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Supporting Information for

Synergistic effects of $SrTiO_3$ nanocubes and Ti^{3+} dual-doping for highly improving photoelectrochemical performance of TiO_2 nanotube arrays under visible light

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1. Experimental

1.1 Chemical reagents and characterization

As substrates for TiO_2 nanotube arrays growth we used titanium foils (>99.9% purity, Bao ji Titanium Industry Co., Ltd.) with a thickness of 0.2 mm. Acetone, ammonium fluoride, AL powders, ethanol, ethylene glycol, hydrofluoric acid, nitric acid, potassium hydroxide, and sodium hydroxide were obtained from Sinopharm Chemical Reagent Co., Ltd, without any further purification. Strontium hydroxide octahydrate ($Sr(OH)_2 \cdot 8H_2O$) was purchased from Alfa. Deionized water (18 MΩ, molecular) was used for preparing all solutions.

A field-emission scanning electron microscope (JSM-6701F, JEOL) was used for the morphological characterization of the electrodes. X-ray diffraction (PANalytical X'Pert PRO) was carried out using graphite monochromized CuKa radiation (40 kV). The XRD patterns were recorded from 20° to 80° at a scanning rate of 0.067°/s. UV-visible diffusion reflectance spectra were measured on a UV-2550 (Shimadzu) spectrometer by using $BaSO_4$ as the reference. Evolved hydrogen gas was detected by a gas chromatograph (GC-2014C, Shimadzu). The elemental composition was determined by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD).

Synchronous illumination X-ray photoelectron spectroscopy (SIXPS).

In the case of in-situ XPS, the sample is placed into the vacuum chamber of the XPS instrument, in which an optical fiber has been seated. The normal XPS is firstly carry out in the dark for one circle and then the optical fiber is turned on for providing the light. The wavelength of the light can be fixed to visible or UV light by put in or out the 420 nm cut-off filter. The changes of XPS spectra were recorded by controlling light on or off at given time intervals.

1.2 Preparation of TiO_2、$SrTiO_3$ nanotube arrays and $SrTiO_3/TiO_2$ heterostructured nanotube arrays.

First, titanium foil was cut into 1 x 3 cm strips. Prior to anodization, these strips were degreased ultrasonically in turn in acetone, ethanol, and deionized water for about 15 min, and then polished in a 1:1 mixture of hydrofluoric acid (24 M) and nitric acid (10 M), and rinsed extensively with deionized water. The titanium strip was placed in a plastic beaker equipped with a platinum slice negative electrode and continuous current power supply. Ammonium fluoride (0.3 wt %) and deionized water (3 wt %) diluted in ethylene glycol (200 ml) was used as electrolyte. A constant potential of 60 V was supplied between the two electrodes for 30 min. Subsequently, the strip was washed with ethylene glycol and sonicated for 30 s, and then washed with deionized water and sonicated for 15 s to remove the surface deposit. To obtain TiO_2 NTs, these strips were annealed at 450 °C for 2 h with a programming rate of 5 °C/min for both warming up and cooling down. Well aligned crystalline anatase TiO_2 nanotube arrays with the average length of 3.8 um were obtained.

The TiO_2 nanotube arrays obtained in the above step were used as both substrate and reactant for the fabrication of heterostructured $SrTiO_3/TiO_2$ nanotube arrays. In a typical synthesis, 0.025 g $Sr(OH)_2{\cdot}8H_2O$ and 5 g NaOH were dissolved in 40 ml deionized wateras the precursor solution, following by stirring for 0.5 h. The TiO_2 strip was put in a 50 mL Teflon-lined stainless steel autoclave filled with the precursor solution. The hydrothermal reaction was carried out at 150 °C for 25, 35, 45 and 55 min in an electric oven, respectively. After the autoclave was cooled to room temperature, the sample was taken out and rinsed extensively with deionized water, and then dried at 60 °C for 1 h. The synthesis $SrTiO_3$ nanotube arrays were similar to that of $SrTiO_3/TiO_2$ heterostructures, except that the hydrothermal reaction was carried out at 180 °C for 60 h.

1.3 Preparation of $SrTiO_{3-x}/TiO_{2-x}$ heterostructures and TiO_{2-x}、 $SrTiO_{3-x}$ nanotube arrays.

A certain amount of AL powders and heterostructured $SrTiO_3/TiO_2$ nanotube arrays obtained in the above step were separately placed in an evacuated two-zone furnace of 800 °C (molten AL) and 450 °C ($SrTiO_3/TiO_2$) for 6 h in a 5×10^{-4} Pa pressure. The synthetic approach of TiO_{2-x} (The Al-reduced TiO_2, $SrTiO_3$ and $SrTiO_3/TiO_2$ samples are denoted as TiO_{2-x}, $SrTiO_{3-x}$ and $SrTiO_{3-x}/TiO_{2-x}$, respectively) and $SrTiO_{3-x}$ was similar to that of $SrTiO_{3-x}/TiO_{2-x}$ heterostructures, except that the 450 °C-zone was corresponding to TiO_2 and $SrTiO_3$.

1.4 Photoconversion and photoelectrochemical hydrogen production.

A three-electrode configuration was used in the PEC measurement, with the heterostructure nanotube arrays as the working electrode (photoanode), a saturated calomel electrode (SCE) as the reference electrode, and a platinum foil as the counter electrode. 1 M KOH aqueous solution was used as an electrolyte. The TiO_2, $SrTiO_3$ nanotube arrays, $SrTiO_3/TiO_2$ heterostructures, TiO_{2-x}, $SrTiO_{3-x}$ nanotube arrays, $SrTiO_{3-x}/TiO_{2-x}$ heterostructures were used as the photoanodes, respectively. Photocurrent response under visible-light irradiation was recorded with a CHI-660D potentiostat in a sandwich-type configuration with a Pt slice as counter electrode, an SCE reference electrode, and 1M NaOH solution as electrolyte. A 300 W xenon arc lamp equipped with an UV cutoff filter (HSX-F300, Beijing NBeT Technology Co., Ltd) calibrated to 200 $mWcm^{-2}$, which was measured with a radiometer (CEL-NP2000, Beijing Au-light Co., Ltd), served as light source. The photocurrent response under monochromatic light was measured by using a 300 W Xe lamp and a monochromator (71SWS, Beijing 7-Star Optical Instruments Co., Ltd) at 0.6 V vs SCE. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky curves were performed by using of Zahner IM6. EIS measurements were performed by applying 0.6 V_{SCE} at a frequency range of 100,000 Hz to 0.01 Hz with amplitude of 10 mV in the dark. The Mott-Schottky curves were obtained under dark conditions at a frequency of 5k Hz in 1 M NaOH solution, amplitude +/- 10 mV. All experiments were carried out under ambient conditions.

Photoelectrochemical H_2 evolution was studied in a self-made photoreactor (Figure S6A), in which the photoanode and the counter electrode were separated by an Amberplex membrane. KOH (1 M) was utilized as electrolyte in the presence of methanol, and a Ti slice loaded with Ti^{3+}self-doped $SrTiO_{3-x}/TiO_{2-x}$ heterostructures was used as photoanode. A saturated calomel electrode was used as reference electrode. Evolved H_2 gas was collected and measured according to the standard H_2 evolution curve, which is shown in Figure S6B of the Supporting Information.

Additional figures and discussions

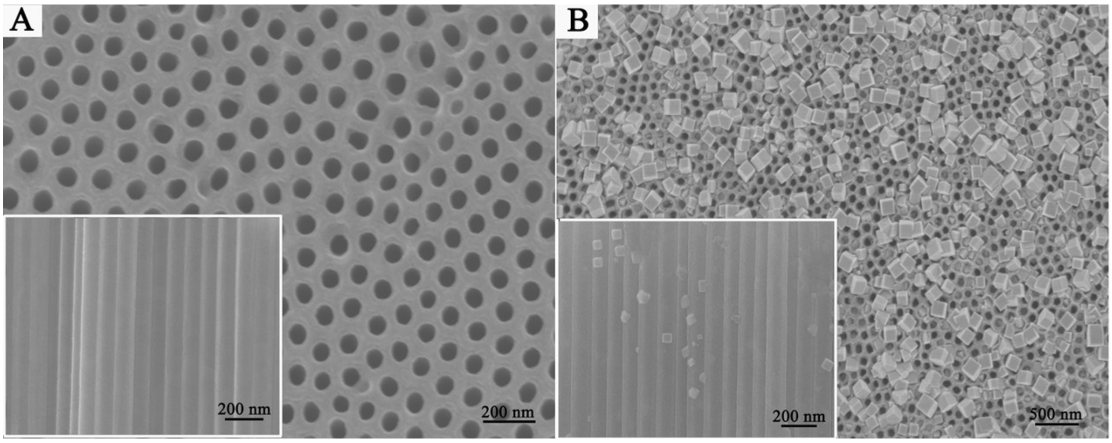

Figure S1. SEM top and cross sectional images of A) TiO_2 nanotube arrays, B) pristine $SrTiO_3/TiO_2$ after hydrothermal reaction times 35 min.

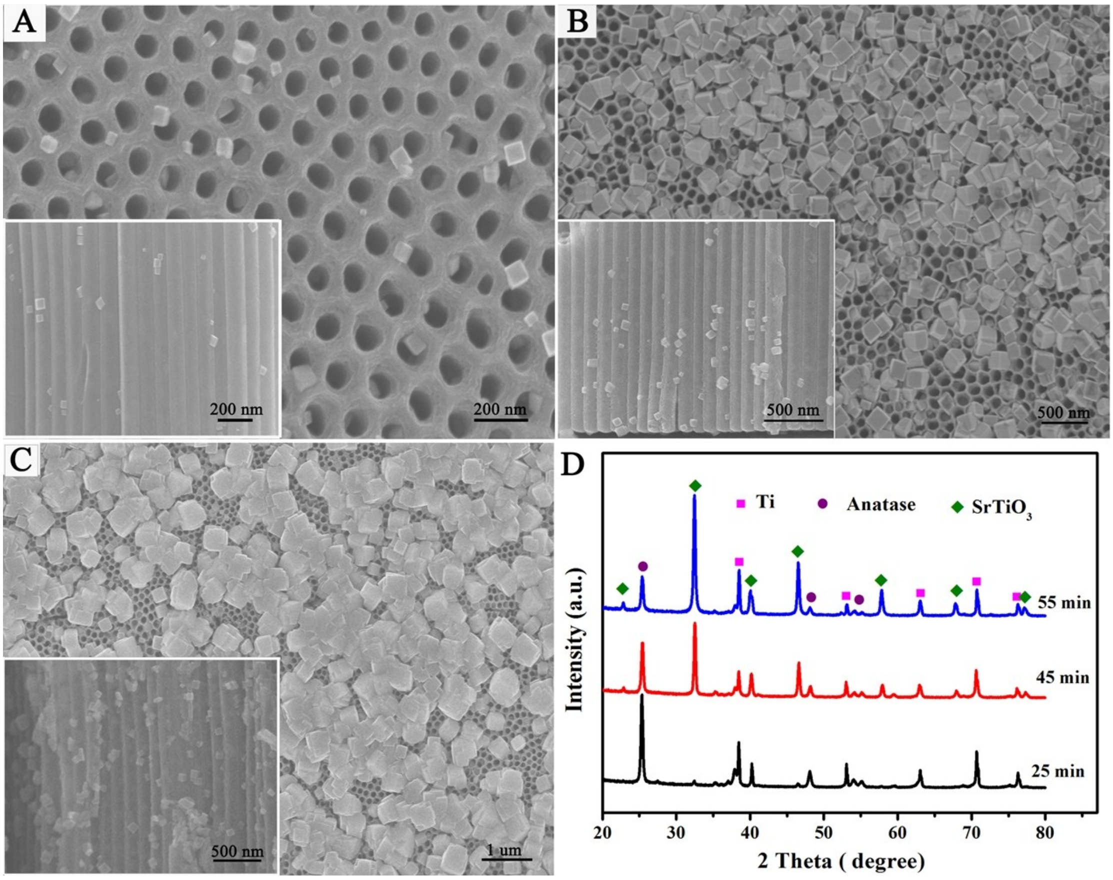

Figure S2. SEM top and cross sectional images of A), B), C) reduced $SrTiO_3/TiO_2$ after hydrothermal reaction times 25 min, 45 min, 55 min, respectively. D) XRD patterns of reduced $SrTiO_3/TiO_2$ after different hydrothermal reaction times.

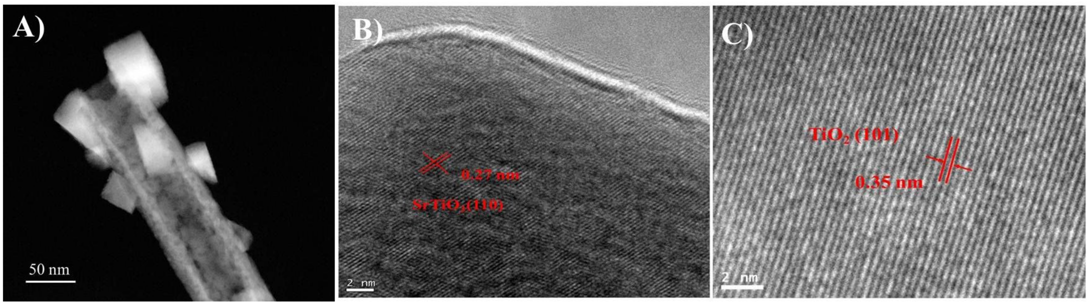

Figure S3. TEM images of A) pristine $SrTiO_3/TiO_2$; HRTEM images of B) Ti^{3+} doped $SrTiO_3$ and C)Ti^{3+} doped TiO_2.

TEM results and discussions

The TEM image of Ti^{3+} dual-doping $SrTiO_3/TiO_2$ heterojunction has been shown in Figure S3A. It can be seen that after hetero-coupling of $SrTiO_3$ nanocubes and Ti^{3+}-doping, the TiO_2 nanotubes generally kept their original tubular structure. Moreover, the HRTEM images of $SrTiO_{3-x}$ and TiO_{2-x} in the Ti^{3+} dual-doped heterostructures have been also tested and shown in the Figure S3B,C. After the reduction treatment, $SrTiO_{3-x}$ nanocubes exhibit well crystalline structure throughout the whole particles (Figure S3B), and the lattice plane distances are about 0.27 nm, which is consistent with the lattice plane (110) of pure $SrTiO_3$.[1] In addition, the HRTEM image of TiO_2 nanotube was shown in Figure S3C, and the measured lattice fringe fringe space is about 0.35 nm indexed to the (101) plane of the anatase crystal structure of TiO_2.[2] These results clearly reveal that after Ti^{3+} dual-doping, the lattice fringe spacing of both $SrTiO_3$ and TiO_2 have no evident changes, which is consistent previous work [3,4].

References

[1] H. Tan, Z. Zhao, W. Zhu, E. Coker, B. Li, M.Zheng, W.Yu, H. Fan, Z. Sun, *ACS Appl. Mater. Interfaces*, 2014, 6, 19184.

[2] H. Cui, W. Zhao, C. Yang, H. Yin, T. Lin, Y. Shan, Y. Xie, H. Gu, F. Huang, *J. Mater. Chem. A*, 2014, 2, 8612.

[3] J. Du, J. Qi, D. Wang, Z. Tang, *Energy Environ. Sci*. 2012, 5, 6914.

[4] K. Zhu, N. R. Neale, A. Miedaner, A. J. Frank, *Nano Lett*. 2007, 7, 69.

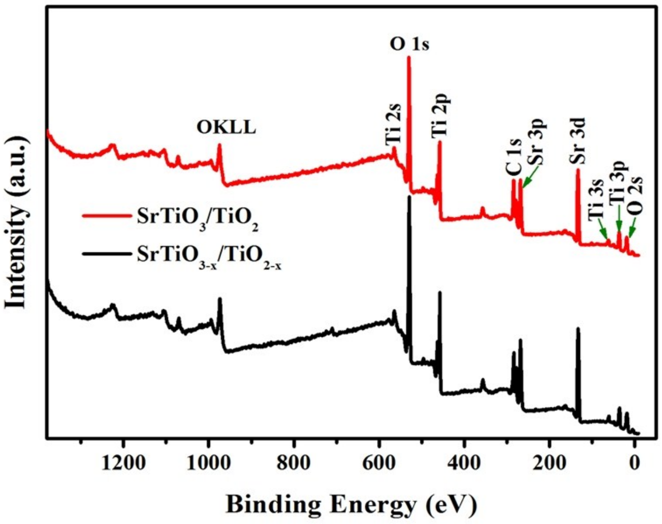

Figure S4. Full-scan XPS spectrum of pristine and reduced $SrTiO_3/TiO_2$ heterostructured nanotube arrays after hydrothermal reaction times 35 min.

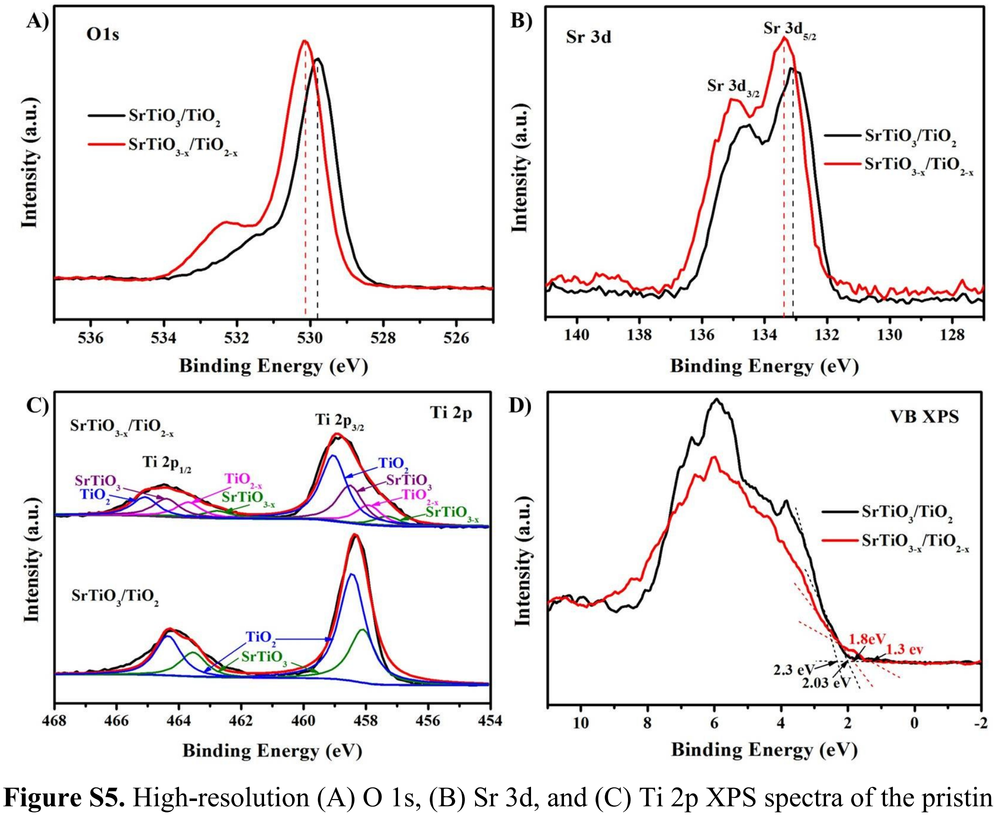

Figure S5. High-resolution (A) O 1s, (B) Sr 3d, and (C) Ti 2p XPS spectra of the pristine $SrTiO_3/TiO_2$ and $SrTiO_{3-x}/TiO_{2-x}$ heterostructured nanotube arrays after hydrothermal reaction times 35 min. (D) XPS valence band spectra of the pristine $SrTiO_3/TiO_2$ and $SrTiO_{3-x}/TiO_{2-x}$ heterostructured nanotube arrays after hydrothermal reaction times 35 min. Dashed lines highlight the linear extrapolation of the curves, deriving two band edge position of 2.03 eV and 1.3 eV.

XPS results and discussions

The X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemical composition, surface chemical bonding, and position of electronic valence band. For comparison, the XPS measurements on $SrTiO_3/TiO_2$ samples without reduction have also been performed. The fully scanned spectra (Figure S4) clearly demonstrate the presence of Ti, Sr, and O elements in the obtained hetero-structure. However, it is worth mentioning that no signal about Al element has been detected. Herein, we consider that the melted aluminum, as a thermite, may only provide reducing atmosphere for pristine $SrTiO_3/TiO_2$ heterostructures and do not dope or coat them.[1] Figure S4 shows the high-resolution spectra of Ti, Sr, and O elements. As shown in Figure S5A and B, a shift to the higher binding energy of the O 1s and Sr 3d peaks are observed for the Ti^{3+} doped $SrTiO_3/TiO_2$ compared with raw $SrTiO_3/TiO_2$. The Ti 2p spectrum of the pristine $SrTiO_3/TiO_2$ shown in Figure S5C suggests that the characteristic peaks centered at 458.33 eV (Ti $2p_{3/2}$) and 464.09 eV (Ti $2p_{1/2}$), indicating a Ti^{4+} oxidation state in the $SrTiO_3/TiO_2$ heterostructures.[2, 3] However, in the case of Ti^{3+} doped $SrTiO_3/TiO_2$ heterostructures, the wide and asymmetric peaks of Ti 2p spectrum indicates that there should be more than two chemical states according to the binding energy. It was considered that Al reduction introduced a considerable amount of Ti^{3+} states in the $SrTiO_3/TiO_2$ heterostructures and naturally resulted in the shifted of the peak. Furthermore, the Ti 2p XPS spectrum could be fitted to four kinds of chemical states (the black curve experimental data, the red line fitted data). More specifically, the spectrum shows eight peaks ascribed to $Ti^{3+}/SrTiO_{3-x}$ (Ti $2p_{3/2}$, 457.31eV; Ti $2p_{1/2}$, 462.76 eV), Ti^{3+}/TiO_{2-x} (Ti $2p_{3/2}$, 457.91 eV; Ti $2p_{1/2}$, 463.81 eV), and $Ti^{4+}/SrTiO_3$ (Ti $2p_{3/2}$, 458.51 eV; Ti $2p_{1/2}$, 464.46 eV), $Ti^{4+}/$ TiO_2 (Ti $2p_{3/2}$, 459.03 eV; Ti $2p_{1/2}$, 464.98 eV).[4] This result clearly confirms the existence of Ti^{3+} (oxygen vacancies), and consistent with the above-described speculation. The valence band spectra of $SrTiO_3/TiO_2$ and Ti^{3+} dual-doped $SrTiO_3/TiO_2$ are shown in Figure S5D. As calculated by linear extrapolation of the peaks to the baselines, the band edge positions of $SrTiO_3/TiO_2$ and Ti^{3+} dual-doped $SrTiO_3/TiO_2$ are 2.03 and 1.80 eV, respectively. More specifically, as a result of Ti^{3+} doping, the VB maximum energy of Ti^{3+} doped $SrTiO_{3-x}/TiO_{2-x}$ showed notable blue-shift about ~1.80 eV following by a band tail further toward 1.30 eV, which leads to a noticeable band gap narrowing (about0.5 eV) in the Ti^{3+} dual-doped $SrTiO_3$ /TiO_2 heterostructures.

References

[1] C. Yang, Z. Wang, T. Lin, H. Yin, X. Lü, D. Wan, T. Xu, C. Zheng, J. Lin, F. Huang, X. Xie, M. Jiang, *J. Am. Chem. Soc*. 2013, *135*, 17831-17838.

[2] Q. Kang, J. Cao, Y. Zhang, L. Liu, H. Xu, J. Ye, *J. Mater. Chem. A*. 2013, *1*, 5766-5774.

[3] T. S. Yang, M. C. Yang, C. B. Shiu, W. K. Chang , M. S. Wong, *Appl. Surf. Sci*. 2006, *252*, 3729.

[4] H. Cui, W. Zhao, C. Yang, H. Yin, T. Lin, Y. Shan, Y. Xie, H. Gu, F. Huang, *J. Mater. Chem. A*. 2014, *2*, 8612-8616.

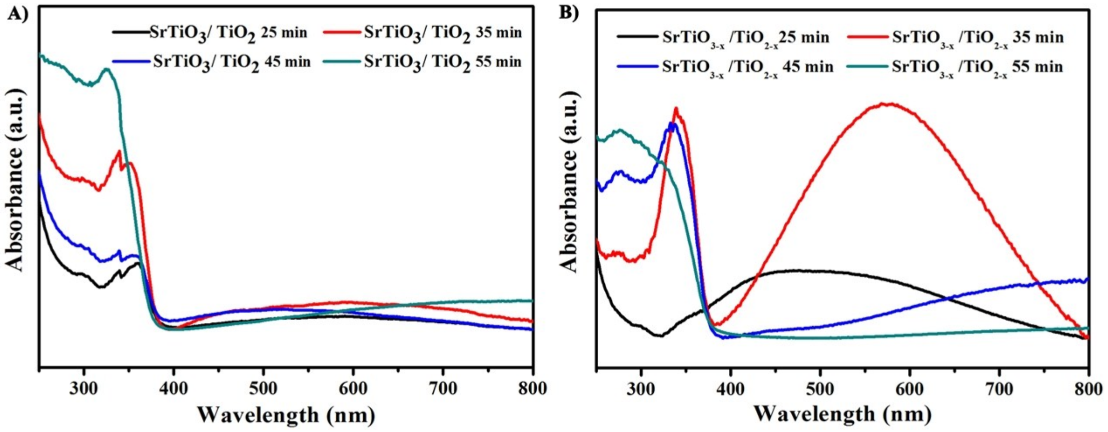

Figure S6. UV-Vis diffusive absorption spectra of A) pristine $SrTiO_3/TiO_2$ heterostructures and B) $SrTiO_{3-x}/TiO_{2-x}$ heterostructures after different hydrothermal reaction time.

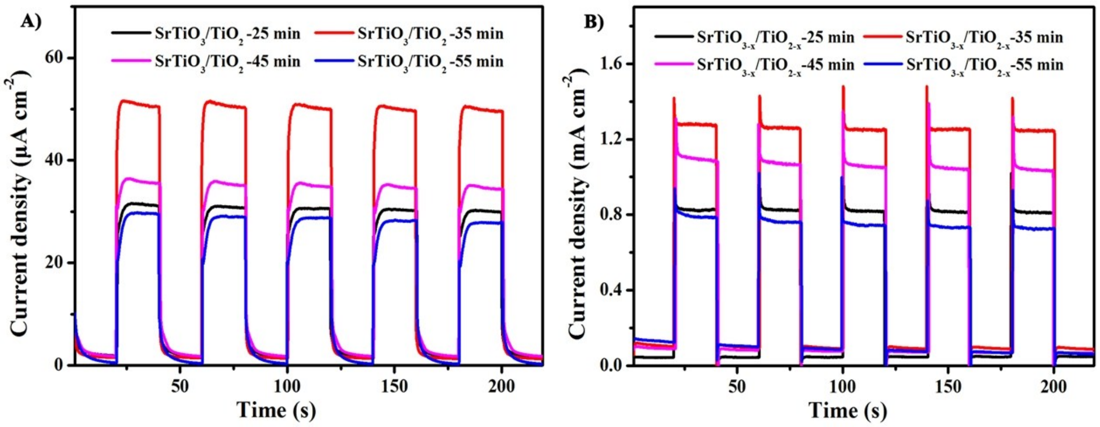

Figure S7. I–t curves of A) pristine $SrTiO_3/TiO_2$ heterostructures and B) $SrTiO_{3-x}/TiO_{2-x}$ heterostructures after different hydrothermal reaction time.

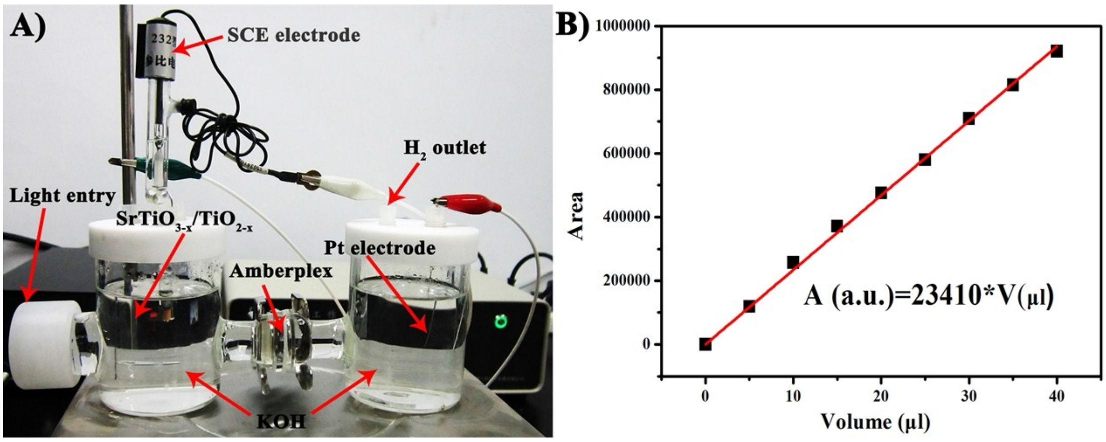

Figure S8. A) Digital photo of the self-made H_2 generation and collection system. B) Standard H_2 evolution curve. The equation between the volume of H_2 and the corresponding peak area can be expressed as follows: A (a.u.) = 23410 × V (μl).

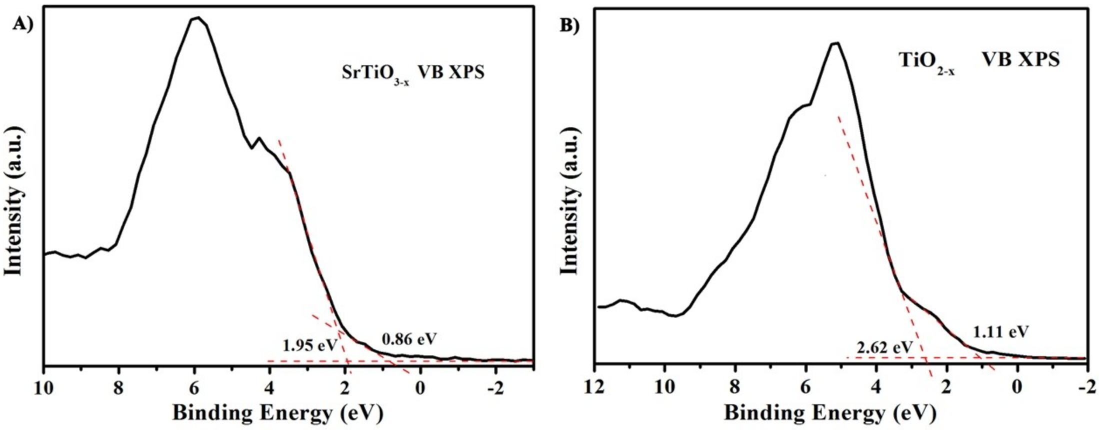

Figure S9. XPS valence band spectra of A) $SrTiO_{3-x}$ and B) TiO_{2-x}. Dashed lines highlight the linear extrapolation of the curves, deriving two band edge position of ~0.86 eV and ~1.11 eV.

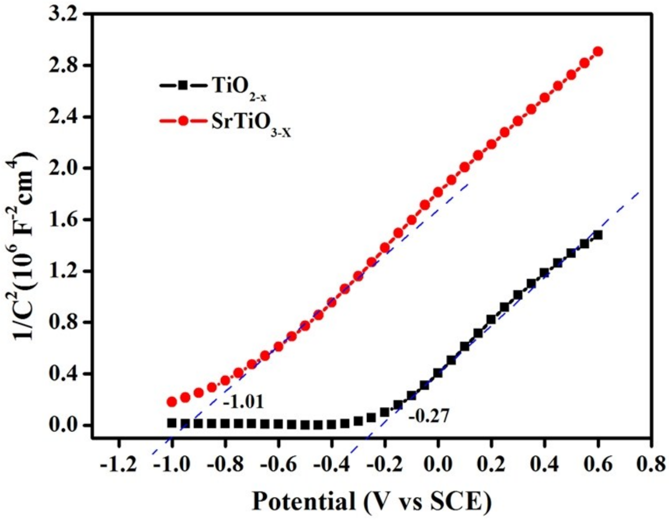

Figure S10. Mott–Schottky plots for $SrTiO_{3-x}$ and TiO_{2-x}.