Supporting Information

Enhanced Photoelectrochemical Water Splitting of In-Doped TiO_2 Nanorods with Oxygen Vacancies: Synergistic Effects of Band Structure and Charge Carrier Dynamics Engineering

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1.1 Materials for the experiments

Fluorine-doped tin oxide substrates (FTO) coated glasses, acetone, ethanol, deionized water, acetylacetone, tetrabutyl titanate, hydrochloric acid and Indium chloride ($InCl_3$).

1.2 Preparation of TiO_2 seed layer by spin-coating method

Add 0.015M acetylacetone, 0.05M tetrabutyl titanate and 0.05M ethanol to 50ml deionised water to prepare the spin coating solution. A clean 1.5*3 cm FTO is fixed on the spin coater at 2000 rpm for 60 s and spin coated three times. After spin coating, the FTO is removed and heated at 60 °C for 10 minutes on a heating table. The sample was then transferred to a muffle furnace and annealed at 450 °C for 30 min. After cooling, the sample was removed and repeatedly rinsed with deionised water and heated on a heating table at 60 °C for 10 min.

1.3 Preparation of TiO_2 NRs

To 30 ml of deionised water add 30 ml of hydrochloric acid and 0.05 M tetrabutyl titanate. Transfer the FTO with the TiO_2 seed layer to the above solution, placing the side with the seed layer towards the bottom. Transfer to an oven and hold at 160 °C for 6 h. After completion of hydrothermal heating remove the FTO and wash repeatedly, dry by heating at 60 °C on a heating table and then transfer to a muffle furnace to anneal at 450 °C for 2 h.

1.4 Preparation of In/TiO_2 nanorod arrays (NRs)

To 30 ml of deionised water add 26 ml of hydrochloric acid with tetrabutyl titanate and indium chloride in the ratios 2:10, 4:10, 6:10 and 9:10. Transfer the FTO with the TiO_2 seed layer to the above solution, placing the side with the seed layer towards the bottom. Transfer to an oven and hold at 160 °C for 6 h. After completion of hydrothermal heating remove the FTO and wash repeatedly, dry by heating at 60 °C on a heating table and then transfer to a muffle furnace to anneal at 450 °C for 2 h.

1.5 Characterization

The scanning electron microscope (SEM, JEOL JSM-7800 F) and transmission electron microscopy (TEM, JEOL JEM-2100) were utilized to study the morphology of the prepared samples. An X-ray diffractometer (PANalytical X'pert PRO, Cu Kα irradiation (λ = 0.154184 nm)) was employed to study the crystal structure of the hybrid films. Raman spectra (Jobin Yvon LabRAM Solei) were collected using a confocal laser Raman spectrometer equipped with a wavelength of 532 nm for STR500.The chemical elements and states of the films were recorded with an X-ray photoelectron spectrometer (XPS, AXIS ULtrabld) using Al Ka (1486.6 eV) radiation as X-ray source and calibrated by C 1s (284.8 eV). A double-beam UV 4100 UV–vis-NIR spectrophotometer was used to investigate the UV–vis absorption spectra of the hybrid structure films. The PL spectra was obtained by using a FLS 980 fluorescence spectrophotometer at room temperature.

1.6 PEC measurements

The PEC measurements of photoanodes were performed using an electrochemical workstation (CHI 760E) in a standard three-electrode system. An as-obtained photoanode working electrode, a saturated Ag/AgCl reference electrode and a Pt foil counter electrode were used. A 0.5 M Na_2SO_4 buffer solution (pH = 6.8) was used as the electrolyte. The intensity density of simulated sunlight is controlled at 100 mW cm^{-2} by a 350 W Xenon lamp with an AM 1.5 G filter. All photoanodes were illuminated by simulated sunlight through the sample side (i.e., a front illumination). The tested area of the photoanode was about 0.196 cm^2. Current density-potential and linear sweep voltammograms measurements were performed using the scan rate of 20 mV s^{-1}. The tested cyclic voltammetry of the photoanode at scan rates from 20 mV/s to 200 mV/s.

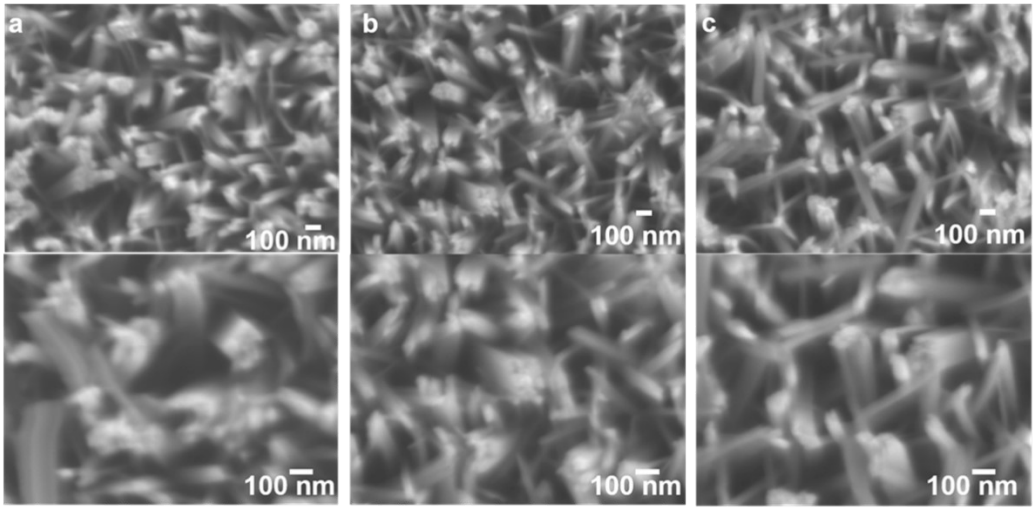

Figure S1. Low- and high-magnification SEM images of 2-In/TiO_2 NRs (a), 4-In/TiO_2 NRs(b) and 9-In/TiO_2 NRs(c).

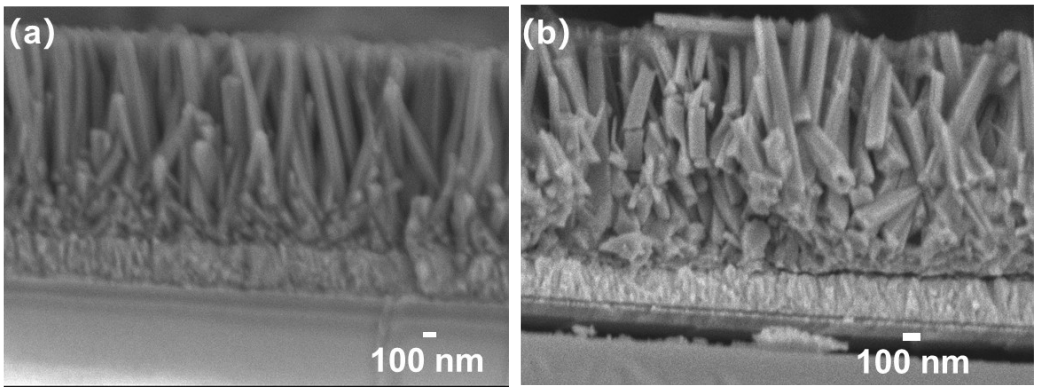

Figure S2. Cross-sectional SEM image of (a) pure TiO_2 NRs and (b) 6-In/TiO_2 NRs.

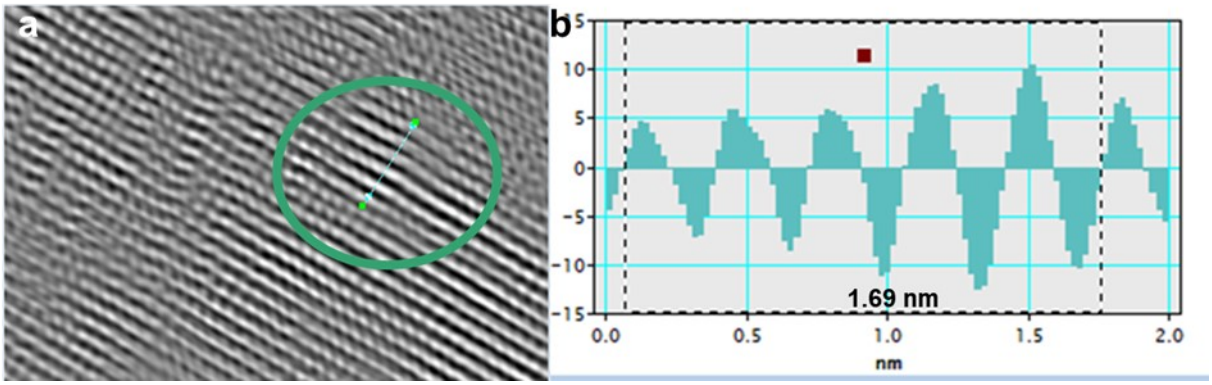

Figure S3.（a,b）IFFT image of 6-In/TiO_2 NRs.

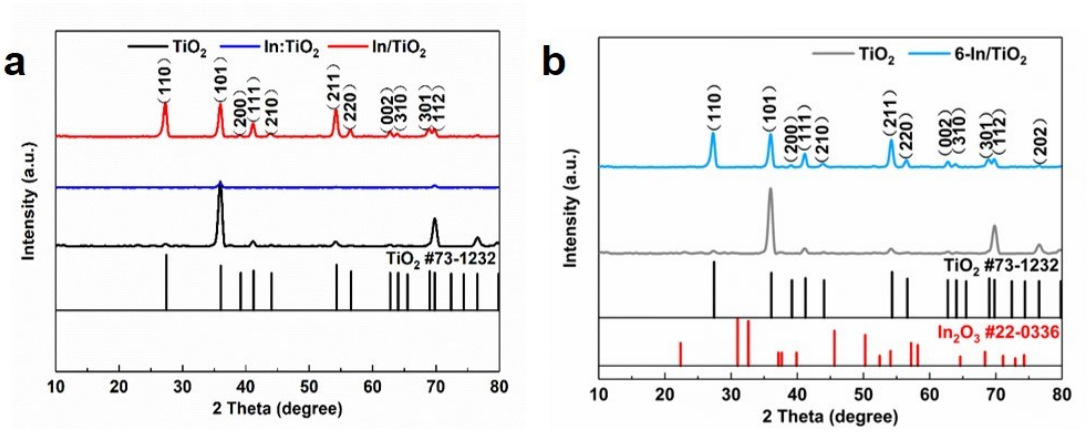

Figure S4. (a)XRD patterns of bare TiO_2 NRs, 6-In:TiO_2 and 6-In/TiO_2 NRs;(b) XRD patterns of pure TiO_2 NRs and 6-In/TiO_2 NRs .

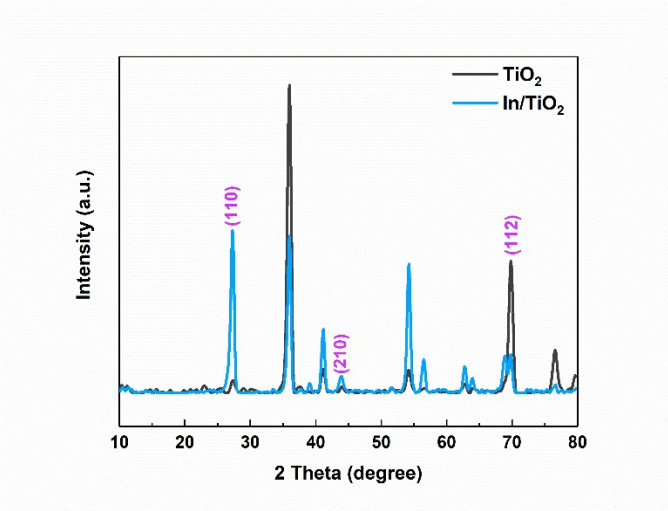

Figure S5. XRD patterns of pure TiO_2 NRs and 6-In/TiO_2 NRs

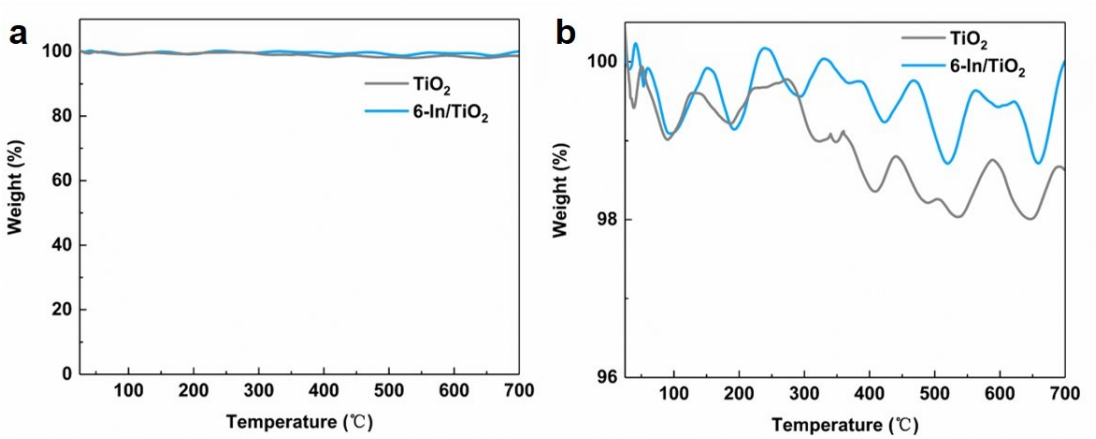

Figure S6. Thermogravimetric curves of TiO_2 NRs and 6-In/TiO_2 NRs.

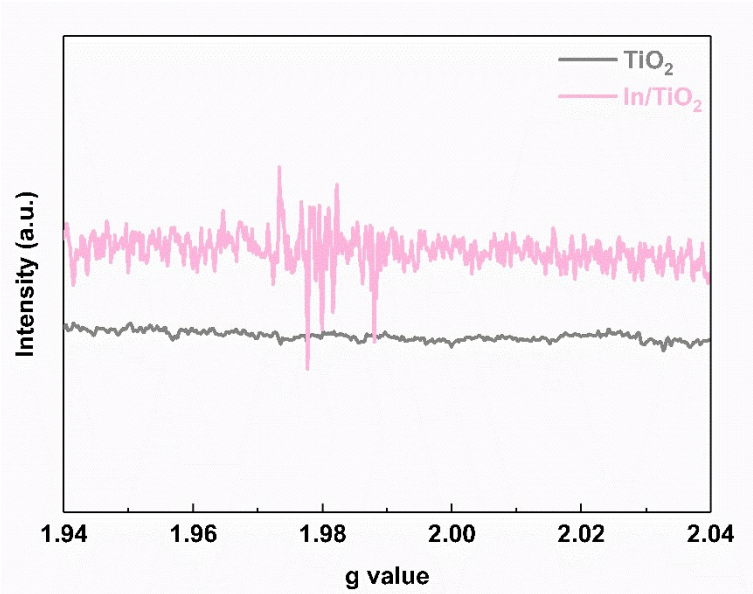

Figure S7. EPR spectrum of bare TiO_2 and 6-In/TiO_2 nanorod arrays.

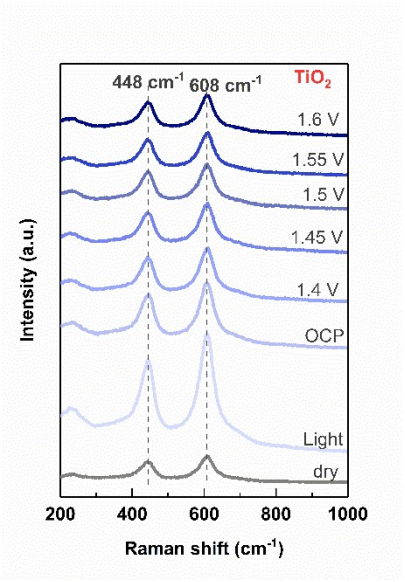

Figure S8. Operando Raman spectra of pure TiO_2 NRs under various applied potentials vs RHE.

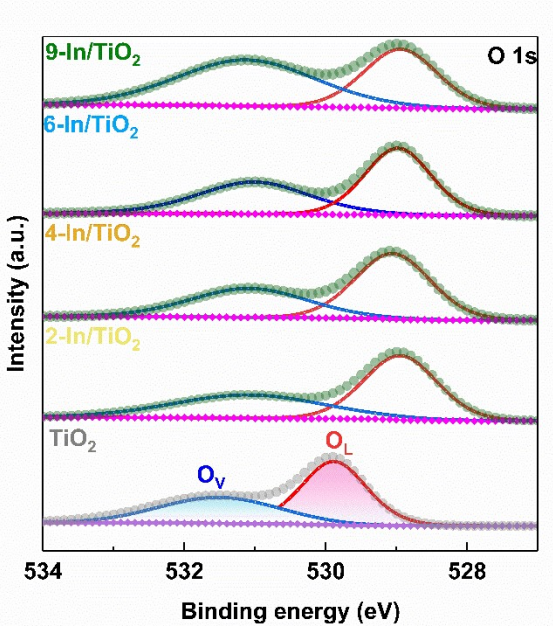

Figure S9. O 1s spectrum of bare TiO_2 and In-doped In/TiO_2 nanorod arrays.

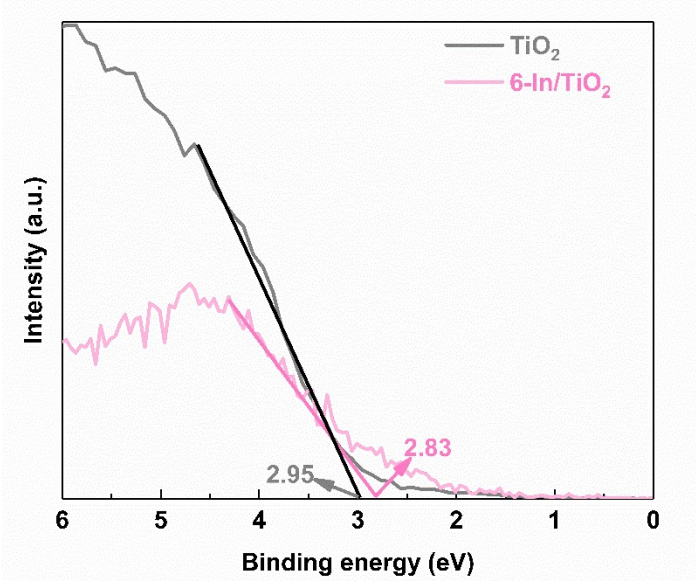

Figure S10. High-resolution VB XPS spectra of bare TiO_2 NRs and 6-In/TiO_2 NRs.

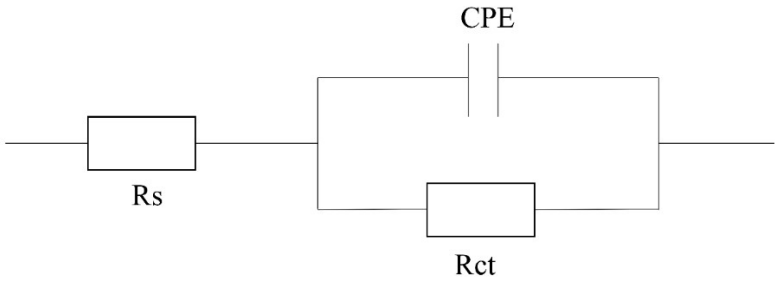

Figure S11. Simplified equivalent circuit used to fit EIS data in Nyquist plots.

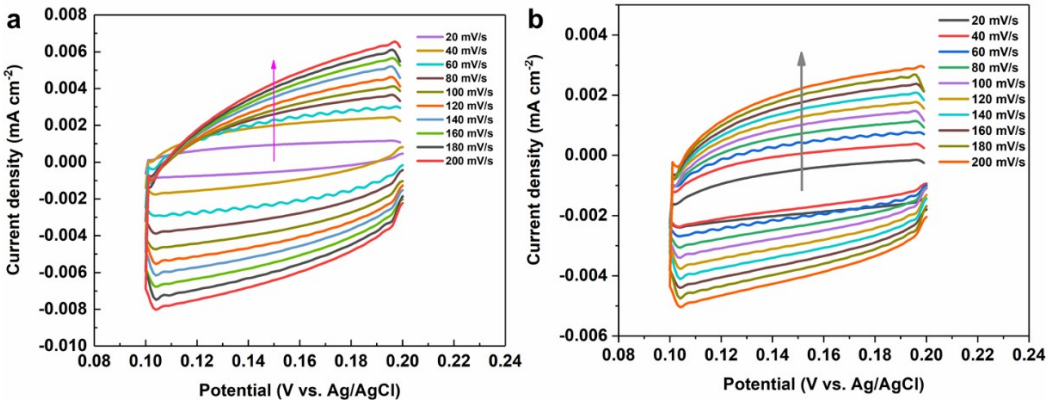

Figure S12. Cyclic voltammetry curves of the (a) 6-In/TiO_2 and (b) bare TiO_2 electrodes from 20 to 200 mV/s.

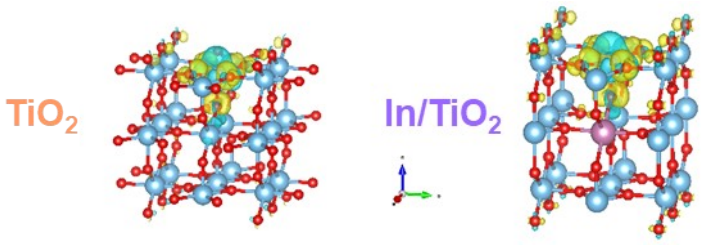

Figure S13. Differential charge density for pure TiO_2 NRs and 6-In/TiO_2 NRs.

Table S1. O_V/O_L ratio of different samples.

Sample	O_V/O_L
TiO_2	0.728:1
2-In/TiO_2	0.753:1
4-In/TiO_2	0.795:1
6-In/TiO_2	0.812:1
9-In/TiO_2	1.479:1

Table S2. In/Ti atomic ratio of different samples.

Sample	In/Ti
TiO_2	0
2-In/TiO_2	0.64%
4-In/TiO_2	2.72%
6-In/TiO_2	3.4%
9-In/TiO_2	6.15%

Table S3. Fitted values of PL decay kinetics of pure TiO_2 and 6-In/TiO_2

Sample	B_1	τ_1(ns)	B_2	τ_2(ns)	τ (ns)
TiO_2	2182.2	1.0516	226.7	5.2279	2.4738
6-In/TiO_2	2018.4	0.9491	252.7	4.7163	2.3940

Table S4. Fitted values of EIS data of different samples.

Sample	$R_s(\Omega)$	CPE(μF)	$R_{ct}(\Omega)$
TiO_2	105.9	9.7	5593
2-In/TiO_2	139.7	5.0	4155
4-In/TiO_2	108.3	5.3	3380
6-In/TiO_2	84.2	13.3	2340
9-In/TiO_2	106.4	2.1	5611