Supporting information for

Elucidating Charge Separation in Particulate Photocatalysts Using Nearly-Intrinsic Semiconductors with Small Asymmetric Band Bending

Zhenhua Pan, Jason A. Röhr, Zuyang Ye, Zachary S. Fishman, Qianhong Zhu, Xin Shen, Shu Hu*

1 Department of Chemical and Environmental Engineering, Yale University, New Haven, CT 06520 (USA)
2 Energy Sciences Institute, Yale University, 810 West Campus Drive, West Haven, CT 06516 (USA)

Corresponding Author
*E-mail: shu.hu@yale.edu, Tel: +1-203-737-6521. Fax: +1-203-432-4387

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**Table S4** Physical input parameters of SrTiO₃ and the window layer used in SCAP3307.
Supporting Results and Discussions
S1. Depletion width and intensity of electric field in photoelectrodes vs. uniform particulate photocatalysts

In this section, a single-side pn diode equation was used to estimate depletion width and the intensity of electric field in a p⁺/n-Si junction which is commonly used as a photoelectrode. The results were compared with those from particulate photocatalysts to quantitatively elucidate the knowledge gap of current understanding for the charge separation in photocatalysts. Supposing that a n-type Si with an electron concentration of 10^{16} cm⁻³ (N_D) forms a heterojunction with a p⁺-Si with a hole concentration of 10^{19} cm⁻³ (N_A), the built-in potential across the junction is 0.87 V using Eq. S1. The width of depletion region (l) located in n-Si is 0.34 μm using Eq. S2. Therefore, the average electric filed in the depletion region of n-Si is 2.5 × 10^4 V cm⁻¹.

\[ V_{bi} = \frac{k_B T}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right) \tag{1} \]

\[ l = \sqrt{\frac{2e_ε_0 V_{bi}}{q} \frac{N_A}{N_D} \left( \frac{1}{N_A + N_D} \right)} \tag{2} \]

Where \( ε_0 \) is electric constant; \( ε_r \) (11.7) is the dielectric constant of Si; \(^1 n_i \) (1.5*10^10 cm⁻³) is the intrinsic carrier concentration of Si at 300 K.

If the size of particle is much larger than the width of depletion layer formed in the semiconductor/water junction, only the electrons in the vicinity of surfaces are depleted, and electron distribution inside the bulk is not affected. In this case, band bending in particles can be described by interfacial charge equilibrium, similar to that in semiconductor/liquid junction.² In contrast, if the size of particle is smaller, the depletion layer will penetrate through the whole particle, and electron distribution in the whole particle will be influenced. The band bending in this case will be determined by the doping concentration of particle. The lower the doping concentration is, the flatter the energy bands are, as depicted in Eq. S3 developed Albery and Bartlett.³ For example, the depletion layer thickness of a n-type SrTiO₃ thin film with an electron concentration of 1 × 10¹⁷ cm⁻³ in water is about 600 nm according to Eq. S4. When SrTiO₃ particles of 200 nm with the same doping concentration are dispersed in water, the band bending from the particle center to particle surfaces is only ca. 10 mV at room temperature, and the average electric field is 1.0 ×10³ V cm⁻¹. Table S1 listed the band bending condition of several photocatalysts that could achieve overall water splitting. If the band bending in
particles is weak and symmetric, there should not be any charge separation for water splitting, but this deduction contradicts experimental results. This issue motivated us to conduct this study to elucidate the underlying driving force for charge separation.

\[ V_{BB} = \frac{e_r^2 N_D}{6\varepsilon, \varepsilon_0} \]  

(3), when \( r_0 < \sqrt[3]{3} W_{dep} \)

Where \( V_{BB} \) is the band bending from surface to the center; \( r_0 \) is the radius of particle.

\[ W_{dep} = \sqrt{2\varepsilon, \varepsilon_0 \left( \frac{V_{bi}}{qN_D} \right)} \]  

(4)

Where \( \varepsilon_r \) (300) is the dielectric constant of SrTiO\(_3\); \( N_D \) is the donor concentration; \( aV_{bi} \) of 1.0 V is used.

**S2. Hall coefficient measurements by the van der Pauw Method.**

\[ R_H = \frac{V_H}{IB} = \frac{R_{CH}}{B} = -\frac{1}{ne} \]  

(5)

\[ R_{CH} = \frac{V_H}{I} \]  

(6)

\( R_H \) was measured in different contact configurations. For example, \( R_{H13,24} \) indicates \( V^+, V^-, I^+, \) and \( I^- \) were connected to point 1, 3, 2 and 4, respectively. The value of \( R_H \) was obtained by averaging \( R_{H13,24}, R_{H31,42}, R_{H24,13} \) and \( R_{H24,31} \). The size of sample was \( 0.5 \times 0.5 \) cm\(^2\). The thickness (t) was 100 nm. The results were shown in Fig. S1 and summarized in Table S2.

![Contact placement for Hall measurement](image)

**S3. Electrochemical properties of TiO\(_2\) films without a Ni layer**

It has been previously shown that hole transfer from as-grown TiO\(_2\) to the electrolyte is not possible without the addition of Ni. As expected, almost no anodic current was observed through TiO\(_2\) (as-grown) without the addition of a Ni
layer (shown in Fig. S4). Using TiO$_2$/p$^+$-Si as an example (Fig. S4a): even when the applied potential was as positive as 1.5 V vs. NHE, about 1 V more positive than the potential of the Fe(CN)$_6^{3-/4-}$ redox couple, negligible current density was observed. When the applied bias was more negative than -0.22 V vs. NHE, a cathodic current was observed. This observation indicates that electron transfer through the conduction band was possible when a negative bias was applied. In contrast, after annealed at 800 °C, the TiO$_2$ film became conductive both anodically and cathodically and the onset potentials for both electron and hole transfer shifted to 0.63 V vs. NHE, indicating that TiO$_2$(800 °C) film is an n-type degenerately doped semiconductor. For the ohmic behaviour, p$^+$-Si/TiO$_2$(800 °C) and n$^+$-Si/TiO$_2$(800 °C) are supposed to form a tunnel junction type interface.

S4. External quantum yields (EQYs) of n$^+$-Si/i-Si/TiO$_2$(as-grown)/Ni and p$^+$-Si/i-Si/TiO$_2$(800 °C)/Ni electrodes.

The external quantum yields (EQYs) of n$^+$-Si/i-Si/TiO$_2$(as-grown)/Ni and p$^+$-Si/i-Si/TiO$_2$(800 °C)/Ni electrodes, in 1 M KOH(aq) electrolytes, were measured as shown in Fig. S6. During the measurement, 2.52 V vs. RHE and -0.38 V vs. RHE were applied to n$^+$-Si/i-Si/TiO$_2$(as-grown)/Ni and p$^+$-Si/i-Si/TiO$_2$(800 °C)/Ni, respectively, where saturation currents were achieved. Under 1-Sun ELH-type W-halogen simulated solar illumination, the photocurrent density of the n$^+$-Si/i-Si/TiO$_2$(as-grown)/Ni at 2.52 V vs. RHE and p$^+$-Si/i-Si/TiO$_2$(800 °C)/Ni at -0.38 V vs. RHE were 32.6 mA cm$^{-2}$ and -10.9 mA cm$^{-2}$, respectively. These current densities were in accordance with expected light-limiting current densities (32.3 mA cm$^{-2}$ and -12.1 mA cm$^{-2}$, respectively) based on an integration of the measured spectral response. The light-dependent $J$-$E$ behaviour of n$^+$-Si/i-Si/TiO$_2$(as-grown)/Ni and p$^+$-Si/i-Si/TiO$_2$(800 °C)/Ni were shown in Fig. S7. The normalized saturation photocurrent decreased as the light intensity increased, indicating that the EQYs of these diffusion-driven photoelectrodes are negatively correlated to the light intensity. This phenomenon was also observed in RhCrO$_x$/GaN:ZnO photocatalytic water splitting reactions. As the intensities of laser for EQY measurement are not identical at different wavelengths, the EQYs above 650 nm fluctuated as shown in Fig. S6. The EQY loss of the devices at these applied potentials is mostly attributed to the parasitic absorption of TiO$_2$ layers as shown in Fig. S8.

S5. Photocurrent directions and electron and hole charge flow of i-Si electrodes under illumination

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For the n⁺-Si/i-Si/TiO₂(as-grown), the photocurrent induced by both electron and hole migration was flowing in the same direction in most part of the i-Si layer, from the back interface to the front interface (0 – 349.7 µm), as shown in Fig. S12.1(c). Furthermore, the electron current increased from the front interface to a maximum value at the back side, while the hole current decrease at a maximum value from the front interface to 0 mA cm⁻² at the back interface. This observation indicates that most of the holes, generated at the front side, tended to migrate to the front contact rather than the back contact. In contrast, most electrons diffused across the whole i-Si layer, eventually reaching the back contact, which phenomenon is also supported by the electron and hole distributions shown in Fig. S12.1(d). As the n⁺-Si and TiO₂(as-grown) layers are electron and hole selective, respectively, a combination of both layers enables n⁺-Si/i-Si/TiO₂(as-grown) to work as an efficient photoanode, as shown in Fig. 4.

For the p⁺-Si/i-Si/TiO₂(800 °C) photocathodes, both the electrons and holes migrated from the front side to the back side within the i-Si layer as shown in Fig. S12.2(c). The values for both the electron and the hole current reached maximum at around 8 µm away from the front interface. From that position to the back interface, both electron and hole currents were decreasing due to recombination. Although the electron current decreased to 0 mA cm⁻² at the back interface, there was still a hole current of -5.9 mA cm⁻². The p⁺-Si back contact was hole-selective, but its effect was limited by the charge recombination in the bulk of the i-Si layer. Most of the charges were generated around the front interface, but from the position at around 8 µm away from the front interface, both the electron and hole currents were decreasing because the TiO₂(800 °C) front contact is not selective to neither electrons nor holes.

For the non-energy-converting p⁺-Si/i-Si/TiO₂(as-grown) electrode, all the electrons generated in the i-Si layer migrated to the front interface, while most of the holes migrated to the front interface and a small amount toward the back interface, as shown in Fig. S12.3(c). The TiO₂(as-grown) front contact is hole-selective and almost all holes accumulate near the front interface. As the p⁺-Si back contact is also hole-selective, a small population of holes are attracted to the back interface, leading to a net photocurrent. The electrons rarely migrate to the back interface; instead, they migrate to the nearby front interface for recombination. Since most of the photo-generated charge carriers recombined in this case, the efficiency of the p⁺-Si/i-Si/TiO₂(as-grown) electrode is much lower than that of the n⁺-Si/i-Si/TiO₂(as-grown) electrode as a photoanode.
The trend of the current distribution of the non-energy-converting n⁺-Si/i-Si/TiO₂(800 °C) electrode is shown in Fig. S12.4(c). The n⁺-Si back contact only attracts a small population of electrons, whereas most of the electrons migrate to the TiO₂(800 °C) front contact for recombination. Our observations suggest that the TiO₂(800 °C) contact, with a high electron concentration, favors charge recombination rather than hole transportation. As a result, the charge separation efficiency of i-Si in the n⁺-Si/i-Si/TiO₂(800 °C) electrode was poor as compared to that of the p⁺-Si/i-Si/TiO₂(800 °C) electrode, even though the Fermi level difference between the n⁺-Si and TiO₂(800 °C) contacts is as high as -0.43 V.

From the above discussions, it is further supported that an asymmetric electric field in a light absorber was the driving force for charge separation. However, from the n⁺-Si/i-Si/TiO₂(800 °C) electrode, it is observed that the charge separation not only requires the right internal energy landscape, but also need suitable contacts to extract the charge carriers without too many recombination losses.

S6. Simulated photovoltaic behaviour of i-Si/model contact junction

As shown in Fig. S13, even with a bare Si contact (contact 1), a photovoltage of 0.00004 V was generated. This photovoltage was induced by the difference in the electron and hole mobilities."\textsuperscript{13} When the electron and hole mobilities of TiO₂ was used for the model contact (contact 2), the photovoltage became -0.009 V which indicates that the difference of the charge-carrier mobilities between i-Si and TiO₂ made the contact selective for holes. When the effective density of states of the energy bands of TiO₂ were used for the model contact (contact 3), the photovoltage dropped to 0.0002 V, this indicates that these parameters had little effects on the selectivity of the contact. When the dielectric constant (contact 4), the energy band positions (contact 5) and the Fermi level position (contact 6) of TiO₂ were applied on the model contact, the photovoltages were 0.001 V, 0.002 V and 0.008 V, respectively. The conduction band offset between Si and TiO₂, and the electric field induced by the Fermi level offset, facilitated electron transfer, consistent with a previous study."\textsuperscript{13} With all the parameters of TiO₂ applied except the Fermi level position (contact 7), the photovoltage was only 0.0001 V. It means a Fermi level offset generating a photovoltage over 0.0001 V can inverse the direction of charge carrier migration. When all the above parameters were used for the contact (which would correspond to using a TiO₂ (800 °C) layer, contact 8), the contact induced a photovoltage of only 0.004 V, showing their negligible effects on electron selectivity.
For a given TiO$_2$ front contact, its Fermi level and the induced interfacial electric field are major variables, and their effect on the selectivity was further studied by systematically varying the doping level. Moreover, the Fermi level from TiO$_2$(as-grown) and TiO$_2$(800 °C) spans a range of 0.5 eV. Similarly, the Fermi level from p$^+$- to n$^+$-Si back contacts spans 1.1 eV. The photovoltaic behaviour of i-Si/TiO$_2$, with TiO$_2$ having various doping concentrations, were displayed in Fig. S14. Two types of devices were simulated: i-Si/TiO$_2$ as described (Fig. S14a and b), and i-Si/TiO$_2$ whose space-charge region (or ×3) was turned transparent (Fig. S14c-f), and both configurations showed similar photovoltaic behaviour. If drift of charge carrier dominated charge separation at the space-charge regions, making the space-charge region in i-Si transparent would drastically reduce the photocurrent, while this hypothesis was observed. Furthermore, as the thickness of transparent region in i-Si increases, $J_{sc}$ began to decrease. These results indicate that the photovoltages were induced by diffusion-dominated carrier collection. When the donor concentration was set to 7×10$^{20}$ cm$^{-3}$, the Fermi level of TiO$_2$ was located at its conduction band minimum, similar to that of TiO$_2$(800 °C), and the model gave a positive value for the photovoltage of 0.001 V. When the Fermi level of TiO$_2$ was lowered as the donor concentration was decreased and the acceptor concentration was increased, the charge flow direction was inversed. When the acceptor concentration was set as 7×10$^{20}$ cm$^{-3}$, the Fermi level of TiO$_2$ was located around the intermediate charge-transport band of “leaky” TiO$_2$. The model showed a photovoltage of approximately -0.43 V. This photovoltage is much more significant than those contributed by the aforementioned trivial parameters (shown in Fig. S13).

Additional figures and tables
Diffusion-driven i-Si photoelectrodes

Selective contacts

- Back contacts: p*/n*-Si with different Fermi levels
- Front contacts: protective ALD TiO\textsubscript{2} layers

Fermi level modulation on contacts

Defect tuning on contacts

As-grown TiO\textsubscript{2}: low electron concentration due to self-trapping by Ti\textsuperscript{4+};

TiO\textsubscript{2} annealed in H\textsubscript{2}: high electron concentration due to the introduction of O\textsubscript{2} vacancies.

(a)
Fig. S1 Flowcharts of (a) designing i-Si photoelectrodes with various front and back carrier-selective contacts, and (b) developing devices simulation based on experimental results.
**Fig. S2** Fabrication procedures for i-Si photoelectrodes

**Fig. S3.1** Hall resistance vs. magnetic field for TiO$_2$ (as-grown).
Fig. S3.2 Hall resistance vs. magnetic field for TiO$_2$(600 °C).

Fig. S3.3 Hall resistance vs. magnetic field for TiO$_2$(700 °C).
by a Pt wire because the surface chemistry of TiO

The scan speed for the cyclic voltammetry measurements was 20 mV s\(^{-1}\). The open
circuit potentials of electrodes were not equal to the potential of Fe(CN)\(_6\)\(^{3/-4}\) measured
by a Pt wire because the surface chemistry of TiO\(_2\) layers was different from that of a
Pt wire.

**Fig. S3.4** Hall resistance vs. magnetic field for TiO\(_2\)(800 °C).

**Fig. S4** Charge transfer current density-potential behaviour from TiO\(_2\)(as-grown) and
TiO\(_2\)(800 °C) films on (a) p\(^+\)-Si or (b) n\(^-\)-Si substrates to Fe(CN)\(_6\)\(^{3/-4}\) redox couple.

The scan speed for the cyclic voltammetry measurements was 20 mV s\(^{-1}\). The open
circuit potentials of electrodes were not equal to the potential of Fe(CN)\(_6\)\(^{3/-4}\) measured
by a Pt wire because the surface chemistry of TiO\(_2\) layers was different from that of a
Pt wire.
Fig. S5 Photovoltaic current density-potential ($J–E$) characteristics of (a) p$^+$-Si/n-Si/TiO$_2$(as-grown)/Ni electrodes and (b) n$^+$-Si/p-Si/TiO$_2$(800 °C)/Ni electrodes in 1 M KOH(aq) electrolytes. Blue Dash line: water oxidation behaviour of (a) a p$^+$-Si/TiO$_2$(as-grown)/Ni electrode and (b) a p$^+$-Si/TiO$_2$(800 °C)/Ni electrode. Scan speed: 20 mV s$^{-1}$.

Fig. S6 External quantum yield and overlay of the normal-incidence optical absorptance for (a) n$^+$-Si/i-Si/TiO$_2$(as-grown)/Ni at 2.52 V vs. RHE and (b) p$^+$-Si/i-Si/TiO$_2$(800 °C)/Ni at -0.38 V vs. RHE. The potentials were chosen for approximate light-limited current densities.

Fig. S7 Light-dependent photovoltaic current density-potential ($J–E$)
characteristics of (a) p⁺-Si/i-Si/TiO₂(as-grown)/Ni and (b) n⁺-Si/i-Si/TiO₂(800 °C)/Ni in 1 M KOH(aq) under simulated 0.1 – 1.3 sun illumination. Scan speed: 40 mV s⁻¹.

**Fig. S8** Absorption (in percentage) of TiO₂ (as-grown) and TiO₂(800 °C). The absorbance of TiO₂(800 °C) was substantially larger than that of TiO₂ (as-grown) due to a higher Ti³⁺ concentration.

**Fig. S9** Photovoltaic behaviour of (a) n⁻-Si/i-Si/TiO₂(as-grown)/Ni, (b) p⁺-Si/i-Si/TiO₂(800 °C)/Ni, (c) p⁺-Si/i-Si/TiO₂(as-grown)/Ni, and (d) n⁻-Si/i-Si/TiO₂(800 °C)/Ni. The plots show the current density vs. applied bias for different conditions: under illumination and dark condition.
°C)/Ni evaluated in a typical solar-cell-measurement configuration. $V_{oc}$, $J_{sc}$, and $FF$ represent open-circuit photovoltage, short-circuit photocurrent-density and fill factor, respectively. Scan speed: 40 mV s$^{-1}$.

![Image of a photovoltaic cell curve](image)

**Fig. S10** Photovoltaic behaviour of n$^+$-Si/i-Si/TiO$_2$(as-grown)/Ni, in which top electrical contacts were formed via bonding of 15 Al wires with 15 metal pads. Scan speed: 40 mV s$^{-1}$. Electrode area: 0.9 cm$^2$.

![Image of photovoltaic behaviour curves](image)

**Fig. S11** Photovoltaic behaviour of (a) n$^+$-Si/i-Si/TiO$_2$(as-grown), (b) p$^+$-Si/i-
Si/TiO$_2$(800 °C), (c) p$^+$-Si/i-Si/TiO$_2$(as-grown), and (d) n$^+$-Si/i-Si/TiO$_2$(800 °C) by simulation.

**Fig. S12.1** (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in n$^+$-Si/i-Si/TiO$_2$(as-grown). The electron and hole quasi Fermi levels are drawn close near the contact due to recombination at contacts, resulting in zero photovoltage in short circuit conditions.
Fig. S12.2 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p⁺-Si/i-Si/TiO₂ (800 °C). The electron and hole quasi Fermi levels are drawn close near the contact due to recombination at contacts, resulting in zero photovoltage in short circuit conditions.
Fig. S12.3 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p⁺-Si/i-Si/TiO₂(as-grown). The electron and hole quasi Fermi levels are drawn close near the contact due to recombination at contacts, resulting in zero photovoltage in short circuit conditions.
Fig. S12.4 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in n⁺-Si/i-Si/TiO₂(800 °C). The electron and hole quasi Fermi levels are drawn close near the contact due to recombination at contacts, resulting in zero photovoltage in short circuit conditions.

Fig. S13 Simulated photovoltaic behaviour of i-Si with model contacts with its
parameter updated from that of TiO$_2$ (800 °C): (1) i-Si, (2) i-Si with the electron and hole mobilities of TiO$_2$, (3) i-Si with the effective density of states of TiO$_2$, (4) i-Si with the dielectric constant of TiO$_2$, (5) i-Si with the energy band levels of TiO$_2$, (6) i-Si with the Fermi level position from TiO$_2$, (7) all the device parameters for TiO$_2$(800 °C) except the Fermi level, and (8) contact with all the property parameters for TiO$_2$(800 °C). The model contacts were set to be optically transparent.

**Fig. S14** The models for simulating the i-Si/TiO$_2$ junction in which (a) 0 μm, (c) the space-charge region (9 μm) and (e) the space-charge region × 3 (27 μm) at the i-Si/TiO$_2$ junction was set to be optically transparent, and (b), (d) and (f) the corresponding photovoltaic behaviour (the lines for N$_D$ = 7×10$^{12}$ cm$^{-3}$, N$_A$ = 7×10$^{14}$, 7×10$^{12}$ cm$^{-3}$ overlapped each other). The Fermi level of the TiO$_2$ layer was modulated by the donor and acceptor concentrations as indicated in the figure legends. The TiO$_2$
layer was set to be optically transparent.

Figure S15.1 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p⁺-Si/i-Si/TiO₂(800 °C). The thickness of i-Si was set to be 350 μm.
Fig. S15.2 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p⁺-Si/i-Si/TiO₂(800 °C). The thickness of i-Si was set to be 35 μm.
Fig. S15.3 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p⁺-Si/i-Si/TiO₂(800 °C). The thickness of i-Si was set to be 3.5 μm.
Fig. S15.4 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p⁺-Si/i-Si/TiO₂(800 °C). The thickness of i-Si was set to be 0.35 μm.
Fig. S15.5 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p⁺-Si/i-Si/TiO₂(800 °C). The thickness of i-Si was set to be 35 nm.
Fig. S16.1 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p⁺-Si/i-Si/TiO₂ (as-grown). The thickness of i-Si was set to be 350 μm.
Fig. S16.2 (a) The band diagram of i-Si in dark, (b) the band diagram, (c) electron and hole current density distribution, and (d) electron and hole carrier concentration distribution of i-Si in short-circuit conditions under illumination in p+–Si/i–Si/TiO2 (as-grown). The thickness of i-Si was set to be 35 μm.

Fig. S17 Electron and hole current density distribution of i-Si at -0.01 V under illumination in p+–Si/i–Si/TiO2 (as-grown). The thickness of i-Si was set to be (a) 3.5 μm, (b) 0.35 μm and (c) 35 nm.
Fig. S18 The band structures of semiconductors and contacts before contacting. The doping concentration of i-Si, n\textsuperscript{+}-Si, p\textsuperscript{+}-Si and TiO\textsubscript{2}(800 °C) was 1 × 10\textsuperscript{13} cm\textsuperscript{-3} (N\textsubscript{D}), 1 × 10\textsuperscript{19} cm\textsuperscript{-3} (N\textsubscript{D}), 1 × 10\textsuperscript{19} cm\textsuperscript{-3} (N\textsubscript{A}), and 5.9 × 10\textsuperscript{19} cm\textsuperscript{-3} (N\textsubscript{D}), respectively. The relative conduction and valence band offsets of Si/TiO\textsubscript{2} heterojunctions follows the experimental values by photoelectron spectroscopy.\textsuperscript{11}
Fig. S19 Band diagrams of i-Si electrodes with different front and back contacts. $p^+$-Si, with a Fermi level more positive than that of i-Si, will deplete the electrons of i-Si in the vicinity of the heterojunction interface resulting in an upward band bending. In contrast, the Fermi level of $n^+$-Si is more negative than that of i-Si. Electrons will accumulate at the interfaces, resulting in a downward band bending. As the Fermi level of TiO$_2$ is more positive than that of i-Si, it will induce an upward band bending near the interface similar to $p^+$-Si. Almost no band bending will be formed near the interface between i-Si and TiO$_2$(800 °C), since their Fermi levels are nearly identical.
Fig. S20 (a) The model for simulating a one-dimensional SrTiO$_3$ particle with H$_2$ evolution and O$_2$ evolution sites on the left and right, respectively. The parameters for simulation were listed in Table S5. The (b) band diagram, (c) electron and hole current density distribution, (d) electron and hole carrier concentration distribution, and (e) photovoltaic behaviour of the SrTiO$_3$ particle under illumination. The window layer was set to be optically transparent.
### Table S1 Performance and band energy levels of reported photocatalysts for overall water splitting

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Cocatalyst</th>
<th>Apparent quantum yield</th>
<th>Particle size (diameter) / nm</th>
<th>$\sqrt{3} W_{dep}$ / nm</th>
<th>$V_{BB}$ / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile-type TiO$_2$</td>
<td>Pt</td>
<td>1% at 350 nm</td>
<td>~ 50</td>
<td>658</td>
<td>1.4</td>
</tr>
<tr>
<td>GaN:ZnO</td>
<td>RhCrO$_x$</td>
<td>2.5% at 420 - 440 nm</td>
<td>~ 20</td>
<td>118</td>
<td>7.2</td>
</tr>
<tr>
<td>LaMg$<em>{1/3}$Ta$</em>{2/3}$O$_2$N</td>
<td>RhCrO$_x$</td>
<td>0.03% at 440 ± 30 nm</td>
<td>~ 80</td>
<td>173</td>
<td>54</td>
</tr>
<tr>
<td>TaON</td>
<td>Cr$_2$O$_3$/RuO$_x$;</td>
<td>&lt; 0.1% at 420 nm</td>
<td>~ 400</td>
<td>336</td>
<td>354</td>
</tr>
</tbody>
</table>

$V_{be} = 1.0$ V; $N_D = 1 \times 10^{17}$ cm$^{-3}$; $\epsilon_r = 8.85 \times 10^{-12}$ F/m; $\epsilon_r = 130$ (TiO$_2$); 4.2 (GaN:ZnO); 8.91 (LaMg$_{1/3}$Ta$_{2/3}$O$_2$N); or 34 (TaON).

### Table S2 Charge carrier concentration of TiO$_2$ films with and without annealing in H$_2$.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Charge carrier type</th>
<th>Charge carrier concentration / cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (as-grown)</td>
<td>close to intrinsic</td>
<td>Not available</td>
</tr>
<tr>
<td>TiO$_2$ (600 °C)</td>
<td>n</td>
<td>$1.8 \times 10^{19}$</td>
</tr>
<tr>
<td>TiO$_2$ (700 °C)</td>
<td>n</td>
<td>$4.2 \times 10^{19}$</td>
</tr>
<tr>
<td>TiO$_2$ (800 °C)</td>
<td>n</td>
<td>$5.9 \times 10^{19}$</td>
</tr>
</tbody>
</table>

### Table S3 Physical input parameters of Si and TiO$_2$ used in SCAP3307.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Si</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness / μm</td>
<td>i-Si: 350</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>p$^+/n^+$-Si: 0.5</td>
<td></td>
</tr>
<tr>
<td>Bandgap / eV</td>
<td>1.12</td>
<td>0.70$^a$</td>
</tr>
<tr>
<td>Electron affinity / eV</td>
<td>4.05</td>
<td>4.40</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>11.9</td>
<td>130</td>
</tr>
<tr>
<td>CB effective density of states / cm$^{-3}$</td>
<td>$2.80 \times 10^{19}$</td>
<td>$7.00 \times 10^{20}$</td>
</tr>
<tr>
<td>VB effective density of states / cm$^{-3}$</td>
<td>$1.04 \times 10^{19}$</td>
<td>$1.00 \times 10^{20}$</td>
</tr>
<tr>
<td>Electron thermal velocity / cm s$^{-1}$</td>
<td>$2.30 \times 10^{7}$</td>
<td>$5.00 \times 10^{7}$</td>
</tr>
<tr>
<td>Hole thermal velocity / cm s$^{-1}$</td>
<td>$1.65 \times 10^{7}$</td>
<td>$5.00 \times 10^{7}$</td>
</tr>
<tr>
<td>Electron mobility / cm$^2$ V$^{-1}$ S$^{-1}$</td>
<td>1500</td>
<td>10</td>
</tr>
</tbody>
</table>
Table S4 Physical input parameters of SrTiO$_3$ and the window layer used in SCAP3307.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SrTiO$_3$</th>
<th>Window layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>350 nm</td>
<td>1-5 μm</td>
</tr>
<tr>
<td>Bandgap / eV</td>
<td>3.31</td>
<td>3.31</td>
</tr>
<tr>
<td>Electron affinity / eV</td>
<td>4.20</td>
<td>4.20</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>300</td>
<td>10000</td>
</tr>
<tr>
<td>CB effective density of states / cm$^-3$</td>
<td>$7.94 \times 10^{20}$</td>
<td>$7.94 \times 10^{20}$</td>
</tr>
<tr>
<td>VB effective density of states /cm$^-3$</td>
<td>$6.71 \times 10^{20}$</td>
<td>$6.71 \times 10^{20}$</td>
</tr>
<tr>
<td>Electron thermal velocity / cm s$^{-1}$</td>
<td>$5.00 \times 10^{7}$</td>
<td>$5.00 \times 10^{7}$</td>
</tr>
<tr>
<td>hole thermal velocity / cm s$^{-1}$</td>
<td>$5.00 \times 10^{7}$</td>
<td>5.00</td>
</tr>
<tr>
<td>Electron mobility / cm$^2$ V$^-1$ S$^{-1}$</td>
<td>6.0</td>
<td>$6.0 \times 10^5$</td>
</tr>
<tr>
<td>Hole mobility / cm$^2$ V$^-1$ S$^{-1}$</td>
<td>6.0</td>
<td>$6.0 \times 10^3$</td>
</tr>
<tr>
<td>Donor density N$_D$ / cm$^-3$</td>
<td>$1.0 \times 10^{18}$</td>
<td>—</td>
</tr>
<tr>
<td>Acceptor density N$_A$ / cm$^-3$</td>
<td>—</td>
<td>$1.0 \times 10^{10}$</td>
</tr>
</tbody>
</table>

Table S5 Effects of front and back contact combinations on the carrier-collection behaviour types of i-Si photoelectrodes.

<table>
<thead>
<tr>
<th>Front contact</th>
<th>Back contact</th>
<th>Type of photoelectrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$(as-grown)</td>
<td>n$^-$-Si</td>
<td>Photoanode</td>
</tr>
<tr>
<td>TiO$_2$(as-grown)</td>
<td>p$^-$-Si</td>
<td>Photocathode with weak cathodic photoconductivity</td>
</tr>
<tr>
<td>TiO$_2$(800 °C)</td>
<td>n$^-$-Si</td>
<td>Photoconductivity with no photovoltage</td>
</tr>
<tr>
<td>TiO$_2$(800 °C)</td>
<td>p$^-$-Si</td>
<td>Photocathode</td>
</tr>
</tbody>
</table>
References