Supporting Information

Surface polaron states on single-crystal rutile TiO₂ nanorods array enhancing charge separation and transfer

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Fig. S1. (a) TEM image of a nanorod and High-resolution TEM lattice image of different parts of a whole TiO_2 nanorod. The dotted line square indicates the (b) the left, (c) the middle and (d) the right region.



Fig. S2. SEM image of the TiO_2 nanorods arrays after electrochemical doping at -1.7 V for 60 s in 1 M NaOH solution.



Fig. S3. The UV-visible absorption spectra of TiO_2 nanorods array before and after electrochemical doping at -1.7 V for 60 s.



Fig. S4. (a) Photocurrent density curves of TiO_2 nanorods electrode in in 1 M NaOH and 1 M NaOH+0.5 M Na₂SO₃ solution before and after electrochemical doping at -1.7 V for 20 s. (b) Separation and (c) injection efficiency of TiO_2 nanorods array electrode before and after electrochemical doping at -1.7 V for 20 s.

The charge injection efficiency Φ_{inj} and charge separation efficiency Φ_{sep} were calculated through Eq. (1)~(3):

$$J_{PEC} = J_{abs} \times \Phi_{inj} \times \Phi_{sep} \tag{1}$$

$$\boldsymbol{\Phi}_{inj} = J_{H_2O} \,/ \,J_{Na_2SO_3} \tag{2}$$

$$\Phi_{sep} = J_{Na_2SO_3} / J_{abs} \tag{3}$$

Where, J_{PEC} is the measured photocurrent density of the TiO₂ electrode in 1M NaOH, J_{abs} is the photocurrent density when completely converting the absorbed photons into current, J_{abs} is the theoretical photocurrent density of 12 mA·cm⁻² under our experimental conditions,¹⁻³ J_{H_2O} is the photocurrent density when probing H₂O oxidation, and $J_{Na_2SO_3}$ is the photocurrent density with the existence of Na₂SO₃.



Fig. S5. Mott-Schottky plots for TiO_2 nanorods electrode and FTO substrate in 1 M NaOH electrolyte in the dark at 1 kHz.



Fig. S6. Cyclic voltammograms of TiO_2 nanorods electrode before and after electrochemical doping in 1 M NaOH solution at potentials from -1.4 V to -1.7 V for 20 s.

Generally, the interfacial capacitance can be calculated with the cyclic voltammetry (CV) scan curve described as:

$$C = \frac{1}{s \cdot m \cdot \Delta V} \int_{V0}^{V0} \int_{V0}^{+\Delta V} i dV$$

(C is the capacitance, s is the scan rate, m is the mass, V is the applied voltage, i is the current). In other words, the interfacial capacitance was proportional to the integral area of the CV curve.⁴ The CV curves of the samples showed that the interfacial capacitance became larger with more negative applied electrochemical doping bias. Combined with the photocurrent experiment results, we considered that the increased saturated photocurrent of TiO_2 nanorods electrode was due to the enhanced electron capacity caused by electrochemical doping inducing surface polaron states. This may mean that the surface polaron states are an important electron transfer route to promote the charge separation and prolong the life of the photogenerated carriers.



Fig. S7. Transient currents of (a) the pristine TiO_2 nanorods electrode and (b) the electrochemical doping one at -1.7 V for 20 s when varying the potentials with a step of 0.1 V. The insets are partially enlarged view. (c) The integrated charge of the transient current-time curves in a and b.

To confirm our hypothesis of the electron transfer route, the dark transient current response of TiO₂ nanorods electrode was investigated to trace the trapping and filling processes of the electrons. The reported flat band potential (U_{fb}) of the TiO₂ electrode measured by Mott-Schottky equation was -1.14 V (pH 13.6).⁵⁻⁶ In order to completely deplete the charges which may be stored in the space charge region and surface polaron states, the TiO₂ nanorods electrode was polarized for 30 s firstly and the polarization potential was much more positive than its U_{fb}. So, we conducted the electrode polarization at 0 V in 1 M NaOH (pH 13.6). After that, the potential was immediately transferred to a preset potential which was more positive than U_{fb} and the transient current was recorded under the dark.

The dark transient current of the TiO_2 nanorods electrode showed that when the potential shifted from 0 V to a negative one, a cathodic current was observed and then decayed to a stable value depend on the applied potentials. In the pristine sample, the transient current decreased to almost zero quickly at potentials more positive than -0.7 V. And the decay time of the transient current significantly increased as the applied potential more negative than -0.7 V (Fig. S7a). However, after electrochemical doping at -1.7 V for 20 s, the potential at which the decay time increased obviously was -0.6 V more positive than that of the pristine. Meanwhile, the decay time of the electrochemical doping sample became longer than that of the pristine at the same potential negative than -0.6 V (Fig. S7b). The integrated charge of the pristine and electrochemical doping electrodes from the transient current-time curves also revealed that the charge filling and transferring processes were different (Fig. S7c). The accumulated charge of the pristine electrodes increased sharply at -0.7 V while that potential of the electrochemical doping sample was more positive at -0.6 V. Meanwhile, the amount of the accumulated charge of the doping sample was larger than that of the pristine significantly.

When the applied potential was changed, the space charge region induced by high built-in potential can effectively eliminate the charge out of the space charge region because of the rapid charge redistribution, so that the new equilibrium state can be reached quickly, showing the negligible current decay time. However, the occurrence of electron injection into the surface polaron states will prolong the current decay time and increase the charge, depending on whether Fermi level of the semiconductor passes through the surface polaron states. So, the cathodic current decay was mainly attributed to the gradual electron injection process of surface polaron states before reaching a new equilibrium state. Take the pristine electrode for example, when the potential was more positive than -0.7 V, the rapid current decay was attributed to the injection of a small number of electrons into the surface polaron states to establish a new equilibrium state. However, a prolonged current decay time at the potential more negative than -0.7 V would be due to the migration of a large number of electrons to the surface polaron states, which took a long time to reach the new equilibrium. After electrochemical doping, more surface polaron states were induced into the electrode, that is, it needed more positive applied bias to eliminate the charge out of the space charge region and reach to the new equilibrium quickly. The potential at which the new equilibrium state reached rapidly changes from -0.7 V to -0.6 V.



Fig. S8. The model of the nanorods electrode applied to estimate the surface areas (left). The diameter and length are plotted on one nanorod (right).

Illustrated by the top and cross section SEM image (Fig. 1b and 1c), the diameter and the length are 90 nm and 2 μ m, respectively. The number of nanorods per square micrometer was around 30. Here, we estimate the surface areas of TiO₂ nanorods electrode by firstly estimating the number of nanorods per unit area, and then multiplying by the exposed area of a single nanorod (only the sides are calculated) to get the specific reaction area during the catalytic process. The equation as follows:

$$S_{total} = n \cdot S_{single} = n \cdot 4dl$$

where the n is the number of nanorods per unit area, d is the diameter and l is the length. So, the results indicate that the actual reaction area with a projected area of 1 μ m² is approximately 22 μ m², that is the surface areas of TiO₂ nanorods electrodes are about 20 times larger than that of the single crystal wafer electrode.



Fig. S9. (a) Photocurrent density curves and (b) Mott-Schottky plots of rutile single electrode before and after electrochemical doping in 1 M NaOH at -1.7 V for 60 s, 120 s, and 180 s.

Reference

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