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Supporting Information

Hetero-Structured $TiO_2/SrTiO_3$ Nanotube Array Film with Highly Reactive Anatase TiO_2 {001} Facets

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Experimental Section

Vertically oriented TiO_2 nanotube array layer with a Ti substrate was fabricated via anodization, which is similar to our previous work[1]. Before anodization, a Ti foil was soaked into anhydrous ethanol, isopropanol, and distilled water for 10 min with ultrasonic treatment. The anodization at a direct current of 60 V was conducted in a two-electrode electrochemical cell of a Ti substrate (0.5 mm, 1 cm × 4 cm, 99.7%), Pt wire (99.7%), and ethylene glycol electrolyte with 0.5 wt.% NH_4F and 3.0 vol.% tri-distilled water. After 30 min pre-anodization, The Ti substrate with regularly-arranged hexagonal patterns was used as the template to implement 120 min anodization at room temperature, and the as-formed TiO_2 nanotube array layer on the Ti substrate was washed in distilled water and then dried at 120 °C in air.

The anodized TiO_2 layer was used as a structure-directed template and initial reactant to fabricate hetero-structured $TiO_2/SrTiO_3$ (TSr) nanotube arrays via a hydrothermal reaction. The anodized Ti substrate was vertically put in a 50 mL Teflon-lined stainless steel autoclave, filling 40 mL of 0.010, 0.025 and 0.050 M $Sr(OH)_2$ hydrothermal solution, then the autoclave was sealed using a holder and placed in an oven at 200 °C for 30 min. After the hydrothermal reaction, the sample was degreased with 1 M HCl solution to remove residual $Sr(OH)_2$ solution, and then washed with anhydrous ethanol and distilled water several times, followed by annealing at 250 and 450 °C in air for 2 h with the temperature ramp 2 °C/min. The reference TiO_2 nanotube array layer and a Ti substrate was implemented the same annealing. The resulting samples annealing at 450 °C with 0.010, 0.025 and 0.050 M $Sr(OH)_2$ solution, the resulting samples before and after annealing at 250 °C with 0.025 M $Sr(OH)_2$ solution, the reference TiO_2 nanotubes before and after annealing at 450 °C, and Ti substrate were marked as TSr_{300}/Ti,

TSr_{301}/Ti, TSr_{302}/Ti, TSr_{301}*/Ti, TSr_{30}*/Ti, TSr_0*/Ti, TSr_0/Ti and Ti (See **Table. S1**), respectively.

The samples were characterized via XRD (CuKa, D8-Focus, AXS, Germany), FE-TEM with EDX (JEM-2100F, JEOL, Japan) and FE-SEM (S-4800, HITACHI, Japan). The bond energies of the hetero-structured TSr samples were measured via XPS (PHI1600, Perkin Elmer, USA). Raman spectra were acquired with a confocal system with an excitation wavelength of 532 nm and resolution of 2 cm^{-1} (InVia Reflex, RENISHAW, UK).

Photocatalytic and photoelectrocatalytic performance of the hetero-structured and reference samples were evaluated by the concentration difference of "target molecular" methylene blue (MB) aqueous solution. The reaction was employed in a home-made, cylindrical quartz reactor with a water cooling jacket and a Xenon lamp (HSX-F300, 300W, Beijing NBet Technology CO., Ltd.) along with collimated, filtered light ($CuSO_4$ filter, λ=365nm), and the distance between the light source and samples was about 28.0 cm and the average UV intensity impacting the samples surface was measured to be 10.0 mW/cm^2 using a spectroradiometer (USR-40; Ushio Inc., Japan). Beforehand, the hetero-structured and reference TSr_0/Ti samples (active size: 1.0 cm × 2.0 cm) with facing the light source, were vertically placed in the reactor containing 100 ml of 10 mg/L MB solution, and then the reactor was sealed using a rubber stopper with a fixed tube of flowing N_2. During these processes, N_2 was continuously introduced into the cell to keep target MB concentration uniformity, and MB solution was kept in the dark for 30 min to maintain the MB absorption-desorption equilibrium before the decolorizing reaction, then the MB solution with the reactive time was measured with using a UV-Vis spectrophotometer (T6, PERSEE, China) at an intensity of 665 nm.

The catalytic activity and electrochemical properties were investigated in 100 mL of 10 mg/L MB electrolyte (pH = 5) solution containing 0.1 M NaCl solution (supporting electrolyte) using a three-electrode configuration with a hetero-structured sample as a anode, saturated Ag/AgCl as a reference electrode, and a Pt silk as a counter electrode, and the pH of electrolyte was regulated by 1 M HCl and/or NaOH solution. A scanning potentiostat (CH Instruments, model CH 660E) was used to measure currents at a scan rate of 10 mV/s with the voltage range from -1.0 V to 1.0 V and provide the applied voltage (0.5 V) for the photoelectrocatalytic process, ant the other operation is similar to the photocatalysis.

Table S1 the hetero-structured and reference samples are fabricated under different conditions

Samples	Concentration of $Sr(OH)_2$ solution (M)	Annealing (°C)	Hydrothermal time (min)
TSr_{300}/Ti	0.010	450	30
TSr_{301}/Ti	0.025	450	30
TSr_{302}/Ti	0.050	450	30
TSr_{301}*/Ti	0.025	No annealing	30
TSr_{30}*/Ti	0.025	250	30
TSr_0*/Ti	0	No annealing	0
TSr_0/Ti	0	450	0
Ti	0	450	0

Figures Caption:

Fig. S1 XRD patterns of the hetero-structured TSr_{301}*/Ti, TSr_{30}*/Ti samples.

Fig. S2 (a) Top-view and (b) side-view FE-SEM of the template TSr_0*/Ti sample.

Fig. S3 (a) Low-resolution and (b) high-resolution FE-TEM views of the reference TSr_0 sample and the corresponding SAED patterns of the selected area A, B.

Fig. S4 Low-resolution FE-TEM views of the (a) hetero-structured TSr_{302}, the (b-c) SAED patters of selected area B, C and (d) EDX spectra of the sample.

Fig. S5 Raman spectra of the hetero-structured TSr_{301}/Ti and reference TSr_0/Ti samples.

Fig. S6 (a) CV curves of the hetero-structured TSr_{301}/Ti sample for the anode (2 circle); (b) LSV curves of the hetero-structured TSr_{301}/Ti and reference TSr_0/Ti samples for the anode.

Fig. S7 Adsorption spectra of photocatalytic decolorizing MB solution over the reference TSr_0/Ti (a) and hetero-structured TSr_{301}/Ti (b) samples with reaction time.

Fig. S8 Adsorption spectra of photoelectrocatalytic decolorizing MB solution over the reference (a) TSr_0/Ti and hetero-structured (b) TSr_{301}/Ti samples with reaction time.

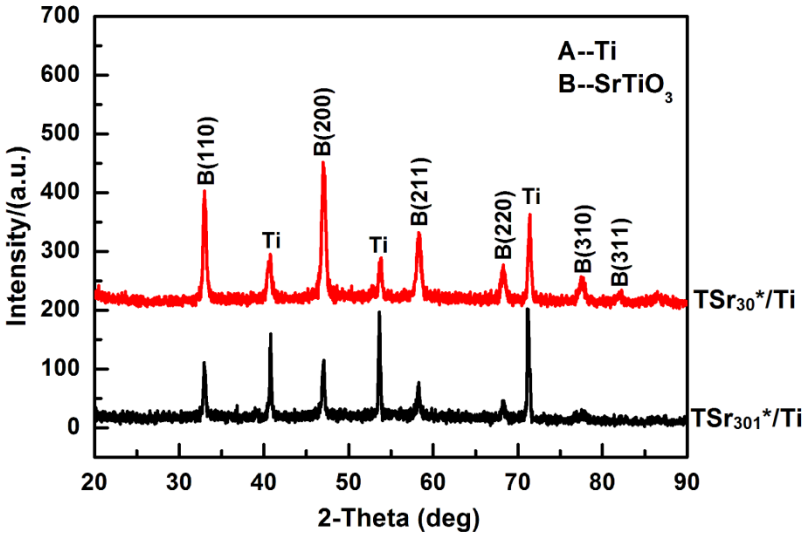
A--Ti
B--SrTiO3
B(110)
Ti
B(200)
Ti
B(211)
B(220)
Ti
B(310)
B(311)
TSr30*/Ti
TSr301*/Ti
Intensity/(a.u.)
2-Theta (deg)
0
100
200
300
400
500
600
700
20
30
40
50
60
70
80
90

Fig. S1

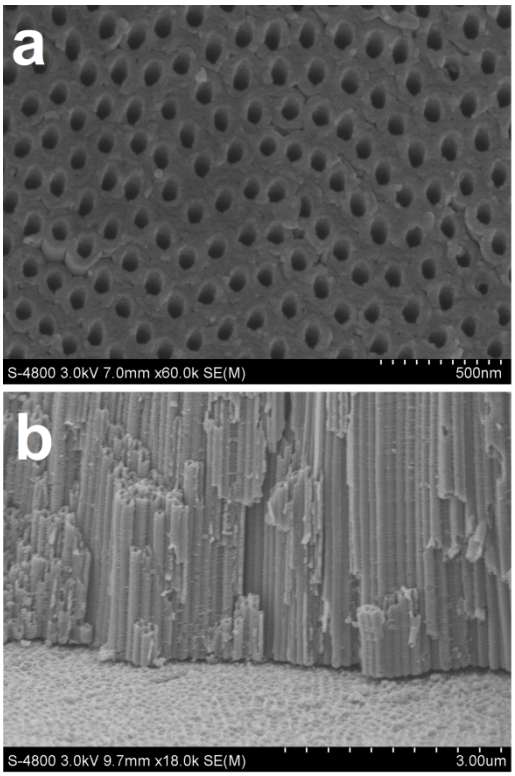
a
S-4800 3.0kV 7.0mm x60.0k SE(M)
500nm
b
S-4800 3.0kV 9.7mm x18.0k SE(M)
3.00um

Fig. S2

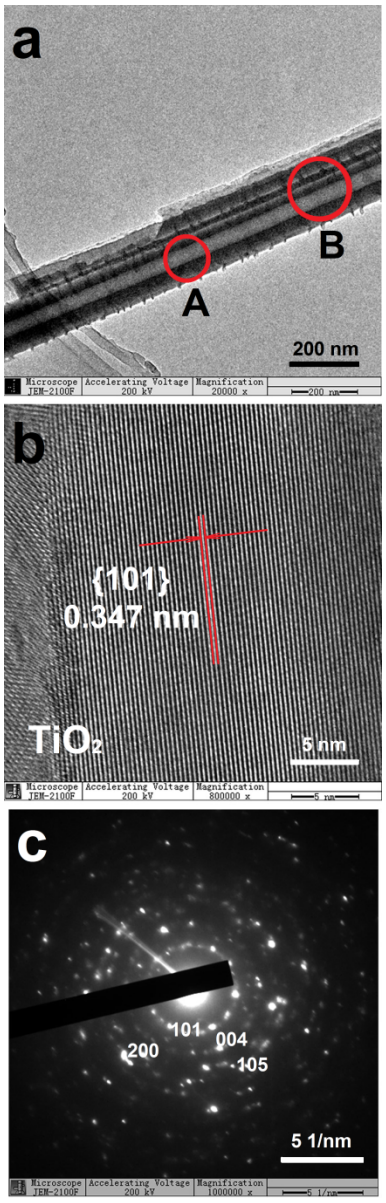
a
A
B
200 nm
Microscope
JEM-2100F
Accelerating Voltage
200 kV
Magnification
20000 x
200 nm
b
{101}
0.347 nm
TiO2
5 nm
Microscope
JEM-2100F
Accelerating Voltage
200 kV
Magnification
800000 x
5 nm
c
101
004
200
105
5 1/nm
Microscope
JEM-2100F
Accelerating Voltage
200 kV
Magnification
1000000 x
5 1/nm

Fig. S3

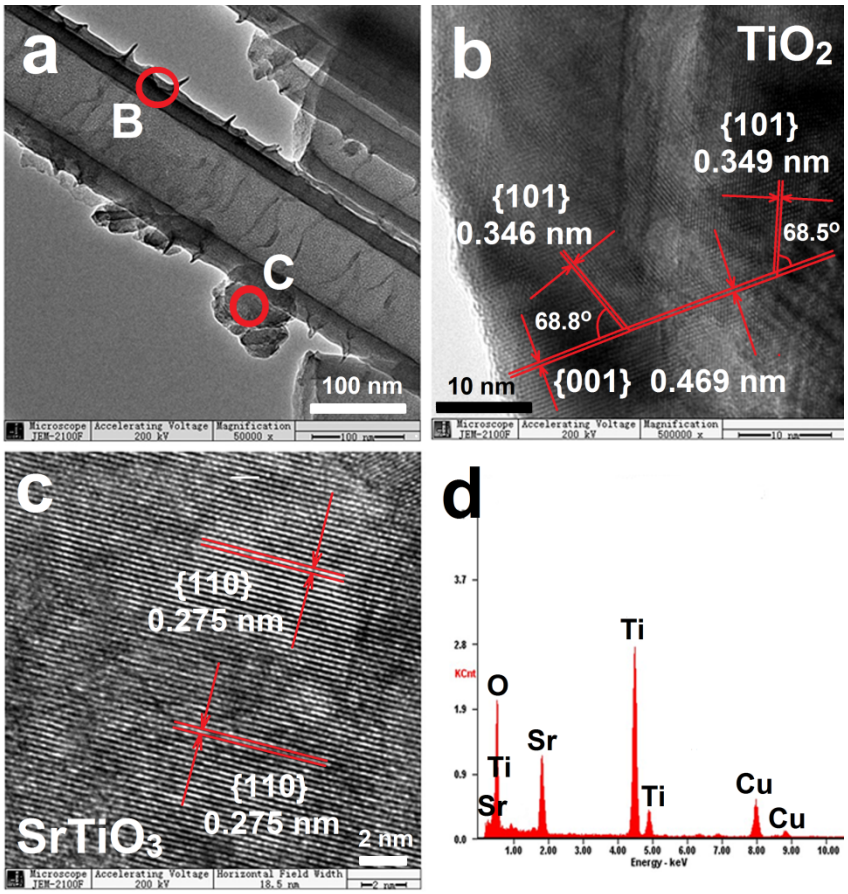
a
B
C
100 nm
b
TiO2
{101}
0.349 nm
{101}
0.346 nm
68.5°
68.8°
10 nm
{001} 0.469 nm
c
{110}
0.275 nm
{110}
0.275 nm
SrTiO3
2 nm
d
Ti
O
Sr
Ti
Sr
Ti
Cu
Cu
KCnt
Energy - keV

Fig. S4

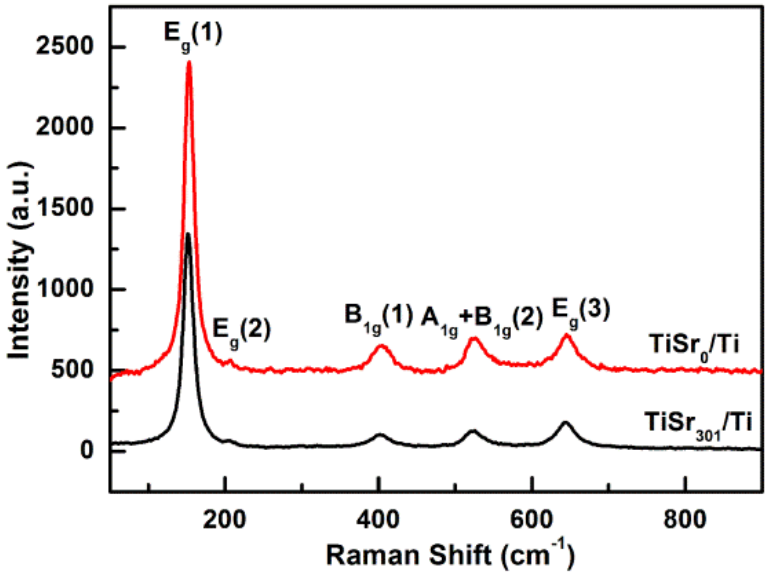
E_g(1)
E_g(2)
B_1g(1) A_1g+B_1g(2) E_g(3)
TiSr_0/Ti
TiSr_301/Ti
Intensity (a.u.)
Raman Shift (cm^-1)
2500
2000
1500
1000
500
0
200
400
600
800

Fig. S5

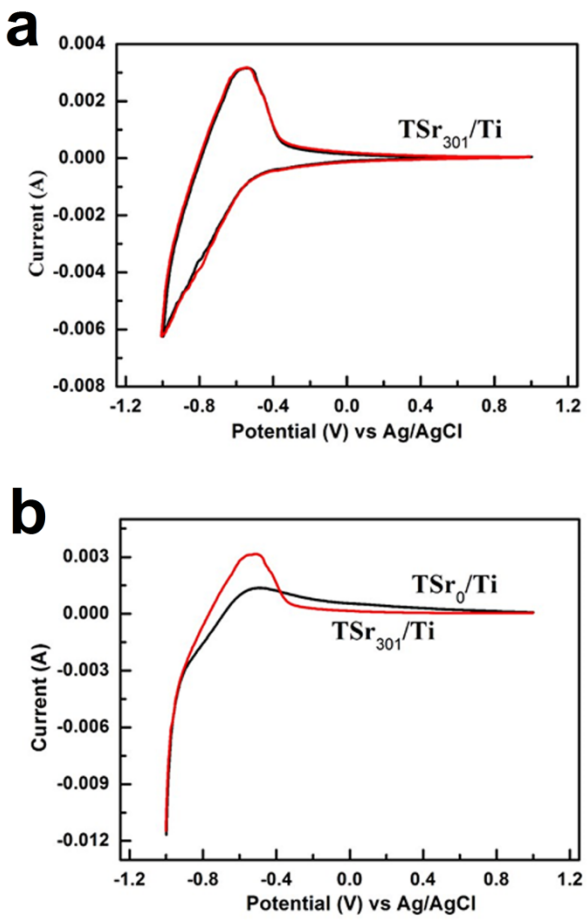
a
0.004
0.002
0.000
-0.002
-0.004
-0.006
-0.008
Current (A)
TSr301/Ti
-1.2
-0.8
-0.4
0.0
0.4
0.8
1.2
Potential (V) vs Ag/AgCl
b
0.003
0.000
-0.003
-0.006
-0.009
-0.012
Current (A)
TSr0/Ti
TSr301/Ti
-1.2
-0.8
-0.4
0.0
0.4
0.8
1.2
Potential (V) vs Ag/AgCl

Fig. S6

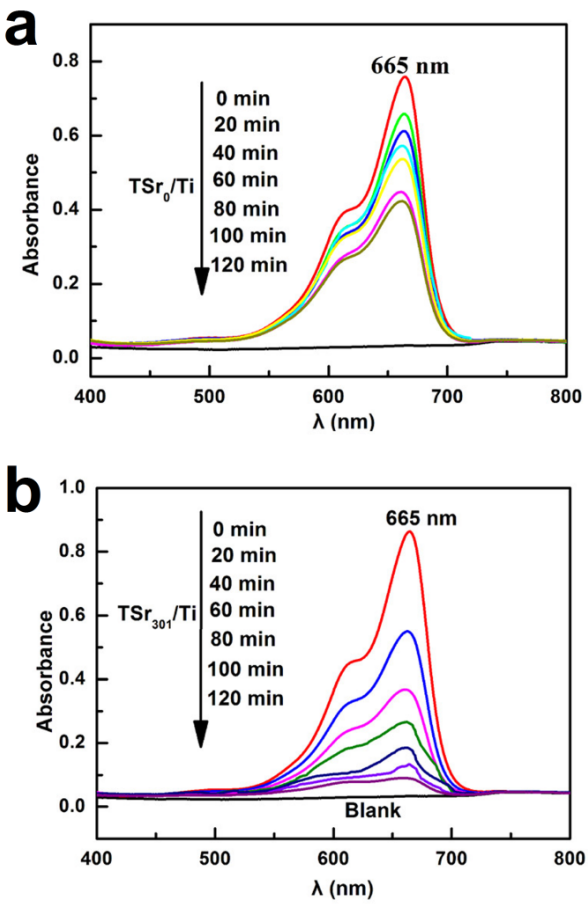
a
665 nm
0 min
20 min
40 min
60 min
80 min
100 min
120 min
TSr0/Ti
Absorbance
λ (nm)
b
665 nm
0 min
20 min
40 min
60 min
80 min
100 min
120 min
TSr301/Ti
Blank
Absorbance
λ (nm)

Fig. S7

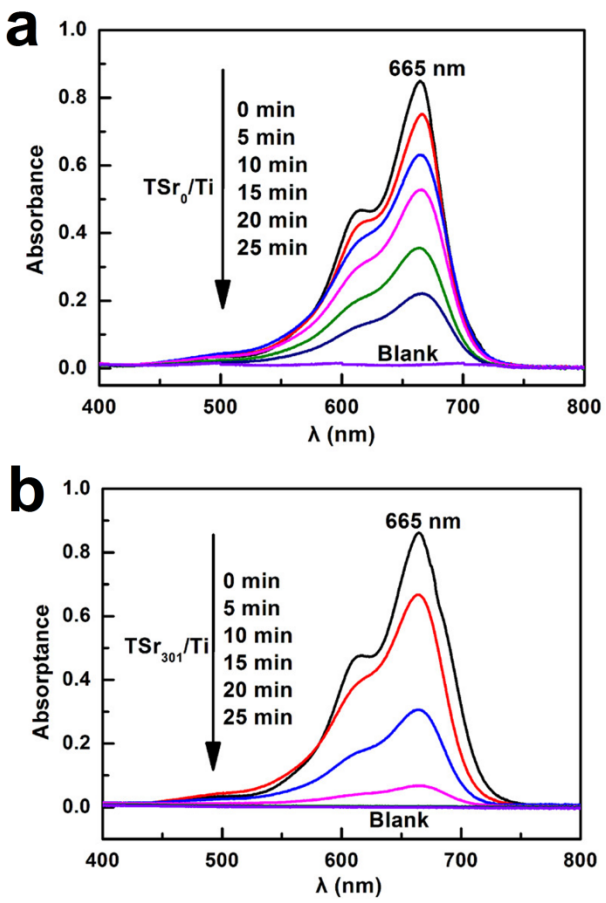

Fig. S8

References

1 J. R. Huang, X. Tan, T. Yu, L. Zhao and S. Xue, *Rsc Adv.*, 2012, 2, 12657-12660.