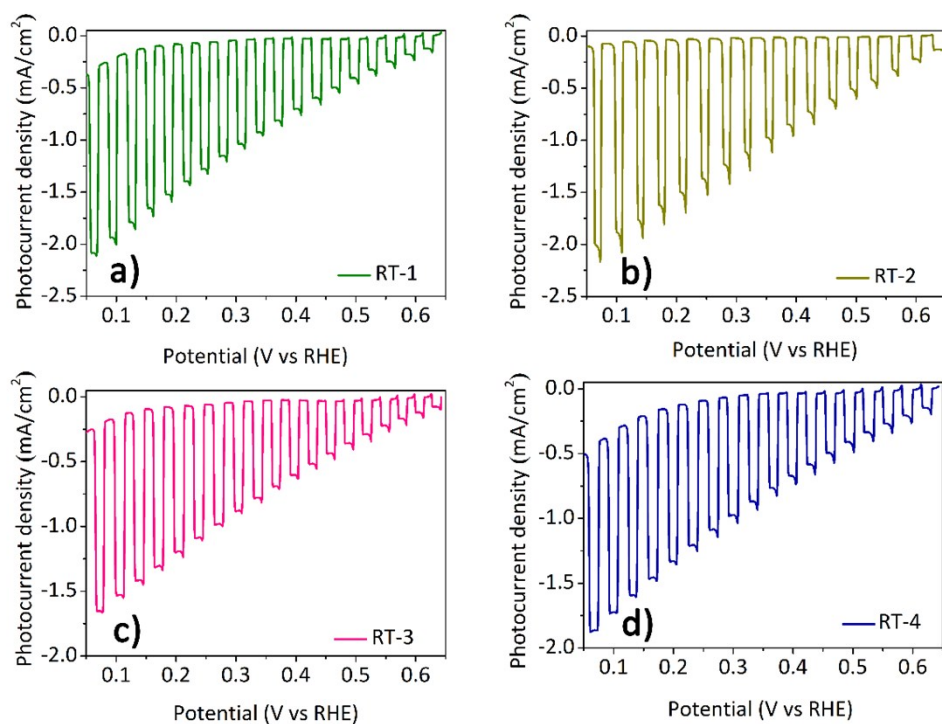


Fig. S8 Photocurrent response of the samples prepared at room temperature.

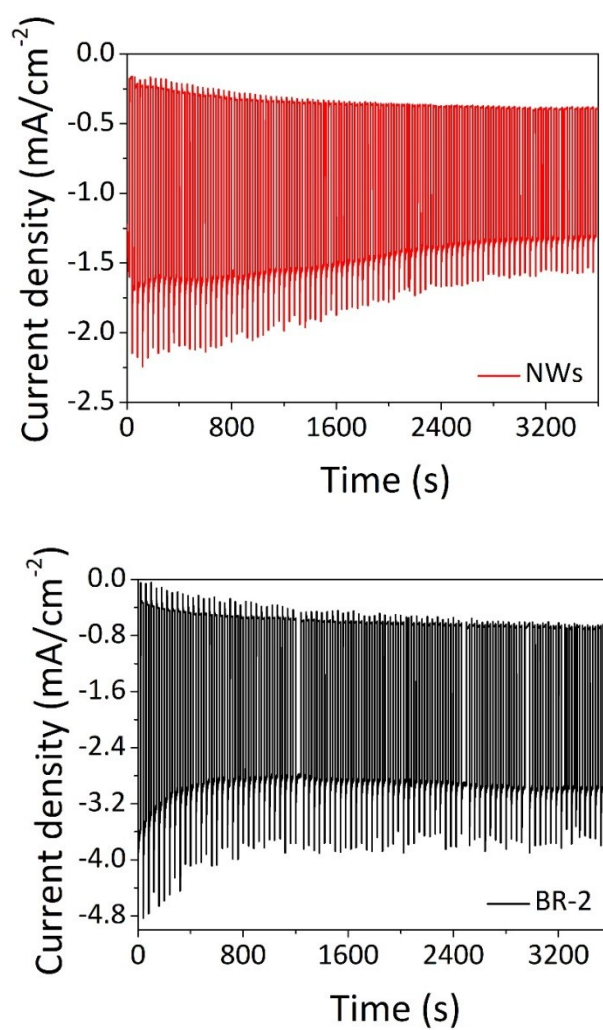


Fig. S11 Photocurrent i-t curve of NWs and BR-2 under AM 1.5G illumination ($100 \text{ mW}\cdot\text{cm}^{-2}$) at 0.2 V vs RHE in 0.5 M Na_2SO_4 , from which we can see the both positive and negative transient photocurrent in two samples.

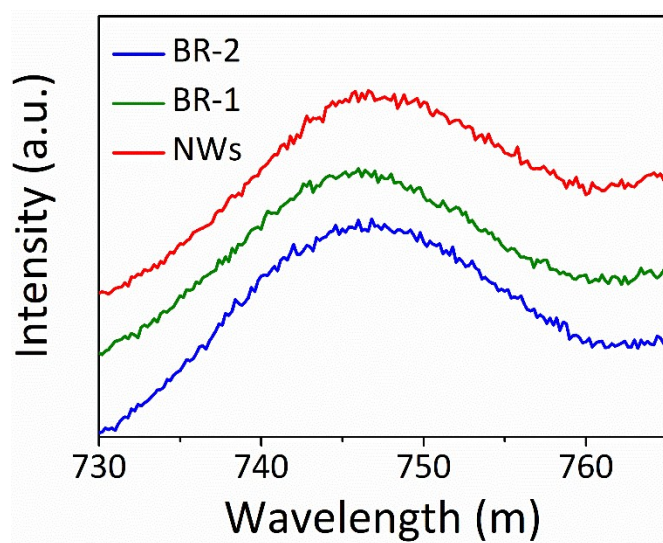


Fig. S12 Steady-state photoluminescence (PL) spectra of the samples, excited at 495 nm.

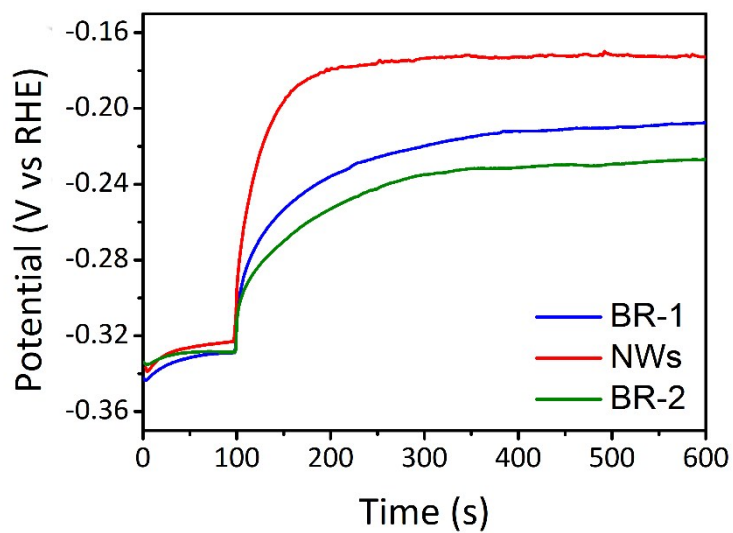


Fig. S13 Open circuit voltage (Voc) decay of the samples.

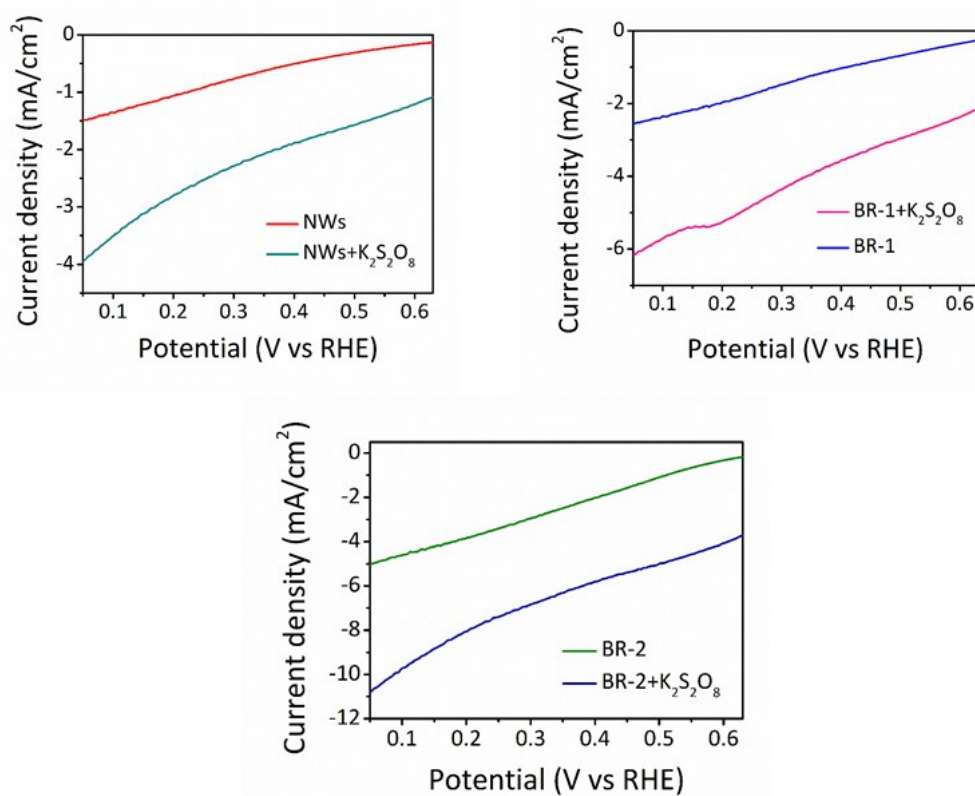


Fig. S14 Photocurrent of the samples obtained in the 0.5 M Na₂SO₄ with and without K₂S₂O₈ (0.02 M). These data are used to calculate the charge injection and separation efficiency.

Table S1 PEC performance of reported CuO and corresponding experimental conditions

Composition of photoelectrode	Photocurrent density (mA·cm ⁻²)	Potential	electrolyte	Illumination condition Light intensity	Year Published	Reference
NWs	1.3	0.2 V (vs. RHE)	0.5 M Na ₂ SO ₄	Xe lamp with AM 1.5 filter	Our work	
BR-1	2.0					
BR-2	3.6					
CuO thin film	-1.8	-0.55 V (vs. Ag/AgCl)	0.1 M Na ₂ SO ₄	150 W solar simulator	2014	1
CuO thin film	-1.8	0 V (vs. RHE)	0.1 M KOH	150 W Xe lamp	2012	2
Ni-doped CuO nanorods	-1.75	-0.55 V (vs. SCE)	1 M KOH	300 W arc Xe-lamp	2018	3
CuO thin film	-0.55	0.05 V (vs. RHE)	0.5 M Na ₂ SO ₄	1 sun (AM1.5G) illumination	2009	4

CuO thin film Au–Pd decorated CuO thin film	-3.1 -3.88	0 V (vs. RHE)	0.1 M Na ₂ SO ₄	1 sun (AM1.5G) illumination	2017	5
CuO nanowire	-0.25	-0.5 V (vs. Ag/AgCl)	0.1 M Na ₂ SO ₄	500 W Xe lamp	2014	6
CuO nanoparticles films	-1.2	-0.7 V (vs. Ag/AgCl)	0.1 M Na ₂ SO ₄	150 W Xenon arc lamp	2012	7
CuO thin film	-2.5	0 V (vs. RHE)	0.1 M Na ₂ SO ₄	300 W Xe lamp	2011	8
heterojunction CuO nanowire	-0.65	-0.45 V (vs. Ag/AgCl)	0.1 M Na ₂ SO ₄	150 W Xe lamp	2016	9
CuO thin film	-1.5	0.6 V (vs. RHE)	0.1 M KOH	300 W Xe arc lamp	2017	10
CuO nanoparticle	-1.2	-0.55 V (vs. Ag/AgCl)	0.5 M Na ₂ SO ₄	1 sun (AM1.5G) illumination	2013	11

Li-doped CuO nanoparticles	-1.7	-0.55 V (vs. Ag/AgCl)	0.1 M Na ₂ SO ₄	150 W Xe lamp	2009	12
FTO/CuONSs	-1.9	0 V (vs. RHE)	0.5 M Na ₂ SO ₄	150 W Xe lamp	2016	13
mpATO@CuONSs	-3.0					
FTO/mpATO@CuONSs	-4.5					
CuO film	-0.85	-0.5 V (vs. Ag/AgCl)	0.1 M KOH	1 kW Xenon lamp	2016	14
CuO NR	-1.13					
CAL CuO	-1.44	0 V (vs. RHE)	0.5 M Na ₂ SO ₄	1.5 G filter (1 sun 100 Mw cm ⁻²)	2015	15
HMA CuO	-4.4					
nanostructured CuO film	-1.5	-0.5 V (vs. SCE)	0.5 M Na ₂ SO ₄	150 W Xenon arc lamp	2006	16
Cu ₂ O-CuO thin films	-0.35	0.05 V(vs. RHE)	0.1 M Na ₂ SO ₄	150 W Xenon arc lamp	2014	17
doped CuO film	-1.52	-0.55 V (vs. Ag/AgCl)	1M KOH	150 W Xenon arc lamp	2014	18

W doped CuO film	-0.25	-0.5 V (vs. Ag/AgCl)	NaOH electrolyte solution (pH=11)	Tungsten–halogen lamp (125 mW cm ⁻²)	2010	19
Ti-alloyed CuO	-0.09	-0.5 V (vs. Ag/AgCl)	1 M Na ₂ SO ₄	250-W quartz tungsten lamp	2012	20
CuO thin film	-0.1	-0.2 V (vs. Ag/AgCl)	0.5 M Na ₂ SO ₄	500 W xenon Lamp ($\lambda > 420$ nm)	2004	21

1. C. G. Morales-Guio, S. D. Tilley, H. Vrubel, M. Gratzel, X. Hu, *Nat. Commun.* 2014, **5**, 3059.
2. C.-Y. Chiang, J. Epstein, A. Brown, J. N. Munday, J. N. Culver, S. Ehrman, *Nano Lett.* 2012, **12**, 6005–6011.
3. J.-W. Ha, J. Oha, H. Choi, H. Ryu, W.-J. Lee, J.-S. Baec, *Journal of Industrial and Engineering Chemistry*, 2018, **58**, 38–44.
4. C. Wadia, A. P. Alivisatos, D. M. Kammen, *Environ. Sci. Technol.* 2009, **43**, 2072–2077.
5. S. Masudy-Panah, R. S. Moakhar, C. S. Chua, A. Kushwaha, G. K. Dalapati, *ACS Appl. Mater. Interfaces*, 2017, **9**, 27596–27606.
6. X. Guo, P. Diao, D. Xu, S. Huang, Y. Yang, T. Jin, Q. Wu, M. Xiang, M. Zhang, *Int. J. Hydrogen Energy*, 2014, **39**, 7686–7696.
7. C.-Y. Chiang, Y. Shin, K. Aroh, S. Ehrman, *Int. J. Hydrogen Energy*, 2012, **37**, 8232–8239.
8. C.-Y. Chiang, K. Aroh, N. Franson, V. R. Satsangi, S. Dass, S. Ehrman, *Int. J. Hydrogen Energy*, 2011, **36**, 15519–15526.
9. S. Masudy-Panah, R. S. Moakhar, C. S. Chua, A. Kushwaha, T. I. Wong, G. K. Dalapati, *RSC Adv.* 2016, **6**, 29383–29390.
10. A. C. Cardiel, K. J. McDonald, K.-S. Choi, *Langmuir*, 2017, **33**, 9262–9270.
11. A. Kargar, Y. Jing, S. J. Kim, C. T. Riley, X. Pan, D. Wang, *ACS Nano* 2013, **7**, 11112–11120.
12. H. Zhang, J.-L. Cao, G.-S. Shao, Z.-Y. Yuan, *J. Mater. Chem.* 2009, **19**, 6097–6099.
13. X.-D. Wang, Y.-F. Xu, B.-X. Chen, N. Zhou, H.-Y. Chen, D.-B. Kuang, C.-Y. Su, *ChemSusChem*, 2016, **9**, 1–8.
14. U. Shaislamov, K. Krishnamoorthy, S. J. Kim, W. Chun, H.-J. Lee, *RSC Adv.* 2016, **6**, 103049–103056.
15. Y. J. Jang, J.-W. Jang, S. H. Choi, J. Y. Kim, J. H. Kim, D. H. Youn, W. Y. Kim, S. Han, J. S. Lee, *Nanoscale*, 2015, **7**, 7624–7631.

16. D. Chauhan, V. R. Satsangi, S. Dass, R. Shrivastav, *Bull. Mater. Sci.* 2006, **29**, 709-716.
17. Y.-F. Lim, C. S. Chua, C. J. J. Lee, D. Chi, *Phys.Chem. Chem. Phys.* 2014, **16**, 25928-25934.
18. C.-Y. Chiang, Y. Shin, S. Ehrman, *Energy Procedia*, 2014, **61**, 1799.
19. L. Chen, S. Shet, H. Tang, H. Wang, T. Deutsch, Y. Yan, J. Turner, M. Al-Jassim, *J. Mater. Chem.* 2010, **20**, 6962.
20. H. Tang, M. A. Matin, H. Wang, S. Sudhakar, L. Chen, M. M. Al-Jassim, Y. Yan, *J. Electron. Mater.* 2012, **41**, 3062
21. K. Nakaoka, J. Ueyama, K. Ogura, *J. Electrochem. Soc.* 2004, **151**, C661.