Supplementary Information
For Journal of Materials Chemistry A

N/Si co-doped Oriented Single Crystalline Rutile TiO_2 Nanorods for Photoelectrochemical Water Splitting

Xiaofan Zhang, Bingyan Zhang, Zhixiang Zuo, Mingkui Wang, Yan Shen*

Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Luoyu Road 1037, Wuhan, 430074, P. R. China.

E-mail: ciac_sheny@mail.hust.edu.cn

Experimental Section:

Fabrication of perovskite solar cell (PSC). The FTO glass was first etched to form two separated electrodes before being cleaned ultrasonically with ethanol. Then, the patterned substrates were coated by a compact TiO_2 layer by aerosol spray pyrolysis, and a 20 nm nanoporous TiO_2 layer was deposited by screen-printing. After being sintered at 500 ˚C for 30 min, the perovskite absorber layer was deposited using the two-step sequential deposition method[2]. The mesoporous TiO_2 films were infiltrated with PbI_2 by spin-coating a PbI_2 solution in DMF (500 mg mL^{-1}) that was kept at 70 ˚C. After drying, the films were dipped in a solution of CH_3NH_3I in 2-propanol (10 mg mL^{-1}) for 20 s and rinsed with 2-propanol. A 1μm ZrO_2 space layer was printed on the top of the nanoporous TiO_2 layer using ZrO_2 slurry, which acts as an insulating layer to prevent electrons from reaching the back contact. Then it was sintered at 500 ˚C for 30 min. Finally, a carbon black/graphite counter electrode with the thickness of about 8μm was coated on the top of ZrO_2 layer by printing carbon black/graphite composite slurry (1:3) and sintering at 400 ˚C for 30 min. After cooling down to room temperature, a 40 wt% perovskite precursor solution was infiltrated by drop casting via the top of the carbon counter electrode. After drying at 50 ˚C for 1h, the perovskite solar cells were obtained.

Assemble of the solar-powered photoelectronchemical device. The fully solar-

powered PEC system was composed of a photoelectrochemical cell using the N/Si co-doped TiO_2 NRs as photoanode and Pt sheet as counter electrode, and a PSC as the solar-powered source. Under light illumination, the PSC provides the bias potential to the N/Si co-doped TiO_2 NRs-based PEC cell for water splitting.

The power conversion efficiency (η) of the perovskite solar cell is calculated according to the following formula:

$$\eta(\%) = P_{out}/P_{in} = (FF \times J_{sc} \times V_{oc})/P_{in} \qquad (S1)$$

where η_{power} presents the photoelectric conversion efficiency, P_{in} (100 mW cm^{-2} herein) and P_{out} is the incident light intensity and output power of the solar cell device, FF is the fill factor, and J_{sc} and V_{oc} stand for the short-circuit current density and open-circuit voltage of the solar cell device, respectively.

The overall solar-to-hydrogen (STH) efficiency of the photoelectrochemical cell is calculated with the following equation:

$$STH = \frac{\eta_F \times J_{PEC\ cell} \times 1.23V}{P_{in} \times (S_{TiO_2} + S_{PSC})} \times 100\% \qquad (S2)$$

where $J_{PEC\ cell}$ is the maximum photocurrent given by the photoelectrochemical cell, S_{TiO2} and S_{PSC} is the area of TiO_2 photoanode and PSC respectively, η_F is the Faradic efficiency for the H_2 evolution that can be calculated with the following equation:

$$\eta_F = \frac{2 \times n_{H_2}(mol) \times 96485(C \times mol^{-1})}{Q_c} \times 100\% \qquad (S3)$$

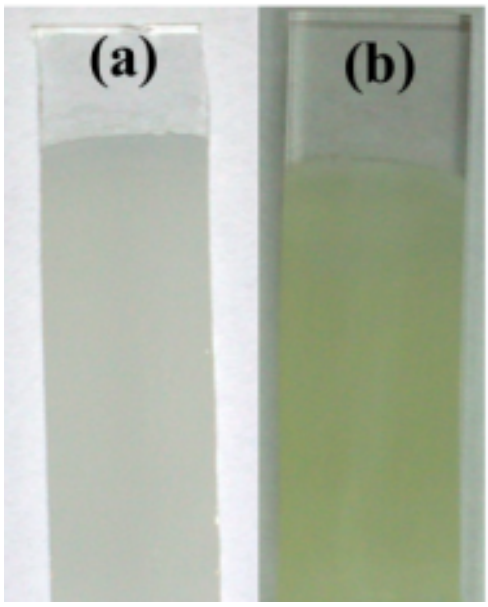

Fig. S1 The optical images of the TiO_2 NRs (a), and (b) the N/Si-codoped TiO_2 NRs deposited on FTO substrate.

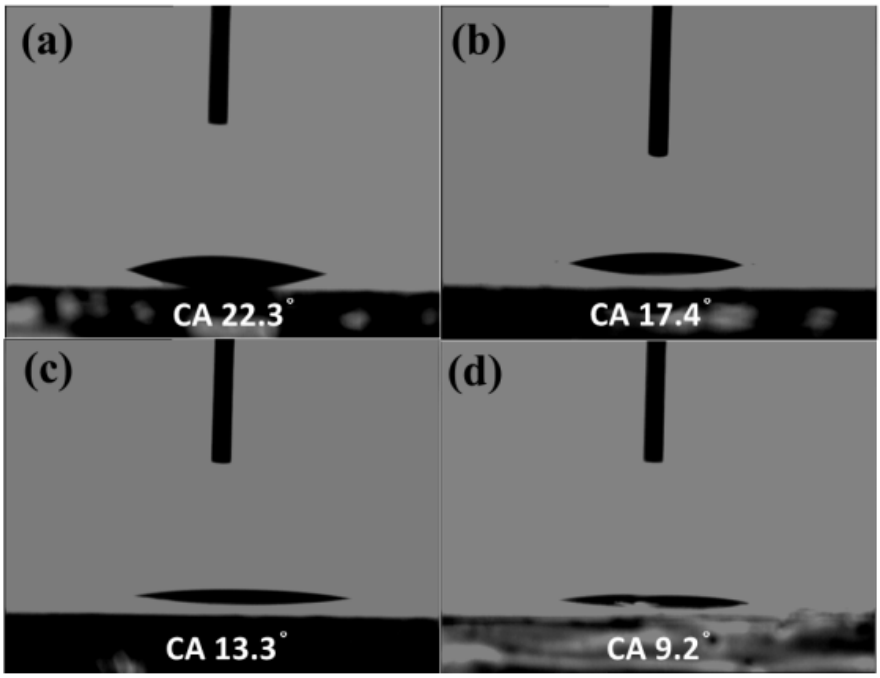

Fig. S2 Photographs showing equilibrium contact angles (CA) of water deposited on the pure TiO_2 NRs (a), the N doped TiO_2 NRs (b), the Si co-doped TiO_2 NRs (c), and (N, Si) co-doped TiO_2 NRs (d), respectively.

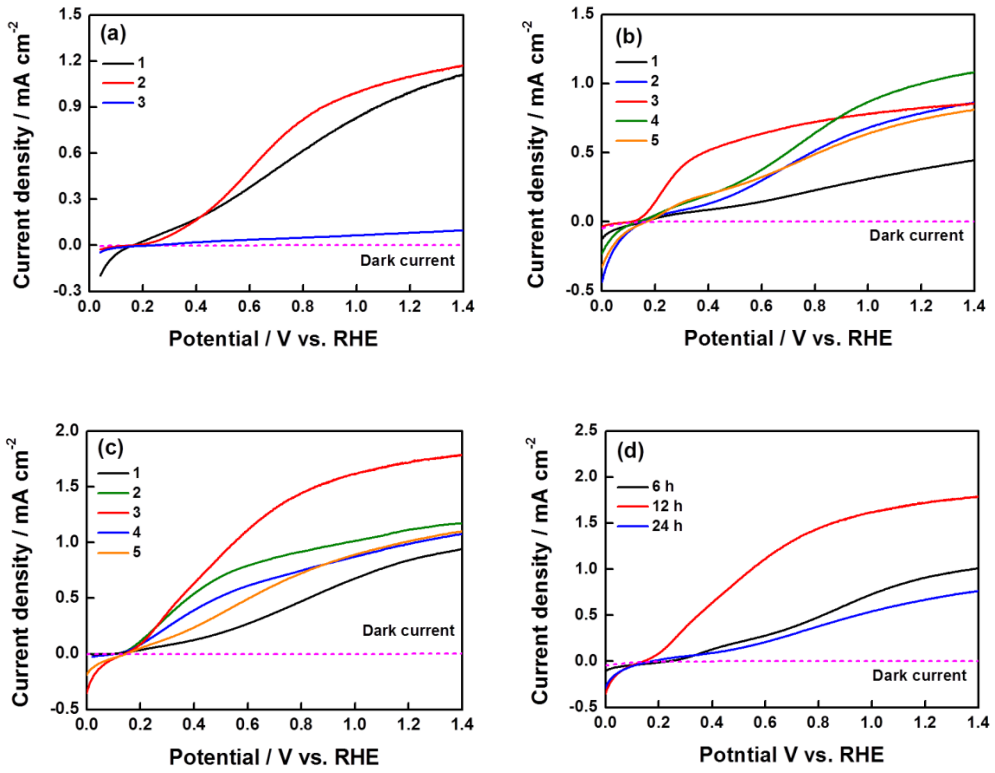

Fig. S3 (a) The LSV plots of N doped TiO_2 NRs prepared with the different content of PI (The Ti/N atomic percent ratio was 4.5%, 3.03%, 0.9% for line 1, 2 and 3, respectively). (b) The LSV plots of Si doped TiO_2 NRs prepared with different content of TEOS (The Ti/Si atomic percent ratio was 20%, 10%, 5%, 4% and 2% for line 1, 2 , 3, 4 and 5, respectively). (c) The LSV plots of (N, Si) doped TiO_2 NRs prepared with different ratio of PI to TEOS (The N/Si atomic percent ratio was 0.2%, 0.4%, 0.8%, 1.6% and 2% for line 1, 2, 3, 4 and 5, respectively). (d) The LSV plots of (N, Si) co-doped TiO_2 NRs prepared with different reaction time under the optimum N/Si atomic percent.

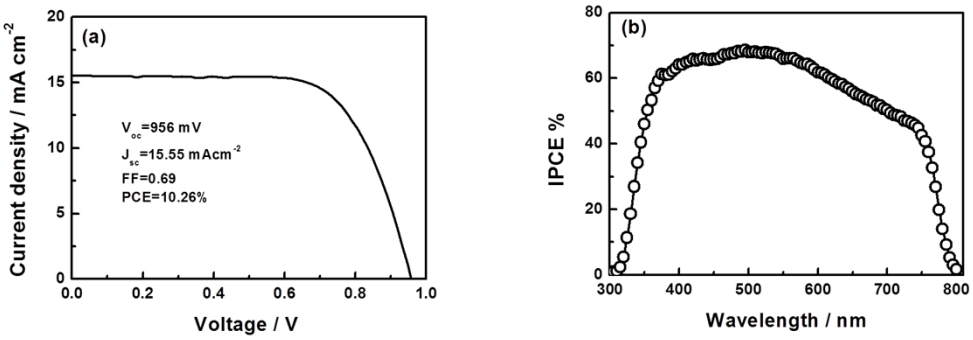

Fig. S4 (a) The J-V curve of the perovskite solar cell under simulated AM 1.5G solar irradiation (100 mW cm^{-2}) measured at room temperature. (b) IPCE plot of the perovskite solar cell.

As shown in Figure S4a, the perovskite solar cell displayed a short-circuit current

density (J_{sc}) of 15.55 mA cm^{-2}, a fill factor (FF) of 0.69, an open-circuit voltage (V_{oc}) of 0.956 V, achieving a PCE of 10.26%. The IPCE reaches a broad maximum at 400 nm remaining at a level over 50% up to 750 nm as shown in Figure S4b.

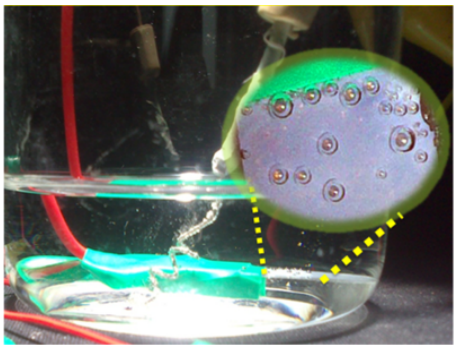

Fig. S5 The image of gas evolution on the surface of the electrode.

The equivalent circuit used for impedance data analysis is shown in Fig. S6.

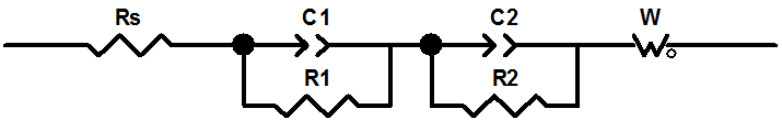

Fig. S6 The equivalent circuit model used for fitting the experimental data in Figure 3d.

Table S1 The fitting results according to the equivalent circuit model.

Samples	*Rs (Ω)*	*R1 (Ω)*	*R2 (Ω)*
TiO_2 NRs	43.3	23	2681
N doped TiO_2 NRs	45.09	57.84	1289
Si doped TiO_2 NRs	30.03	32.45	573
N/Si codoped TiO_2 NRs	27.6	4.09	191

Fig. S7 presents the Mott-Schottky (MS) plot as $1/C^2$ *vs.* potential at a frequency of 1 kHz in the dark. The carrier density (N_d) can be calculated according to the Mott-Schottky equation (S4),

$$\frac{1}{C^2} = \frac{2}{e_0 \varepsilon \varepsilon_0 N_d}\left[\left(E_{app} - E_{fb}\right) - \frac{k_B T}{e}\right] \quad \text{(S4)}$$

where C is the space charge capacitance in the semiconductor; N_d is the electron carrier density; e_0 is the electron charge; E_{app} is the applied potential; ε_0 is the permittivity of the vacuum; ε is the relative permittivity of the semiconductor; E_{fb} is the flat-band potential; T is the temperature; and k_B is the Boltzmann constant.

With e=-1.6×10^{-19}C, ε_0= 8.85×10^{-12} F/m, and ε= 110 for rutile TiO_2, the N_d values are calculated and summarized in Table S2.

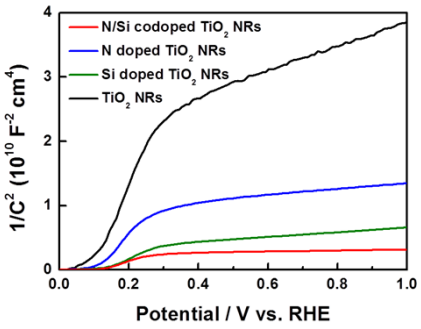

Fig. S7 The Mott-Schottky plots for the bare, mono-doped and co-doped TiO_2 NRs photoanodes collected at a frequency of 1 kHz in the dark.

Table S2 The charge density (N_d) values of the bare, mono-doped and co-doped TiO_2 NRs.

Sample	TiO_2 NRs	N doped TiO_2 NRs	Si doped TiO_2 NRs	N/Si codoped TiO_2 NRs
N_d / 10^{19} cm^{-3}	0.96	2.24	4.61	7.68

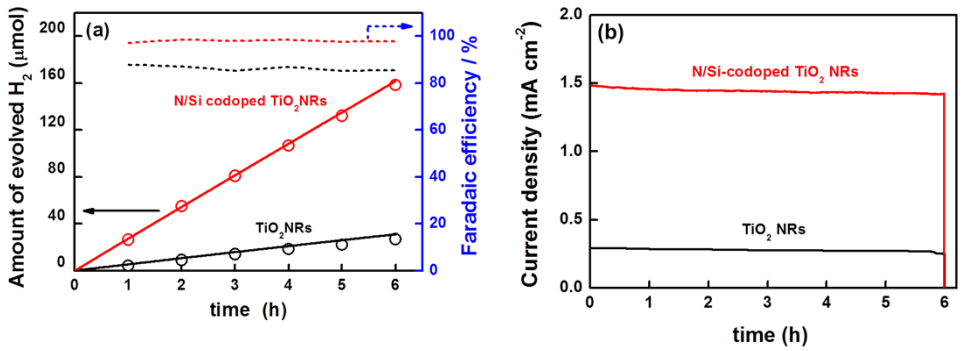

Fig. S8 (a) Faradaic efficiency and quantity of detected hydrogen derived from the tandem assembly cell (PSC+N/Si co-doped TiO_2 NRs and PSC+TiO_2 NRs) under standard one sun AM 1.5 G under irradiation. Black and red lines correspond to the integration of the net photocurrent divided by 2. Black and red circles correspond to the H_2 gas measured by gas chromatography during the experiment. Black and red dash lines correspond to the Faradaic efficiency. (b) The net current measured during the experiment.