Supporting Information

Stable and Efficient Solar-Driven Photoelectrochemical Water Splitting into H_2 and O_2 Based on $BaTaO_2N$ Photoanode Decorated with CoO Microflowers

Shunhang Wei, ‡[a] Shufang Chang, ‡[a] Fan Yang,[b] Zhengping Fu,[c] Gang Liu[d,e] and Xiaoxiang Xu*[a]

[a]*Putuo People's Hospital, Shanghai Key Lab of Chemical Assessment and Sustainability, School of Chemical Science and Engineering, Tongji University, Shanghai, 200060, China.*

[b]*New Energy Automotive Center, School of Automotive Studies, Tongji University, Shanghai, 201804, China.*

[c]*Department of Materials Science and Engineering, CAS Key Laboratory of Materials for Energy Degradation, University of Science and Technology of China, Hefei, 230026, China*

[d]*Shenyang National laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science, 72 Wenhua Road, Shenyang, 110016, China*

[e]*School of Materials Science and Engineering, University of Science and Technology of China, 72 Wenhua Road, Shenyang 110016, China*

*Corresponding author

Xiaoxiang Xu (Email: xxxu@tongji.edu.cn; Tel: +86-021-65986919)

‡These authors contribute equally.

Supporting information content

Number of pages: 22 (S1-S22)

Number of figures: 12 (Figure S1-S12)

Number of tables: 1 (Table S1)

Content

Experimental

Synthesis of $BaTaO_2N$

$BaTaO_2N$ samples were prepared according to previous report[1]. In brief, stoichiometric amounts of $BaNO_3$ (SCR, 99.5%), $TaCl_5$ (Alfa Aesar, 99.99%) were dissolved in 10 ml ethylene glycol (Aladdin, 98%) containing 1.8 g anhydrous citric acid (Aladdin, 99.5%). Heating at 423 K and magnetic stirring was used to facilitate dissolution of all chemicals. The so-formed transparent solution was heated at 573 K which was gradually turned into brown resin due to polymerization. The resin was transferred into alumina crucible and calcined at 823 K for 10 h for the removal of organic species. The resultant white powders were transferred into a tube furnace for ammonolysis. Flowing ammonia gas (Jiaya Chemicals, 99.999%) was introduced into the tube furnace at a flowing rate of 250 ml min^{-1}. The furnace was then ramped to 1273 K, dwelled at 1273 K for 15 h and was cooled naturally to room temperature. The resultant red powders were analyzed by XRD for phase identification.

Photoelectrode preparation

Electrophoretic deposition method was adopted to prepare photoelectrodes[2]: two pieces of fluorine-doped tin oxide (FTO) glass (30 × 10 mm) were inserted in parallel into 50 ml acetone solution containing 70 mg $BaTaO_2N$ powders and 10 mg iodine. 10 mm distance was kept for FTO glass with their conductive sides faced inward. Subsequently, a constant bias (10 V) was loaded for 3 min under a potentiostatic control (Keithley 2450Source Meter). $BaTaO_2N$ powders were quickly deposited onto

FTO glass at the anode side which was then used as the photoelectrodes. These photoelectrodes were calcined in N_2 flow at 673 K for 1 h to remove absorbed iodine. $TiCl_4$ (Alfa Aesar, 99.99%) ethanol solution (10 mM) was dropped onto the photoelectrodes, and were dried at 623 K for 15 min. This treatment was repeated for six times in order to improve particle-interconnection and to reduce exposure of naked FTO. The photoelectrodes were then calcined in N_2 flow at 673 K for another 1 h.

In situ growth of CoO microflowers onto $BaTaO_2N$ photoelectrodes

CoO microflowers were *in situ* grown onto $BaTaO_2N$ photoelectrodes by a hydrothermal method: $Co(NO_3)_2.6H_2O$ (1 mmol) and urea (2 mmol) were dissolved into 30 ml deionized water as a precursor solution. Freshly prepared $BaTaO_2N$ photoelectrodes were immersed into above solution, and were transferred into a Teflon-lined stainless steel autoclave for hydrothermal reactions. Typical reaction temperature is 393 K and reaction time is 5 h. After cooling the autoclave naturally, the photoelectrodes were taken out, and were rinsed by deionized water for a few times. The photoelectrodes were further calcined in N_2 flow at 673 K for 1 h, and was denoted as CoO@$BaTaO_2N$. For comparisons, CoO nanoparticles were also loaded onto $BaTaO_2N$ using conventional impregnation method according to previous reports[3, 4]. Cobalt phosphate (Co-Pi) was also loaded onto $BaTaO_2N$ for comparisons according to previous report[5].

Basic characterization

Phase compositions were analyzed by X-ray powder diffraction (XRD) techniques on a Bruker D8 Focus diffractometer. Incident radiation was Cu Kα1 (λ = 1.5406 Å) and Cu Kα2 (λ = 1.5444 Å). Diffuse reflectance spectra were collected using a UV-Vis spectrometer (JASCO-V750) and were analyzed using JASCO software suite. $BaSO_4$ was used as a non-absorbing reference material. The morphology of the samples was inspected under a field emission scanning electron microscope (Hitachi S4800, Japan) and a transmission electron microscope (JEOL JEM-2100, Japan). Photoluminescence spectra (PL) and time-resolved PL decay spectra were recorded using a spectrofluorometer (FLUOROLOG-3-11) with an excitation wavelength of 260 nm. The soft X-ray absorption spectra (XAS) were collected at the BL10B of the National Synchrotron Radiation Laboratory (NSRL, Hefei, P. R. China). X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD) technique was introduced to investigate the surface state of sample powders. A monochromatic Al K_α X-ray was used as the radiation source. The spectra data was adjusted properly using adventitious C 1s state (284.8 eV)[6].

Photoelectrochemical (PEC) measurements

PEC experiments were performed in a gas-tight PEC cell with a three-electrode configuration connected to a Zahner electrochemical workstation. The photoelectrode, Pt foil (10 × 10 mm) and Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. Potentials are recorded vs. reversible hydrogen electrode (RHE), which is obtained using the formula $E_{RHE} = E_{Ag/AgCl} + 0.059pH +$

0.1976 V. KOH aqueous solution (0.1 M, pH = 13) was used as an electrolyte. A 300 W Xenon lamp (PLX-SXE300, Perfect Light, China) coupled with a cut-off filter ($\lambda \geq$ 420 nm or AM 1.5G) was applied as the light source. The solution was purged with Ar for 20 min prior to the PEC measurement. Incident light was rectified by an electronic timer and shutter (GCI-73 DAHENG, China). The wavelength dependent incident photon-to-current conversion efficiency (IPCE) was calculated according to the following equation:

$$IPCE(\%) = [1240 \times I_{\lambda}]/[\lambda \times P_{Input}] \times 100\%$$

where I_{λ} (mA cm^{-2}) is the steady-state photocurrent density under monochromatic irradiation of wavelength λ, P_{input} (mW cm^{-2}) is the incident photon density measured by a photometer. Tunable monochromatic irradiation was produced by combining a monochromator (TLS300XENON150, NBet, China) with a 300 W Xenon lamp (NBet, China). Gas composition within the PEC cell was analyzed by a gas chromatograph (GC7900 TECHCOMP, China) using Ar as a carrier gas and a TCD detector. Mott-Schottky (MS) analysis was performed using the same three-electrode configuration by analyzing the impedance spectra at 1000 Hz from -0.8 V to 1 V vs NHE. Capacitance was extracted from impedance data and used for MS plot.

Detection of photogenerated holes.

As a chemical probe for detection of hole location[7], MnO_2 was photo-deposited onto

photoelectrodes from manganese (II) chloride aqueous solution (0.2g L^{-1}). A 300 W Xenon lamp (Perfect Light, PLX-SXE300) coupled with AM 1.5G filter was applied as the light source. The photoelectrode was irradiated for 20 min at a bias of 1.23 V vs RHE. After deposition, the photoelectrode was rinsed with deionized water and was dried at room temperature before microscopic analysis.

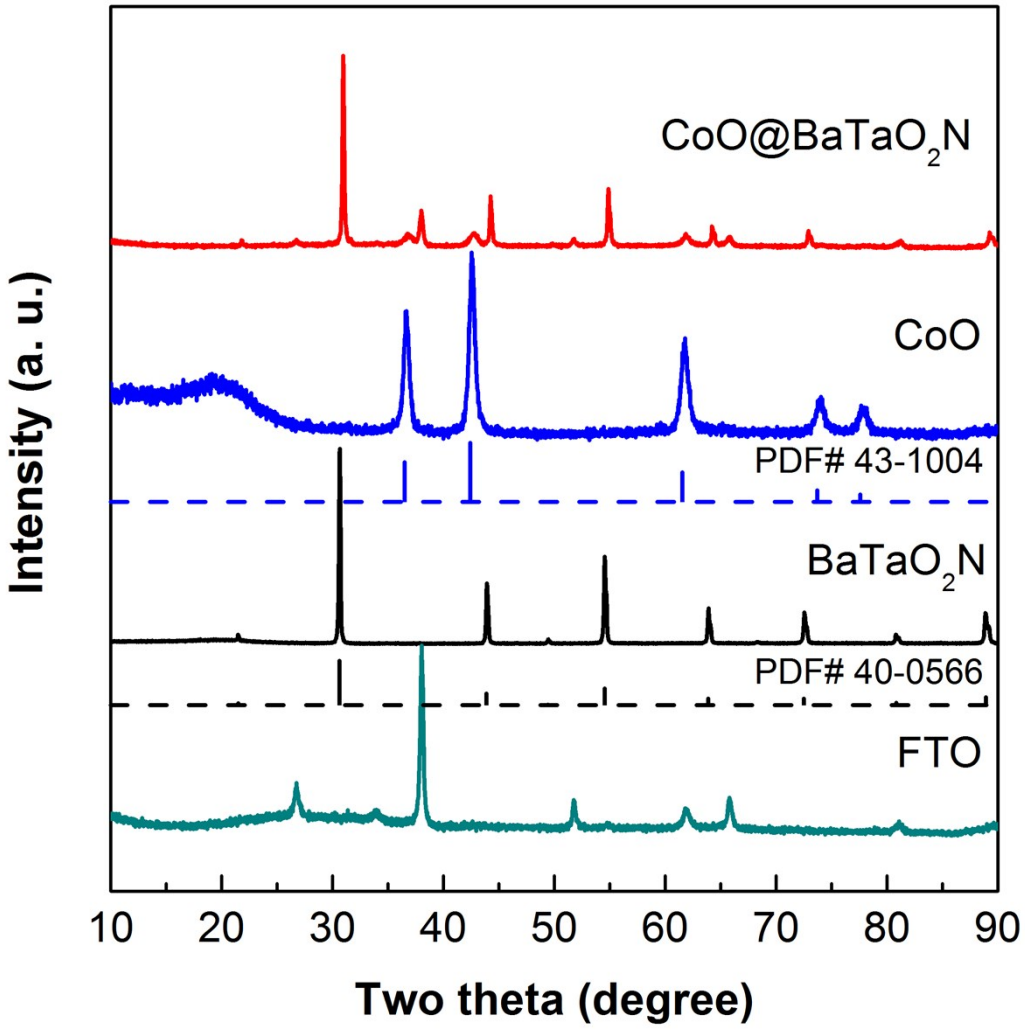

Figure S1. X-ray powder diffraction (XRD) patterns of bare CoO, bare $BaTaO_2N$ and CoO@$BaTaO_2N$ photoanode, standard patterns for CoO, $BaTaO_2N$ and FTO are also included.

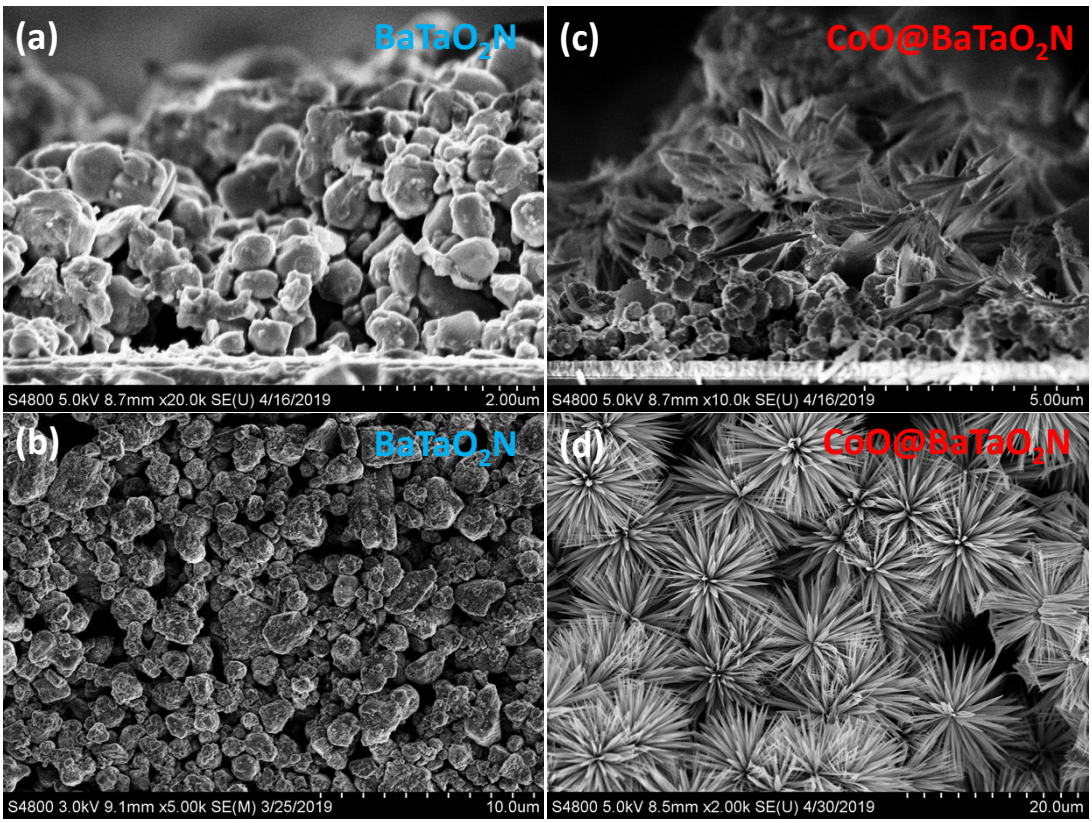

Figure S2. FESEM images of $BaTaO_2N$: (a) cross-section view and (b) top view; FESEM images of $CoO@BaTaO_2N$: (c) cross-section view and (d) top view

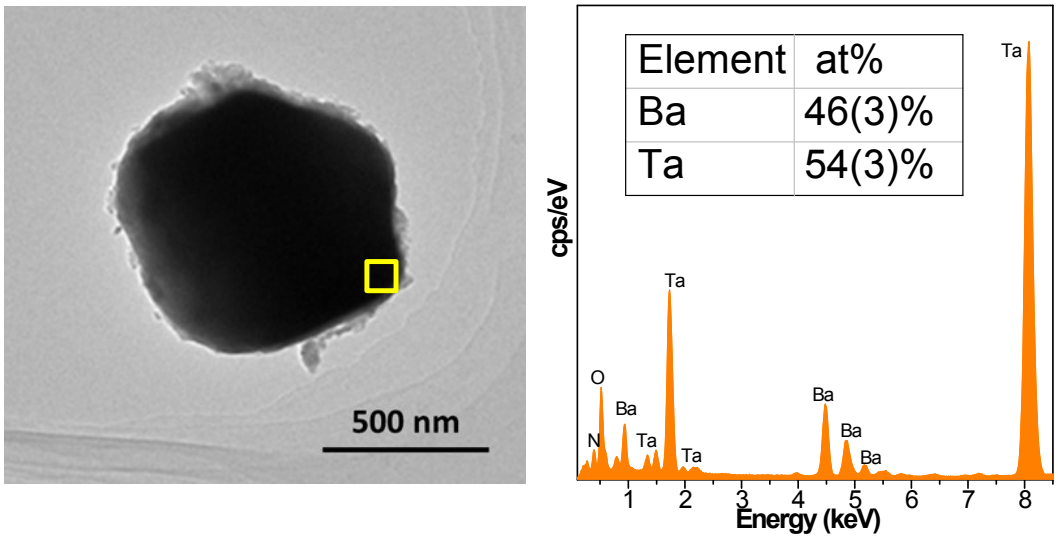

Figure S3. (a) TEM image of $BaTaO_2N$; (b) selected area electron dispersive X-ray spectroscopy (EDS) analysis at marked area of (a), cation compositions are listed in the table inserted, standard deviations are included in the parenthesis.

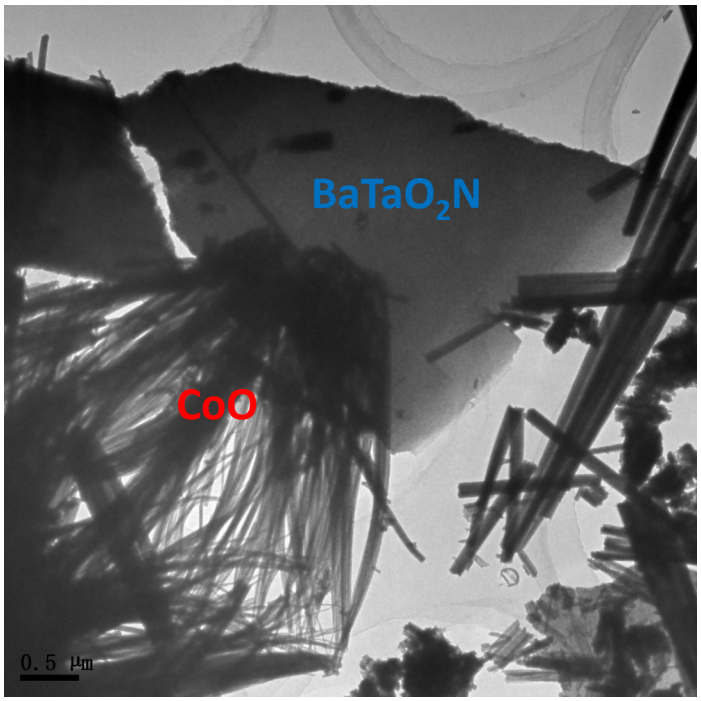

Figure S4. TEM image of CoO@$BaTaO_2N$ after sonication treatment

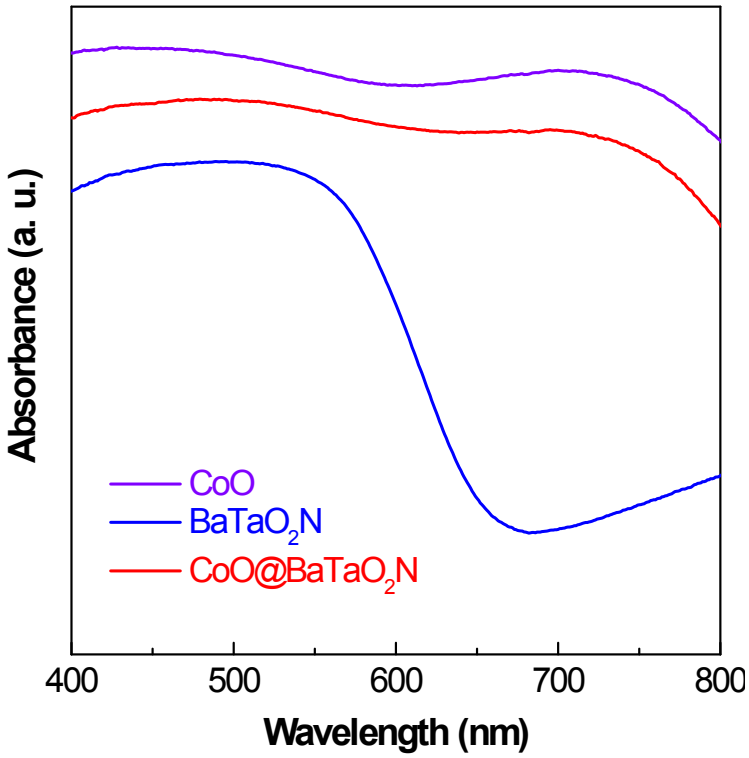

Figure S5. UV-vis absorption spectra of CoO, $BaTaO_2N$ and CoO@ $BaTaO_2N$

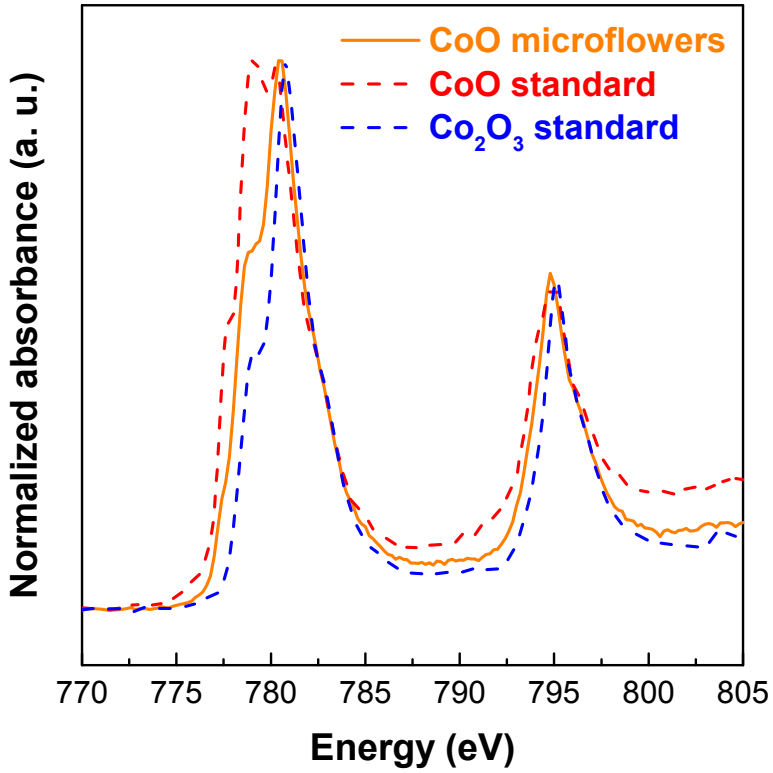

Figure S6. X-ray absorption spectra (XAS) of CoO microflowers, spectra of CoO and Co_2O_3 standard are also shown for comparisons. Linear combination fitting based on the reference spectra suggests a Co^{2+}/Co^{3+} ratio around 2/3.

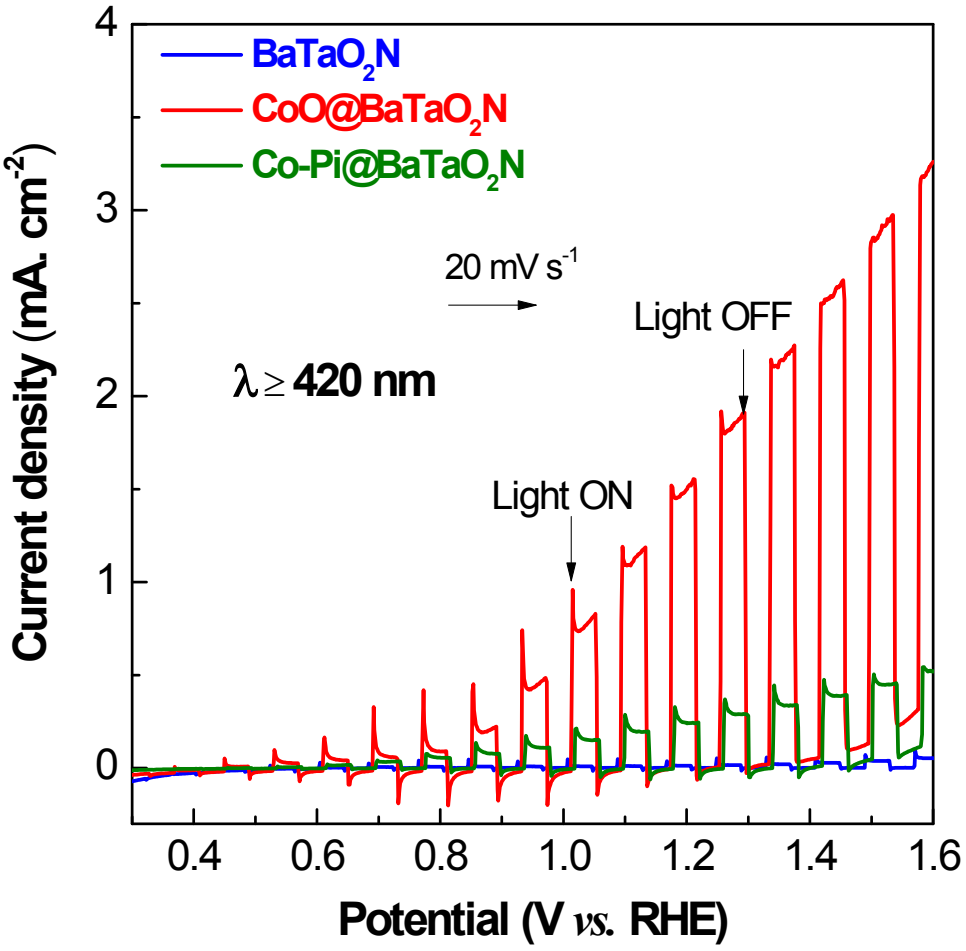

Figure S7. Linear sweep voltammetry of bare $BaTaO_2N$ photoanode, CoO@$BaTaO_2N$ photoanode and Co-Pi@ $BaTaO_2N$ photoanode under chopped visible light illumination ($\lambda \geq 420$ nm)

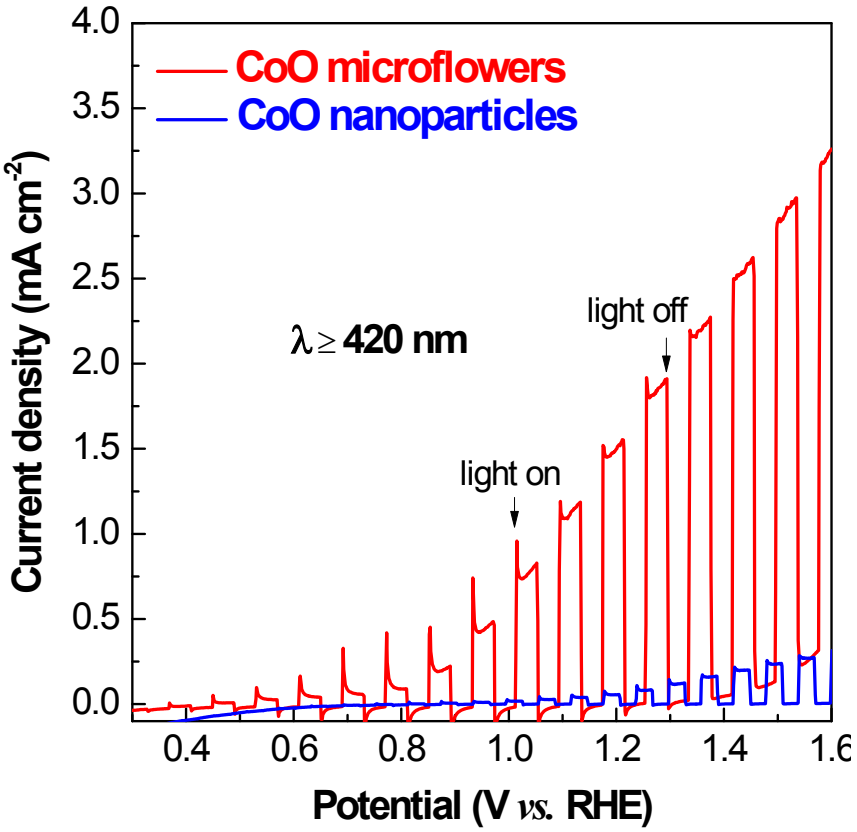

Figure S8. Linear sweep voltammetry of $BaTaO_2N$ photoelectrode deposited with CoO microflowers and CoO nanoparticles under chopped visible light illumination ($\lambda \geq 420$ nm)

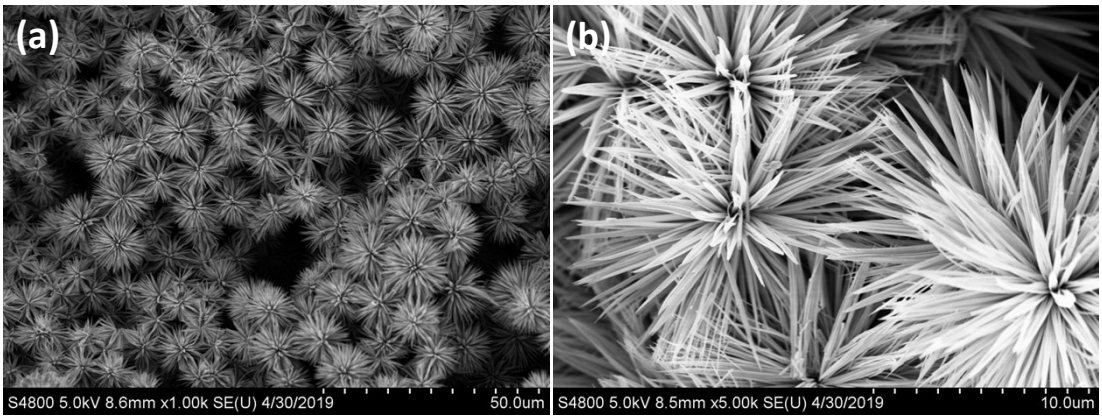

Figure S9. FESEM image of CoO@$BaTaO_2N$ photoelectrode after long tem PEC analysis

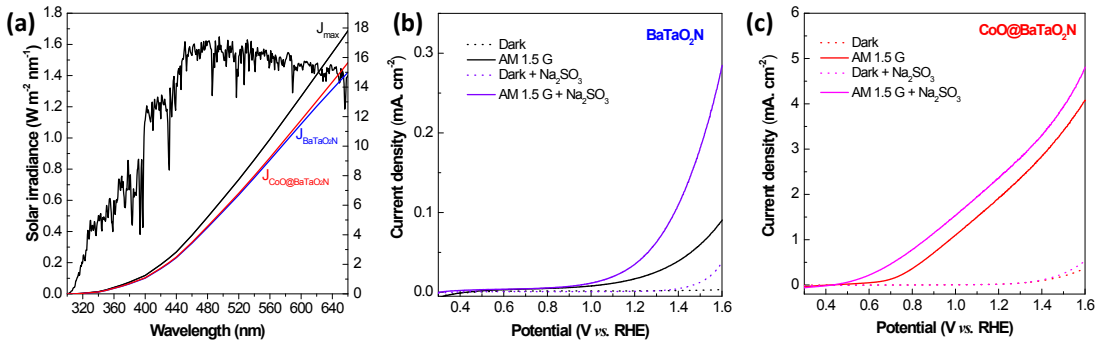

Figure S10. (a) Solar irradiance of AM 1.5 and integrated absorption photocurrent of $BaTaO_2N$ and CoO@$BaTaO_2N$. The integrated absorption photocurrent is obtained by multiplying the AM 1.5 solar spectrum with the absorption spectrum; (b) dark current (dotted line) and photocurrent under AM 1.5 illumination (solid line) of $BaTaO_2N$ with and without Na_2SO_3 (0.05 M) in KOH aqueous solution (0.1 M, pH = 13); (c) dark current (dotted line) and photocurrent under AM 1.5 illumination (solid line) of CoO@$BaTaO_2N$ with and without Na_2SO_3 (0.05 M) in KOH aqueous solution (0.1 M, pH = 13)

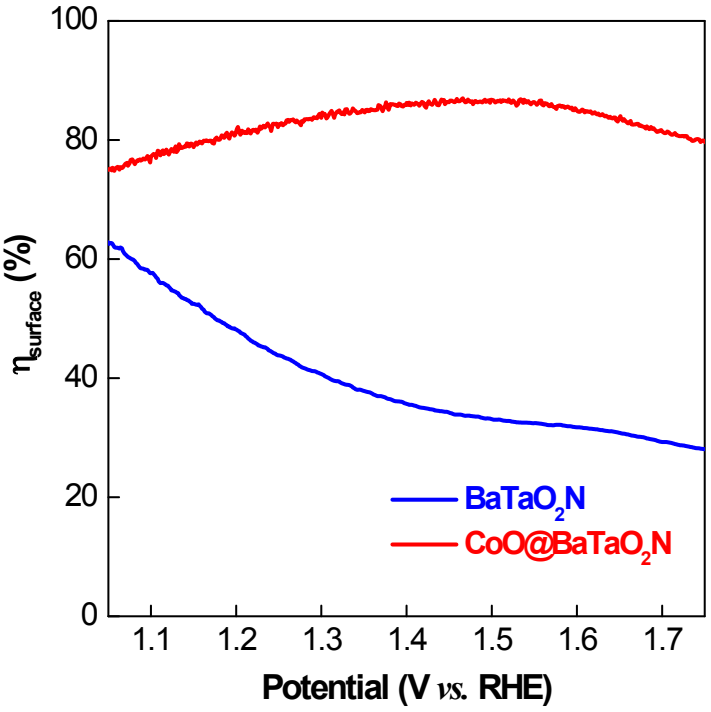

Figure S11. Surface charge transfer efficiency of bare $BaTaO_2N$ and CoO@ $BaTaO_2N$.

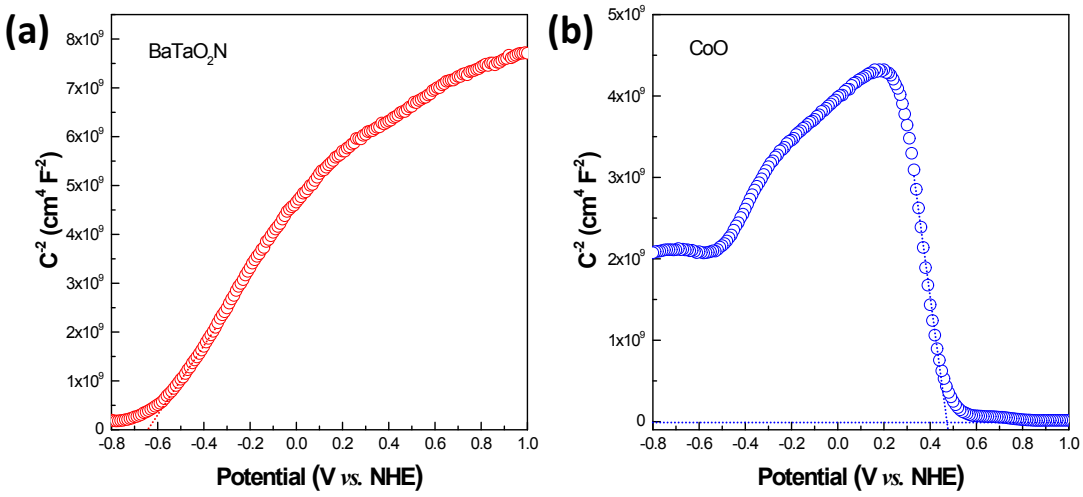

Figure S12. Mott-Schottky (MS) analysis of (a) $BaTaO_2N$ and (b) CoO; their flat band potential can be determined by extrapolating the linear part of MS curves down to the potential axis. $BaTaO_2N$ is a typical n-type semiconductor whilst CoO is p-type one according to the positive and negative MS curve slop, respectively. Assuming a 0.2 eV difference between flat band potential and conduction (valence) band for $BaTaO_2N$ (CoO), the band edge alignment of both compounds can be deduced.

Table S1. Summary of fitted electron lifetime τ and their relative amplitude of $BaTaO_2N$ and CoO@$BaTaO_2N$ deduced from the time-resolved PL spectra

Sample	Fitted electron lifetime (ns)			Relative amplitude (%)			Average lifetime <τ> (ns)	χ^2
	τ_1	τ_2	τ_3	f_1	f_2	f_3		
$BaTaO_2N$	22.2	189.9	1400.6	7.24	27.81	64.95	1332.0	1.02
CoO@$BaTaO_2N$	45.9	279.1	1790.7	7.86	27.89	64.26	1690.1	1.01

The average lifetime is calculated by equation:

$$<\tau> = \frac{f_1\tau_1^2 + f_2\tau_2^2 + f_3\tau_3^2}{f_1\tau_1 + f_2\tau_2 + f_3\tau_3} \quad \text{(S1)}$$

χ^2 : the goodness of fit parameter.

Reference

1. H. Zhang, S. H. Wei and X. X. Xu, *J. Catal.*, 2020, **383**, 135-143.
2. Y. H. Xie, Y. W. Wang, Z. F. Chen and X. X. Xu, *ChemSusChem*, 2016, **9**, 1403-1412.
3. F. X. Zhang, A. Yamakata, K. Maeda, Y. Moriya, T. Takata, J. Kubota, K. Teshima, S. Oishi and K. Domen, *J. Am. Chem. Soc.*, 2012, **134**, 8348-8351.
4. S. H. Wei, G. Zhang and X. X. Xu, *Appl. Catal. B-Environ.*, 2018, **237**, 373-381.
5. S. K. Pilli, T. E. Furtak, L. D. Brown, T. G. Deutsch, J. A. Turner and A. M. Herring, *Energ. Environ. Sci.*, 2011, **4**, 5028-5034.
6. P. Van der Heide, *X-ray photoelectron Spectroscopy - An introduction to principles and practices*, John Wiley & Sons, Inc, Hoboken, New Jersey, 2012.
7. R. G. Li, F. X. Zhang, D. G. Wang, J. X. Yang, M. R. Li, J. Zhu, X. Zhou, H. X. Han and C. Li, *Nat. Commun.*, 2013, **4**, 1432.