Self-Supporting MOF-Derived CoNi@C/Au@TiO₂ Nanotube Array Z-Scheme Heterocatalysts for Plasmon-Enhanced High-Efficiency Full Water Splitting

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Methods

Synthesis of TiO₂ nanotube array

The TiO₂ nanotube with a diameter of \sim 70 nm was prepared by previous report with minor modification.¹ Typically, Titanium foils (0.25 mm thick, 99.9 % purity, Aladdin,) were degreased by sonication in acetone, ethanol and isopropanol, successively followed by rinsing with deionized water; finally, the samples were dried with nitrogen gas. To perform the electrochemical TiO₂ nanotube formation, the foils were anodized by using a high-voltage potentiostat in a two-electrode configuration with a counter electrode made of platinum gauze. The electrolytes were explored using 1.5M lactic acid (LA, DL-Lactic acid, 90%, Aladdin), 0.1 M ammonium fluoride (NH₄F) and 5 wt.% deionized H₂O in ethylene glycol (99 vol. %) electrolytes. Anodization was carried out at room temperatures of electrolyte and 80 voltages for 30 times. After the anodization process, the samples were washed in ethanol and then dried in a nitrogen stream.

Fabrication of CoNi@C-TiO₂ catalyst

The ultra-thin CoNi-MOFs was in situ growth on the as-prepared TiO_2 array by electrostatic adsorption effect. Finally, the compared composite sample was heated to 750 °C at 10 °C min⁻¹ in the Ar atmosphere, kept at the peak temperature for 2 h, and allowed to cool down to room temperature.

Fabrication of CoNi@C-Au/TiO2 catalyst

The monolayer Au nanomembranes were prepared by the method of liquid/liquid interface self-assembly according to previous research.² Then, the nanomembranes were transferred carefully from the "soft" air-water interface onto the as prepared electrodes TiO_2 nanotube array according to previous reported.³ In details, 3 mL of colloidal AuNPs solution was put into a container, and 500 μ L of hexane was added to the solution to form a water/hexane interface; then, 3.7 mL of methanol was added into the mixture rapidly, the nanoparticles aggregate in the interface to form a golden

monolayer nanomembranes, and then the freshly prepared nanomembranes were transferred onto the surface of TiO_2 nanotube array. Then, the ultra-thin CoNi-MOFs were in situ grown on the as-prepared Au/TiO₂ array by electrostatic adsorption. Finally, the compared composite sample was heated to 750 °C at 10 °C min⁻¹ in the Ar atmosphere, kept at the peak temperature for 2 h, and allowed to cool down to room temperature.

Material Characterizations

The detailed microstructure and chemical composition of the samples were investigated by field emission scanning electron microscopy (SEM) using a Hitachi S4800 microscope operated at 10 kV and transmission electron microscopy (TEM) using a JEOL 2010 microscope operated at an accelerating voltage of 200 kV and equipped with an energy dispersive spectrometer. A transmission electron microscope (equipped with an energy-dispersive spectrometer) was used to characterize the detailed microstructures. Chemical compositions of the samples were investigated by X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi, Thermo Fisher Scientific). A 300-W xenon lamp equipped with a filter of $\lambda > 420$ nm (10 kW·m⁻²) was used for the illumination experiments. We study the crystal structure of the as-prepared samples by wide-angle X-ray diffraction (XRD, D8 ADVANCE, Germany BRUKER company) with a Cu target.

Electrochemical Characterizations

Electrochemical measurements were performed by electrochemical workstation (CHI660E) with a three-electrode electrochemical cell. All experiments were tested at room temperature, and KOH aqueous solution (pH=12) or H₂SO₄ (pH = 2) was used as the electrolyte. The as-prepared self-supporting CoNi@C-Au/TiO₂ nanotube array was directly used as work electrode. We used the carbon rod as the counter electrode and Ag/AgCl as the reference electrode. The current density was obtained on the geometrical area of the electrode, and the reversible hydrogen electrode scale was converted by Nernst equation. Before electrochemical measurements, the working electrode was cycling between 0 and 1 V versus Ag/AgCl (100 mV s⁻¹) for 150 cycles at room temperature. The polarization curves were obtained with a sweep rate of 5 mV



Fig. S1. The XRD pattern of the as-prepared TiO_2 nanotube array.



Fig. S2. TEM image of the AuNPs.



Fig. S3. EDX profile of the CoNi-MOF-Au/TiO₂.



Fig. S4. (a) TEM image of CoNi@C and (b) the size distribution of CoNi nanoalloy.



Fig. S5. XRD pattern of the CoNi@C.



Fig. S6. Nitrogen adsorption isotherms of the CoNi@C measured at 77 K.



Fig. S7 (a) CV curves recorded at different scan rate for CoNi@C-Au/TiO₂. (b-d) Plots of the capacitive current densities versus scan rate of the CoNi@C-Au/TiO₂, TiO₂ and CoNi@C-TiO₂ electrodes.



Fig. S8. Polarization curves of the discrete Au/TiO₂ and CoNi@C components, respectively, for (a) HER and (b) OER in 0.1M KOH with a potential scan rate of 5 mV s⁻¹. The current densities was based on the geometric area.



Fig. S9 A photograph of the as-prepared self-supporting $CoNi@C-Au/TiO_2$ electrodes with high O_2 and H_2 evolution performance.



Fig. S10. (a) ESI and (b) Mott-Schottky plots for CoNi@C-TiO₂ and CoNi@C-Au/TiO₂ electrodes with and without light irradiation at 1 kHz frequency in KOH (pH=12) at room temperature. The light source was 300 W xenon lamp equipped with a filter of λ > 420 nm (10 kW·m⁻²).



Fig. S11. EPR spectra of DMPO- \cdot O₂⁻ adduct (formation) with irradiation for 120 s in the presence of CoNi@C-TiO₂ and CoNi@C-Au/TiO₂ nanocomposite.



Fig. S12. Stability test of the as-prepared CoNi@C-Au/TiO₂ water splitting electrode for OER in alkaline solution, measured at 0.8 V (vs. Ag/AgCl).

Materials	Light source	Photocurrent density (mA cm ⁻²)	Conditions for photocurrent	Reference
LDC-S-TiO ₂ /C	500 W Xenon lamp (λ> 400 nm)	0.135	/	Adv. Sci. 2018, 5, 1700870
TiO ₂ nano-branched arrays	simulated AM1.5	0.95	1.23 V _{RHE}	Inter. J. Hydro. Energy 2018 ,43, 21365
10% SrSO ₄ /TiO ₂	simulated sunlight at 100 mW/cm ²	0.3	$0.58 V_{RHE}$	Nano Energy 2019, 59, 129
FH-TiO ₂	300 W high-pressure Hg lamp (λ > 365 nm)	2.7	$1.0 V_{RHE}$	Adv. Mater. 2019, 31,1806596
TiO ₂ hierarchical spheres	300 W Xe lamp	1.64×10 ⁻³	0.78 V _{RHE}	Inter. J. Hydro. Energy 2018, 43, 13190
5% MoS ₂ /10% CdSe/TiO ₂	300 W xenon lamp (AM1.5G)	3.19	$1.0 V_{RHE}$	Micropor. Mesopor. Mater. 2019, 284, 403
CoNi@C-Au/TiO2-NA	300 W Xenon lamp (λ> 420 nm)	3.46	0.9 V _{RHE}	This work

Table S1. Comparison of the photocurrent responses between CoNi@C-Au/TiO₂-NA photocatalysts and previous reports about TiO₂ photocatalysts at bias of 0 V.

References:

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- 2 Y. Shin, J. Song, D. Kim and T. Kang, Adv. Mater., 2015, 27, 4344-4350.
- 3 H. Wu, C. Li, Z. Zhao, H. Li and Y. Jin, *ACS Appl. Mater. Interfaces*, 2016, **8**, 1594-1599.