Supporting Information

CoPi Cocatalyst-Decorated TiO_2/NiO Nanotube Heterojunction Photoanode for Enhanced Photoelectrochemical Performance

Shouyun Zhang [1], Hongjin Chang [1], Dongyu Mei [1], Xu Liu [1], Fujian Lv [2,*], Zhao Wang [3], Qinrong Kang [4] and Ling Wu [1,*]

[1] Hubei Province Key Laboratory of Coal Conversion and New Carbon Materials, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China
[2] College of Chemistry and Environmental Science, Qujing Normal University, Qujing 655400, China
[3] Hubei Provincial Engineering Research Center of Racing Horse Detection and Application Transformation, Equine Science Research and Horse Doping Control Laboratory, Wuhan Business University, Wuhan 430056, China
[4] School of Resources and Safety Engineering, Wuhan Institute of Technology, Wuhan 430074, China

* Corresponding author. E-mail: lvfujian@mail.qjnu.edu.cn (F.L.); wuling2018@wust.edu.cn (L.W.)

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Text S1. Chemicals

Titanium (Ti, 99.9%) was purchased from Xingtai Shengshida Metal Materials Co., Ltd. Ammonium fluoride (NH_4F, A.R.), ethylene glycol ($C_2H_6O_2$, A.R.), sodium dihydrogen phosphate ($NaH_2PO_4·12H_2O$, A.R.), disodium hydrogen phosphate ($Na_2HPO_4·2H_2O$, A.R.), nickel(II) chloride hexahydrate ($NiCl_2·6H_2O$, A.R.), ethanol (C_2H_5OH, A.R.), cobalt(II) nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, A.R.), potassium chloride (KCl, A.R.), sodium hydroxide (NaOH, A.R.), and Boric acid (H_3BO_3, A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. Phosphoric acid (H_3PO_4, A.R.), nickel(II) sulfate hexahydrate ($NiSO_4·6H_2O$, A.R.), and hydrochloric acid (HCl, A.R.) were purchased from Tianjin Tianli Chemical Reagent Co., Ltd.

Text S2. Characterization methods

The morphology of the as-fabricated electrodes was investigated using a field-emission scanning electron microscope (SEM, JSM-7610F Plus, JEOL, Tokyo, Japan) at an accelerating voltage of 5–15 kV, and the elemental composition and distribution were analyzed using an attached energy-dispersive X-ray spectroscopy (EDS) system (JEOL, Tokyo, Japan). Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and EDS elemental mapping were recorded on a JEM-F200 transmission electron microscope (JEM-F200, JEOL., Tokyo, Japan) operated at 300 kV. The crystalline phases were characterized by an X-ray powder diffractometer (XRD, SmartLab SE, Rigaku Corporation, Tokyo, Japan) with Cu K_α radiation (λ = 0.15418 nm) in the 2θ range of 10–90° with a scan step of 1° min^{-1}. The surface elementary composition and chemical state were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000, ULVAC-PHI, Chigasaki, Japan), and all binding energies were calibrated using the C 1s peak at 284.6 eV as a reference. The diffuse reflectance spectra (DRS) were recorded on a UV-2550 spectrophotometer (UV-2550, Shimadzu Corporation, Kyoto, Japan) equipped with an integrating sphere using $BaSO_4$ as a reference, over the wavelength range of 200–800 nm with a slit width of 5 nm.

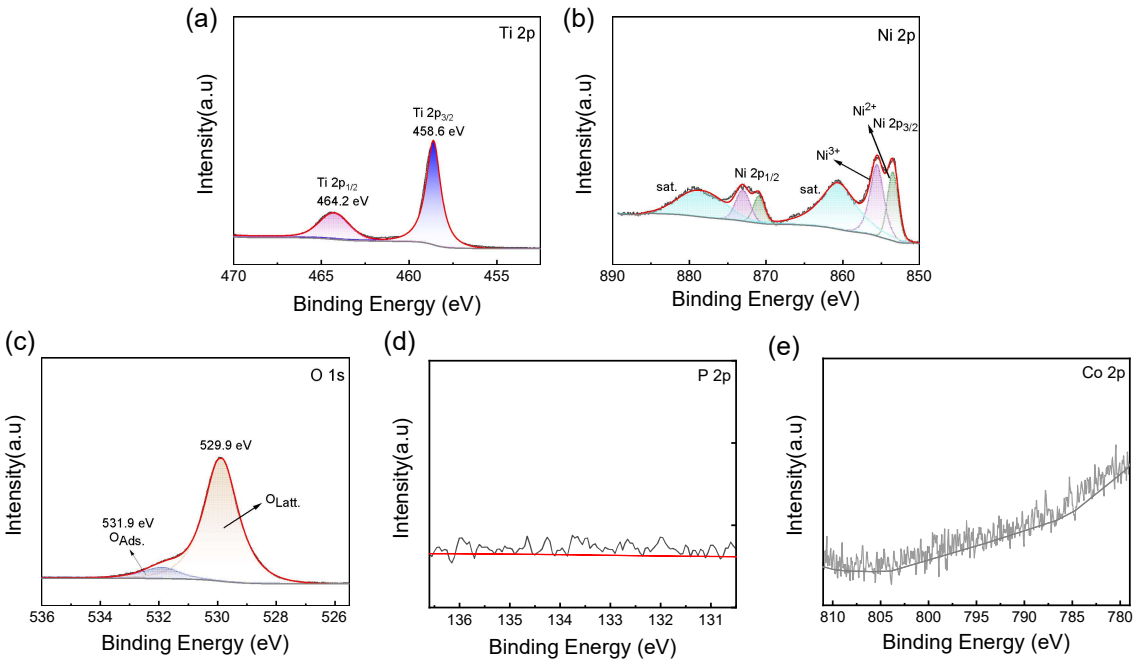


Figure S1. High-resolution XPS spectra of TN electrode: (**a**) Ti 2p, (**b**) Ni 2p, (**c**) O 1s, (**d**) P 2p and (**e**) Co 2p.

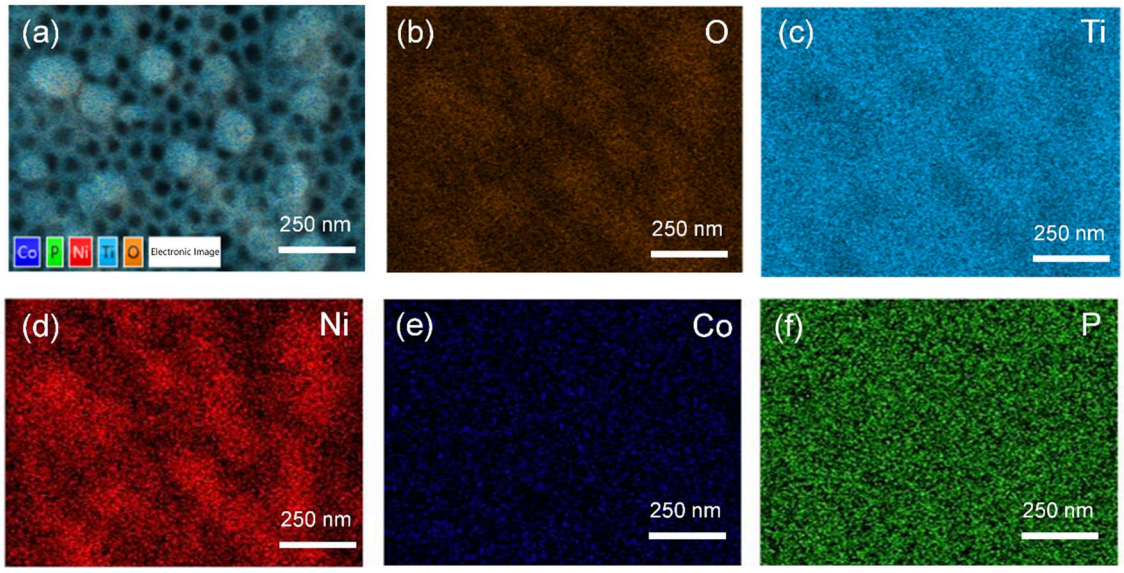


Figure S2. (**a**) SEM image of TNC photoanode, and the corresponding EDS elemental mapping of (**b**) O, (**c**) Ti, (**d**) Ni, (**e**) Co and (**f**) P.

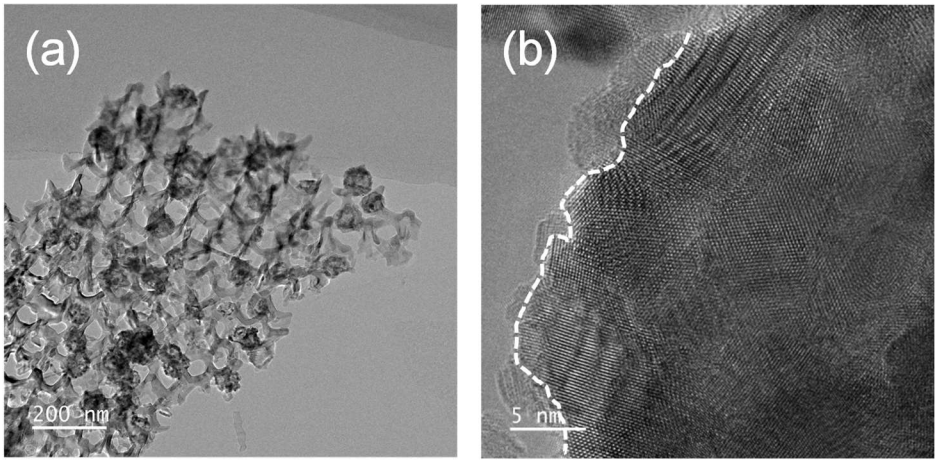


Figure S3. (**a**) TEM and (**b**) HRTEM images of TNC electrode.

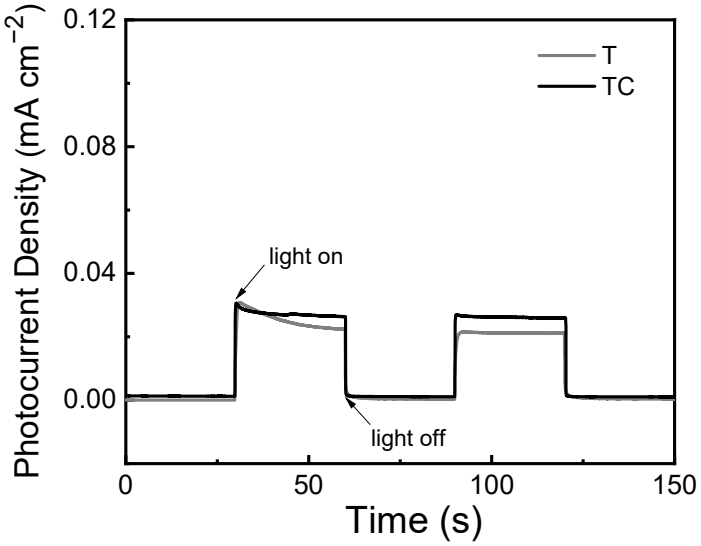


Figure S4. Photocurrent responses of T and TC electrodes.

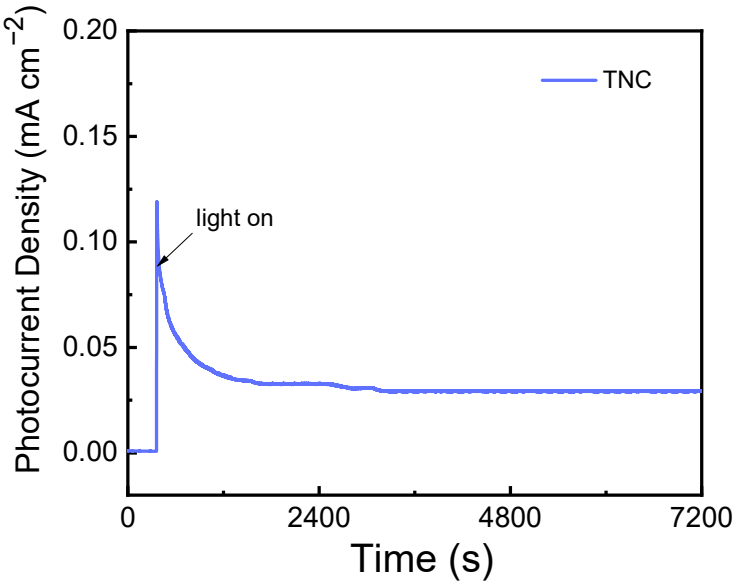


Figure S5. Photocurrent of TNC photoanode recorded at bias voltage of 0.6 V vs. Ag/AgCl under continuous illumination over 7200 s.

Table S1: Comparison of photocurrent enhancement of various photoanodes modified with different cocatalysts under AM 1.5G illumination

Photocatalyst	**Cocatalyst**	**Electrolyte**	**Irradiance (mW cm^{-2})**	**Bias Voltage (V vs. RHE)**	**Photocurrent Enhancement**	**Ref.**
NiO/TiO_2	CoPi	0.1 M Na_2SO_4	100	1.21	2.4-fold	This work
TiO_2/Fe_2O_3	CoPi	0.1 M KOH	100	1.23	1.2-fold	[1]
Au/TiO_2	CoO_x	0.2 M K_3PO_4	180	1.07	3-fold	[2]
$BiVO_4$	CoPi	1.0 M K_3BO_3	100	1.2	1.7-fold	[3]
$P\text{-}Fe_2O_3$	CoPi	1 M NaOH	100	1.23	1.2-fold	[4]
$N\text{-}TiO_2$	MnO_2	1 M NaOH	100	1.23	1.3-fold	[5]
$CdS/Ti^{3+}\text{-}SrTiO_3$	MnO_x	0.1 M Na_2SO_4	100	1.23	1.5-fold	[6]
$Ta{:}Fe_2O_3$	Ni_2P	0.1 M KOH	100	1.23	1.4-fold	[7]
$NiO/BiVO_4$	RuCoV-LDH	0.2 M KPi	100	1.23	1.2-fold	[8]
$BiVO_4/TiO_2$	$Co_2P_2O_7$	1 M KBi	100	1.23	2-fold	[9]

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