Supplementary Information
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N/Si co-doped Oriented Single Crystalline Rutile TiO$_2$ Nanorods for Photoelectrochemical Water Splitting

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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$_3$NH$_3$I 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 photoelectrochemical 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
toxic-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 (\(\eta\)) of the perovskite solar cell is calculated
according to the following formula:

\[
\eta(\%) = \frac{P_{\text{out}}}{P_{\text{in}}} = (\text{FF} \times J_{\text{sc}} \times V_{\text{oc}})/P_{\text{in}} \quad \text{(S1)}
\]

where \(\eta_{\text{power}}\) presents the photoelectric conversion efficiency, \(P_{\text{in}}\) (100 mW cm$^{-2}$ herein)
and \(P_{\text{out}}\) is the incident light intensity and output power of the solar cell device, FF is
the fill factor, and \(J_{\text{sc}}\) and \(V_{\text{oc}}\) 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:

\[
\text{STH} = \frac{\eta_F \times J_{\text{PEC cell}} \times 1.23V}{P_{\text{in}} \times (S_{\text{TiO}_2} + S_{\text{PSC}})} \times 100\% \quad \text{(S2)}
\]

where \(J_{\text{PEC cell}}\) is the maximum photocurrent given by the photoelectrochemical cell,
\(S_{\text{TiO}_2}\) and \(S_{\text{PSC}}\) is the area of TiO$_2$ photoanode and PSC respectively, \(\eta_F\) is the Faradic
efficiency for the H$_2$ evolution that can be calculated with the following equation:

\[
\eta_F = \frac{2 \times n_{\text{H}_2} \text{ (mol)} \times 96485 \text{ (C x mol$^{-1}$)}}{Q} \times 100\% \quad \text{(S3)}
\]
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](image1.png) 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](image2.png) The equivalent circuit model used for fitting the experimental data in Figure 3d.

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>$Rs$ (Ω)</th>
<th>$R1$ (Ω)</th>
<th>$R2$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ NRs</td>
<td>43.3</td>
<td>23</td>
<td>2681</td>
</tr>
<tr>
<td>N doped TiO$_2$ NRs</td>
<td>45.09</td>
<td>57.84</td>
<td>1289</td>
</tr>
<tr>
<td>Si doped TiO$_2$ NRs</td>
<td>30.03</td>
<td>32.45</td>
<td>573</td>
</tr>
<tr>
<td>N/Si codoped TiO$_2$ NRs</td>
<td>27.6</td>
<td>4.09</td>
<td>191</td>
</tr>
</tbody>
</table>
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),

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

where $C$ is the space charge capacitance in the semiconductor; $N_d$ is the electron carrier density; $\varepsilon_0$ is the electron charge; $E_{app}$ is the applied potential; $\varepsilon_0$ is the permittivity of the vacuum; $\varepsilon$ 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 $e=1.6 \times 10^{-19}$ C, $\varepsilon_0=8.85 \times 10^{-12}$ F/m, and $\varepsilon=110$ for rutile TiO$_2$, the $N_d$ values are calculated and summarized in Table S2.

![Mott-Schottky plots](image)

**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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO$_2$ NRs</th>
<th>N doped TiO$_2$ NRs</th>
<th>Si doped TiO$_2$ NRs</th>
<th>N/Si codoped TiO$_2$ NRs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_d / 10^{19}$ cm$^{-3}$</td>
<td>0.96</td>
<td>2.24</td>
<td>4.61</td>
<td>7.68</td>
</tr>
</tbody>
</table>
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 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.