Supporting information

Hydrophilic polypyrrole and g-C₃N₄ co-decorated ZnO nanorod arrays for stable

and efficient photoelectrochemical water splitting

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Experimental section

Materials: Zinc nitrate hexahydrate $(Zn(NO_3)_2) \cdot 6H_2O$, hexamethylenetetramine (HMTA), sodium sulfite (Na₂SO₃), sodium sulfate (Na₂SO₄), ferric chloride hexahydrate (FeCl₃·6H₂O), and pyrrole were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Zinc oxide (ZnO) target (99.99%, purity) was purchased from Beijing Zhongnuo Advanced Material Technology Co., Ltd. Graphitic carbon nitride (g-C₃N₄) aqueous solution (0.1 mg mL⁻¹) was purchased from Jiangsu Xianfeng Nano Technology Co., Ltd.

Synthesis of ZnO photoanode

The ZnO photoanode was prepared by a two-step method. Firstly, the ZnO seed layer was deposited on a clean FTO substrate (1cm×2cm, 7 ohm cm⁻²) using a radio frequency magnetron sputtering system by sputtering the ZnO target for 20 min (working pressure: 2.0 Pa, power: 100 W, Ar flow rate: 55 sccm and O₂ flow rate: 5 sccm). Secondly, the ZnO photoanode was prepared by a hydrothermal method. The precursor solution was prepared by dissolving 50 mM Zn(NO₃)₂ and 50 mM HMTA in 200 ml pure water. Then, the seed-deposited FTO glass was placed into a 50 ml Teflon-lined stainless-steel autoclave containing 20 mL precursor solution, and the FTO was leaned against the wall of the autoclave with the conductive surface facing down. The reaction temperature and time were set as 95 °C and 10 h, respectively. Finally, the resulting samples were washed with pure water and absolute ethanol several times and dried at 60 °C overnight.

Synthesis of ZnO/PC and ZnO/PC-P photoanode

The ZnO/PC photoanode was fabricated by a spin-coating method. Typically, 2 mL g-C₃N₄ ethanol solution was mixed uniformly with 0.2 mL pyrrole. Then, a drop (20 uL) of the mixture was spin-coated onto a ZnO photoanode at 2000 rpm for 20 s. After repeated spin-coating several times, a drop (20 uL) of 0.05 M FeCl₃ ethanol solution was spin-coated onto a ZnO photoanode at 2000 rpm for 20 s. Subsequently, the sample was put in a refrigerator (3 °C) overnight for the completed polymerization of pyrrole to form polypyrrole. Finally, the sample was washed with ultrapure water and dried in an oven at 60 °C for 12 h. The as-obtained sample (polypyrrole and g-C₃N₄ codecorated ZnO nanoarrays) was termed as ZnO/PC photoanode. The ZnO/PC photoanode was further treated by air plasma at 60 W for 10 min to get ZnO/PC-P photoanode. In addition, using the same method, spin-coating g-C₃N₄ ethanol solution onto the ZnO photoanode was denoted as ZnO/g-C₃N₄ photoanode while spin-coating pyrrole and FeCl₃ ethanol solution (the preparation of polypyrrole) was denoted as ZnO/polypyrrole photoanode.

Synthesis of g-C₃N₄ powder

The g-C₃N₄ powder was synthesized by the conventional polymerization method. To be specific, 20 g melamine was put in a crucible and then thermally treated at 550 °C for 4 h. Then, the obtained yellow particles were ground for fine powders. The powders were dispersed in ultrapure water for ultrasonic treatment (100 W, 12 h). After centrifuging and washing treatment, the sample was dried at 60 °C for 6 h. Finally, the as-obtained g-C₃N₄ powders were dispersed in an aqueous solution for experiments.

Synthesis of Polypyrrole

Polypyrrole was synthesized by the self-polymerization of pyrrole. Typically, 0.2 mL pyrrole was mixed with 2 mL ethanol solution uniformly. Then, a drop (20 uL) of the mixture was spin-coated onto an FTO glass at 2000 rpm for 20 s. After repeated spin-coating several times, a drop (20 uL) of 0.05 M FeCl₃ ethanol solution was spin-coated onto the FTO glass at 2000 rpm for 20 s. The polymerization equation of Polypyrrole was listed as follows. After the reaction for 12 h, the sample was washed with ultrapure water and dried in an oven at 60 °C overnight.



Characterization

The morphology of samples was characterized by using a scanning electron microscope (SEM, Carl Zeiss Ultra Plus). The phase and crystal structure of samples were certified by a powder X-ray diffractometer (XRD, Rigaku SmartLab SE) and transmission electron microscopy (TEM, FEI Talos F200X G2). The hydrophilicity of samples was estimated by contact angle (CA) tests (Dataphysics OCA25). The chemical composition and element valence states were detected by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Nexsa). Fourier-transform infrared (FT-IR) spectra were recorded by an FT-IR spectrometer (Thermo Scientific Nicolet iS20). A UV-vis spectrophotometer (Shimadzu UV 3600) was used to investigate the light absorption ability of samples. The photoluminescence (PL) spectra were collected through an optical multichannel analyzer (Acton SP2500i) excited by a 325 nm laser. The time-resolved transient photoluminescence (TRPL) spectra were recorded on an optically

triggered streak camera system (C10910, Hamamatsu) at 325 nm with a repetition rate of 1 kHz (Opera Solo, Coherent). The pulse width of the laser is 150 fs.

Photoelectrochemical (PEC) Measurements

The photoelectrochemical (PEC) measurement was carried out in a three-electrode system using an electrochemical workstation (Chenhua, CHI660B). The as-prepared photoanode, saturated Ag/AgCl electrode, and Pt mesh electrode were used as the working electrode, reference electrode, and counter electrode, respectively. 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte (pH=6.68). The measured potential versus Ag/AgCl (EAg/AgCl) was converted to reversible hydrogen electrode potential (E_{RHE}) by the following Nernst formula: $E_{RHE}=E_{Ag/AgCl}+0.197+0.059pH$. The simulated solar light (100 mW cm⁻²) was provided by a sunlight simulator (NBET, Solar-500) equipped with an AM 1.5G filter. Linear sweep voltammetry (LSV) plots were measured at a scan rate of 10 mV s⁻¹. Photocurrent-time (J-t) curves were performed on a light turn-on/off system with an applied potential of 1.23 V_{RHE}. The incident photon-to-current conversion efficiency (IPCE) was measured at 1.23 V vs. RHE using a 150 W Xe lamp as the simulated light source coupled with a monochromator. Electrochemical impedance spectra (EIS) were collected under illumination at the open-circuit potential in the frequency of 0.1 to 10⁵ Hz with a 5 mV amplitude. Mott-Schottky (M-S) plots were obtained at the potential range of -1 to 1 V vs. Ag/AgCl with a frequency of 1000 Hz. The electrochemically active surface area (ECSA) is proportional to C_{dl}. C_{dl} was measured by cyclic voltammetry (CV) plots in a non-Faradaic potential range of 0.1 to 0.2 V vs. Ag/AgCl at the scan rates of 0.02, 0.04,

0.06, 0.08, and 0.10 V s⁻¹, respectively. The charging current difference (Δj) between the anodic (ja) and cathodic charging current (jc) in the middle of the potential window was plotted against the scan rate, and the linear slope is twice C_{dl}.

Calculations

The applied bias photon-to-current efficiency (ABPE) was calculated according to the following equation:

$$ABPE(\%) = \frac{(1.23V - V) \times J}{P} \times 100\%$$

where J is the photocurrent density (mA cm⁻²), V is the applied bias (V vs. RHE), and P is the incident light density (100 mW cm⁻²).

The incident photon-to-current conversion efficiency (IPCE) was calculated at 1.23 V *vs.* RHE according to the following equation:

 $IPCE(\%) = \frac{1240J(\lambda)}{P(\lambda)\lambda} \times 100\%$

where $J(\lambda)$, λ , and $P(\lambda)$ are photocurrent density (mA cm⁻²) under illumination by monochromatic light, the wavelength of monochromatic light (nm), and the power density of monochromatic light (mW cm⁻²), respectively.

The light-harvesting efficiency (LHE) is calculated based on the following equation:

$$LHE(\lambda) = 1 - 10^{-A(\lambda)}$$

where $A(\lambda)$ is the absorbance at wavelength λ .

The water oxidation photocurrent density could be calculated by the following formula:

$$J_{H20} = J_{abs} \times \eta_{bulk} \times \eta_{surface}$$

where J_{abs} is the photocurrent density when the absorbed photon is completely converted into current. As a hole scavenger, Na₂SO₃ can effectively trap the holes that arrived at the surface, without influencing the charge separation on the electrode ($\eta_{surface}$ assumed to be 100%). Therefore, the charge separation efficiency in the bulk (η_{bulk}) and surface charge injection efficiency ($\eta_{surface}$) could be deduced with the following equations:

$$\eta_{bulk} = J_{SO3}^{2-}/J_{abs}$$

 $\eta_{surface} = J_{H2O}/J_{SO3}^{2-}$

where J_{H20} and J_{S03}^{2-} are the photocurrents achieved in the electrolytes of 0.5 M Na₂SO₄ and 0.5 M Na₂SO₃ + 0.5 M Na₂SO₄, respectively. J_{abs} can be calculated according to the following equation:

$$J_{abs} = \int \frac{\lambda}{1240} \varphi_{AM1.5G}(\lambda) LHE(\lambda) d\lambda$$

where λ is the wavelength (nm), $\varphi_{AM1.5G}(\lambda)$ provides the simulated solar spectral irradiance (W m⁻² nm⁻¹), and *LHE* (λ) is the light-harvesting efficiency.

The photoanode carrier density (N_d) can be quantified by the equation:

$$N_d = \frac{2}{e_0 \varepsilon \varepsilon_0} \left[\frac{d\left(\frac{1}{C^2}\right)}{dV} \right]^{-1}$$

where *C* is the space charge capacitance, e_0 is electron charge (1.602 × 10⁻¹⁹ C), ε_0 is the dielectric constant of ZnO (10), ε is permittivity in vacuum (8.85 × 10⁻¹² F m⁻¹), N_d is the charge donor density (cm⁻³), *V* is the applied potential of photoanode.



Fig. S1 HADDF and elemental mapping images of ZnO/PC-P photoanode.



Fig. S2 XPS survey spectra of ZnO, ZnO/PC, and ZnO/PC-P photoanodes.



Fig. S3 (a) UV/visible diffuse reflectance spectra of ZnO, ZnO/PC, ZnO/PC-P, $g-C_3N_4$, and polypyrrole, respectively. The inset is the digital photograph of ZnO, ZnO/PC, and ZnO/PC-P photoanodes. (b) Tauc plots of ZnO, ZnO/PC, and ZnO/PC-P photoanodes for the calculation of direct bandgap. (c) Tauc plots of $g-C_3N_4$ and polypyrrole for the calculation of indirect bandgap.

Table S1 Bandgaps of different samples.

				-	
Sample	ZnO	ZnO/PC	ZnO/PC-P	g-C ₃ N ₄	polypyrrole
$E_{g}(eV)$	3.262	3.253	3.251	2.73	2.35

Additional discussion

The light-harvesting capabilities were investigated using UV-vis diffuse reflectance spectra, as presented in **Fig. S3**. The ZnO/PC, and ZnO/PC-P samples present enhanced absorption capacity of visible light compared to the pristine ZnO, originating from the modification by polypyrrole and g-C₃N₄. The photograph in **Fig. S3** indicates that the white ZnO photoanode turns pale yellow after the decoration of polypyrrole and g-C₃N₄. The bandgaps of samples were evaluated by the Tauc plot, as shown in **Figs. S3b** and **c**. The bandgaps of samples were listed in **Table S1**. It is seen that the bandgaps of pure ZnO, g-C₃N₄, and polypyrrole are similar to that reported in the literature.



Fig. S4 LSV curves of different samples.



Fig. S5 (a) LSV curves of ZnO and ZnO/polypyrrole photoanodes with different spincoating times of polypyrrole, e.g., ZnO/polypyrrole-5 represents that this sample is prepared by spin-coating polypyrrole 5 times on the ZnO photoanode. (b) LSV curves of ZnO and ZnO/g-C₃N₄ photoanodes with different spin-coating times of g-C₃N₄, e.g., ZnO/g-C₃N₄-5 represents that this sample is prepared by spin-coating g-C₃N₄ 5 times on the ZnO photoanode.



Fig. S6 CV curves of (a) ZnO, (b) ZnO/PC, and (c) ZnO/PC-P photoanodes at different scan rates from 20 to 100 mV s⁻¹.



Fig. S7 LSV curves of ZnO, ZnO/PC, and ZnO/PC-P photoanodes measured in 0.5 M $\,$

 Na_2SO_4 and 0.5 M Na_2SO_3 electrolyte.



Fig. S8 (a) UV-vis absorption spectra and (b) LHE of ZnO, ZnO/PC, and ZnO/PC-P photoanodes. (c) Energy density flux of the standard solar spectrum of the AM 1.5G. (d) Calculated current density flux and integrated current density (J_{abs}) of ZnO, ZnO/PC, and ZnO/PC-P photoanodes.



Fig. S9 TEM images of (a) a ZnO nanorod before testing, (b) a ZnO nanorod after testing, (c) a ZnO/PC-P nanorod before testing, and (d) a ZnO/PC-P nanorod after testing.



Fig. S10 O 1s spectra of (a) the ZnO/PC photoanode before and after testing, (b) the ZnO/PC-P photoanode before and after testing.



Fig. S11 Long-term *j*-t curves of ZnO/polypyrrole-7 and ZnO/g- C_3N_4 -7 photoanodes.



Fig. S12 O_2 amount of ZnO/PC and ZnO/PC-P photoanodes at 1.23 V_{RHE} under AM

1.5~G illumination in $0.5~M~Na_2SO_4$ solution.

Dhataanada	Flootrolyto	Irradiated light and	Photocurrent	Ref.	
Filotoanode	Electionyte	intensity	density (bias)		
		AM 1.5G simulated	0.4 mA cm ⁻²		
Y:ZnO/PCN	Na_2SO_4	solar light, 100	(1.23 V vs.	S 1	
		mW cm ⁻²	RHE)		
		AM 1.5G simulated	0.95 mA cm ⁻²		
ZnO/CNNS	KH_2PO_4	solar light, 100	(1.23 V vs.	S2	
		mW cm ⁻²	RHE)		
		AM 1.5G simulated	0.25 mA cm ⁻²		
$ZnO/g-C_xN_y$	КОН	solar light, 100	(1.23 V vs.	S3	
		mW cm ⁻²	RHE)		
	$N_{2} S^{\perp}$	AM 1.5G simulated	0.7 mA cm ⁻²		
$ZnO/g-C_3N_4$	Na_2ST	solar light, 100	(1.23 V vs.	S4	
	1Na ₂ SO ₃	mW cm ⁻²	RHE)		
		AM 1.5G simulated	0.12 mA cm ⁻²		
ZnO/Pt/g-C ₃ N ₄	Na_2SO_4	solar light, 100	(0.5 V vs.	S5	
		mW cm ⁻²	Ag/AgCl)		
		AM 1.5G simulated	0.66 mA cm ⁻²		
ZnO/ZnS/g-C ₃ N ₄	Na_2SO_4	solar light, 100	(1.23 V vs.	S6	
		mW cm ⁻²	RHE)		
		AM 1.5G simulated	1.21 mA cm ⁻²	Thic	
ZnO/PC-P	Na_2SO_4	solar light, 100	(1.23 V vs.	1 1115	
		mW cm ⁻²	RHE)	WOIK	

Table S2 PEC performance of ZnO/g-C₃N₄-based photoelectrodes.

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