

**Construction of WO₃ quantum dots / TiO₂ nanowire arrays type II
heterojunction via electrostatic self-assembly for efficient solar-driven
photoelectrochemical water splitting**

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Characterization

The crystalline phases of the prepared samples were examined by a DX-2700BH X-ray powder diffractometer (XRD). The morphology was recorded by a field emission scanning electron microscope (FESEM, SIGMA 300) and a high-resolution transmission electron microscope (HRTEM, JEM-2100F) equipped with an energy dispersive X-ray spectrometer (EDS). The elemental chemical states of the samples were examined using an X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) with a monochromatic Al K α source (1486.6 eV). All the binding energies were calibrated using the C1s peak at 284.8 eV as the reference. The diffuse reflection spectra (DRS) of the samples were recorded using a scan UV-vis spectrophotometer (Shimadzu UV-3600 plus) equipped with an integrating sphere assembly, and BaSO₄ was used as the reference.

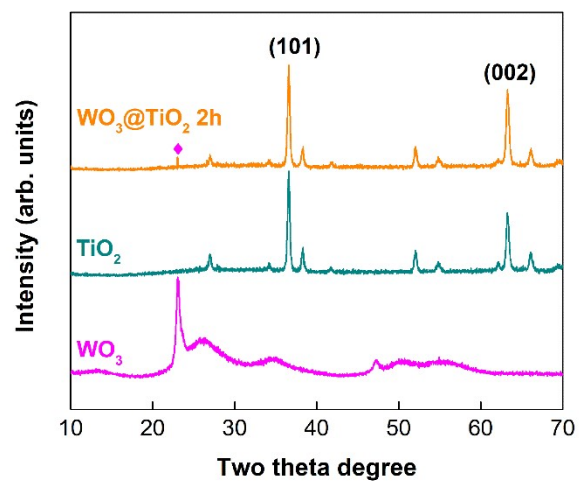


Fig. S1 XRD pattern of the as-prepared samples.

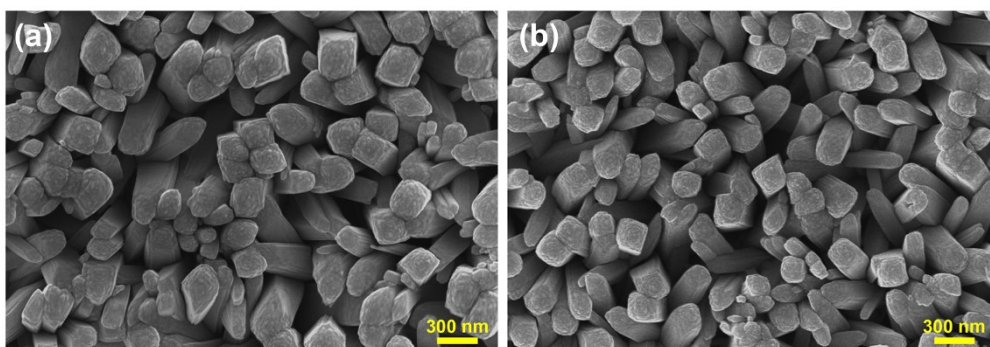


Fig. S2 FESEM images (top view) of the (a) TiO_2 nanowire arrays and (b) $WO_3@TiO_2$ 2h samples.

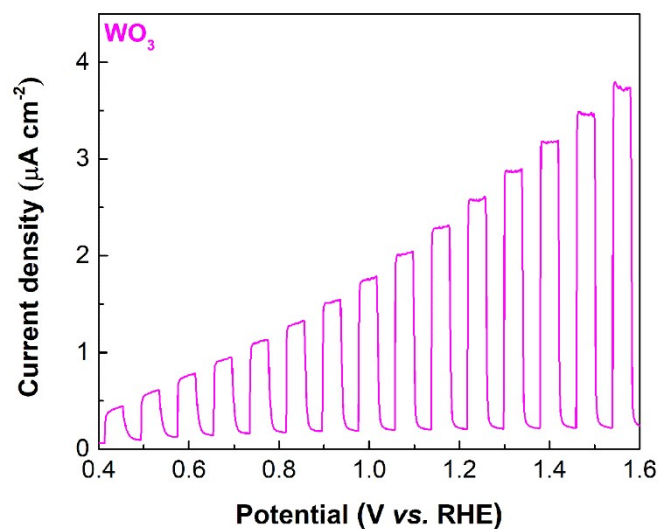


Fig. S3 Photocurrent density-potential curves of the WO₃ electrode.

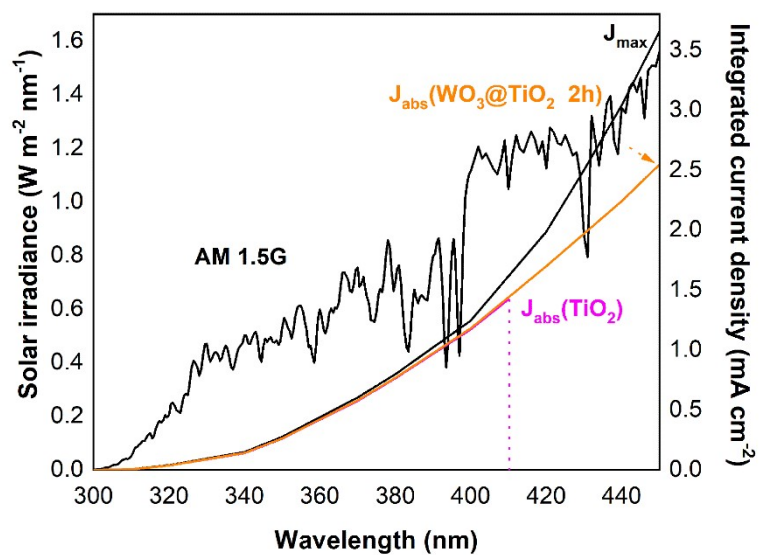


Figure S4. J_{\max} and J_{abs} of the TiO₂ and WO₃@TiO₂ 2h electrodes under AM 1.5G irradiation. J_{\max} curve is calculated using a trapezoidal integration of AM 1.5G spectrum. The J_{abs} curve was obtained via multiply the AM 1.5G solar spectrum with absorption spectrum and then integrate.

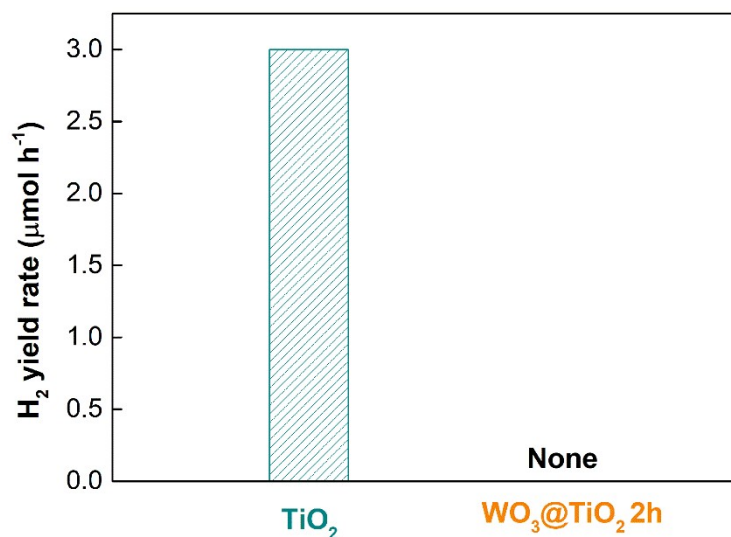


Fig.S5 Photocatalytic performance of different electrodes (methanol (10 vol.%) as sacrificial agent; 300W Xenon lamp; photodeposition of Pt (2 wt.%)).

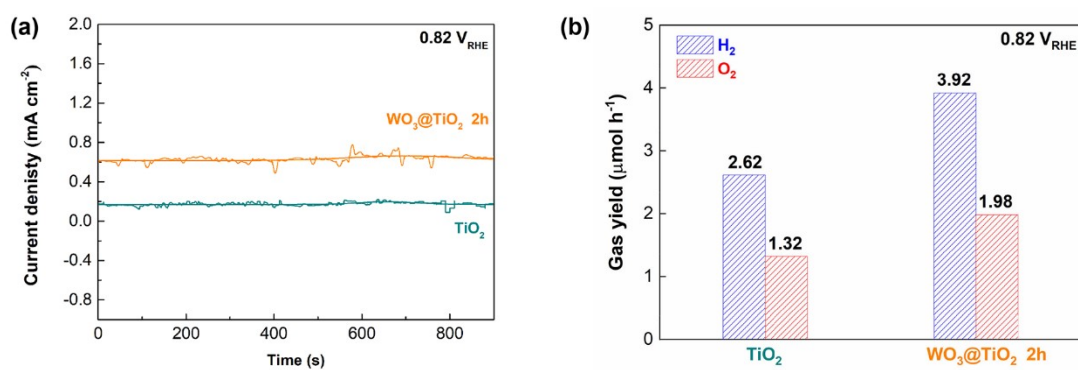


Fig. S6 (a) Steady-state photocurrent density at 0.2 V vs. Ag/AgCl (0.82 V vs. RHE) for the TiO₂ and WO₃@TiO₂ 2h photoanodes; (b) Photoelectrocatalytic overall water splitting with the TiO₂ and WO₃@TiO₂ 2h as photoanodes at 0.2 V vs. Ag/AgCl (0.82 V vs. RHE).

Table S1 Summary of PEC performance of WO₃-based and TiO₂-based photoanodes

Photoanode	Light	Photocurrent density at 1.23 V _{RHE} (mA cm ⁻²)	H ₂ yield rate (μmol h ⁻¹) at 1.23 V _{RHE}	O ₂ yield rate (μmol h ⁻¹) at 1.23 V _{RHE}	Ref.
γ-graphyne/TiO ₂	AM1.5 G (100 mW cm ⁻²)	0.75	/	/	1
WO ₃ /TiO ₂ nanoplates	AM1.5 G (100 mW cm ⁻²)	0.25	/	/	2
TiO ₂ @g-CN nanorods arrays	AM1.5 G (100 mW cm ⁻²)	0.91	/	/	3
WO ₃ @α-Fe ₂ O ₃	AM1.5 G (100 mW cm ⁻²)	1.66	/	/	4
WO _{3-x} @TiO _{2-x}	500 W Xe lamp (100 mW cm ⁻²)	~3.2	56	27	5
TiO ₂ /BiVO ₄ /SnO ₂	AM1.5 G (100 mW cm ⁻²)	~2.3	/	/	6
WO _{3-x} /TiO ₂	300 W Xe lamp (320 mW cm ⁻²)	4.16	69.6 (1.2 V _{RHE})	~34.8 (1.2 V _{RHE})	7
BN ZnO/TiO ₂	AM1.5 G (100 mW cm ⁻²)	2.75	45.6	21.8	8
α-Fe ₂ O ₃ /Au/TiO ₂	AM1.5 G (100 mW cm ⁻²)	1.05	18.67	9.24	9
WO₃@TiO₂ 2h	AM1.5 G (100 mW cm ⁻²)	~1.5	14.42	7.25	This work

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