

Supporting Information

Ultra-fast synthesis of the high performance photocatalytic Ti³⁺ self-doped strontium titanate by an electrochemical assist in molten salt : Effect of electrochemical potential

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Experimentation

Materials and reagent

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and NaCl (AR, Tianjin Damao Chemical Co.Ltd.) reagents as electrolytes. SrO and SrTiO_3 (AR, Shanghai McLean Biochemical Technology Co. Ltd.) provided the source of Sr^{2+} and comparison, respectively. Fe_2O_3 (AR, Tianjin Damao Chemical Co.Ltd.), Ti rod (diameter: 2 mm, length: 20 mm, purity > 99.99%), Ag wire (length: 15 mm, diameter: 1 mm, purity > 99.99%), Mo wire (length: 150 mm, diameter: 1 mm, purity > 99.99%).

Preparation of self-doped SrTiO_3

Ti^{3+} self-doped SrTiO_3 was prepared using an electrolysis process in a three-electrode system. The Fe_2O_3 powders were pressed (2 MPa) into cylindrical pellets (weight: 2g, diameter: 16 mm, height: 4 mm), and the pellet was wrapped with foamed nickel connected with a Mo rod to serve as the cathode. The working electrode was a Ti rod, and the counter electrode was an Ag wire. The SrCl_2 - NaCl (Sr: Na=2:3 M ratio) was used as an electrolyte. Before electrolysis, SrCl_2 and NaCl were homogeneously mixed and dried for about 6 h at 220 °C under vacuum to remove crystalline water. The mixed salt was placed in an alumina ceramic crucible (OD:90 mm, ID:85 mm, Height: 110 mm) and placed in a sealed reactor heated at a rate of 5 °C·min⁻¹ up to 700 °C to heat the SrCl_2 - NaCl with SrO mixture salt into a molten state. In addition, high-purity argon (Ar~99.999 vol%) was purged into the reactor to keep an inert atmosphere. Electrolysis was performed at electrolysis potential (1.0 V, 1.5 V and 1.8 V) using an electrochemical workstation (CHI 1140C Shanghai Chenhua Instrument Co. Ltd.). After the molten salt has cooled to room temperature, wash the SrCl_2 - NaCl and excess SrO present in the molten salt with deionized water and HCl , respectively. After washing the salt, filter the sample and dry it in a vacuum drying oven at a constant temperature of 70 °C for 8 h. According to the changes in the applied electrolysis potential, The samples were STO-1.0, STO-1.5, and STO-1.8. STO-1.0, STO-1.5, and STO-1.8 are collectively referred to named STO-U. Commercial strontium titanate named STO-C.

Characterization

The crystal structures were recorded by Rigaku Ultima type IV X-ray diffractometer (XRD) and Cu K α radiation ($\lambda = 1.54056\text{\AA}$). The Perkin Elmer Lambda 750s spectrophotometer was used to collect UV-vis diffuse reflectance spectra in the range of 200-800 nm (UV-vis-DRS) to characterize the optical absorption properties. The morphology and microstructure of the samples were analyzed by TESCAN MIRA LMS scanning electron microscope (SEM) and FEI TalosF200x transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) was performed on Thermo ESCALAB 250 XI using monochromatic Al K α at $h\nu = 1486.6$ eV to analyze the valence state of the Ti element and the type of surface oxygen vacancies. The specific surface area of the sample was determined by Mac ASAP 2460 Specific Surface Area and Porosity Analyzer (BET), and the average pore size and pore size distribution were obtained by Barrett-Joyner-Halenda (BJH) desorption method.

Photocatalytic activity

The photocatalytic performance of the prepared samples was evaluated by the photocatalytic degradation rate of a typical dye RhB. In a typical experiment, 0.1 g of the sample was added to 100 mL RhB dye solution (10 ppm) and then stirred in a dark photocatalytic device to achieve adsorption-desorption equilibrium. The light source for photocatalysis is provided by a 300W Xenon lamp. During the photocatalytic experiments, approximately 4 ml of solution was removed, each time the catalyst was separated from the dye by centrifugation, and the concentration of RhB was determined by UV spectrophotometer at the characteristic wavelength of 554 nm. In several cycles of stability testing, the catalyst was centrifuged from the dye solution, the bottom precipitate was collected, washed with deionized water several times, and then dried at a constant temperature for 8 h in a vacuum oven at 70 °C. The catalyst and dye solution were separated by centrifugation, the lower precipitate was collected and washed with deionized water several times.

Table S1 Reduction potential of titanium at 700 °C (vs O^{2-}/O_2)

Electrode potential	Ti²⁺/T	Ti³⁺/T	Ti⁴⁺/T	Ti³⁺/Ti²	Ti⁴⁺/Ti²	Ti⁴⁺/Ti³
	i	i	i	+	+	+
Reduction potential/V	-2.33	-2.16	-1.99	-1.82	-1.65	-1.48

Table. S2 Mass fraction of each element

Sample	Sr	Ti
STO-1.8	46.32%	23.74%

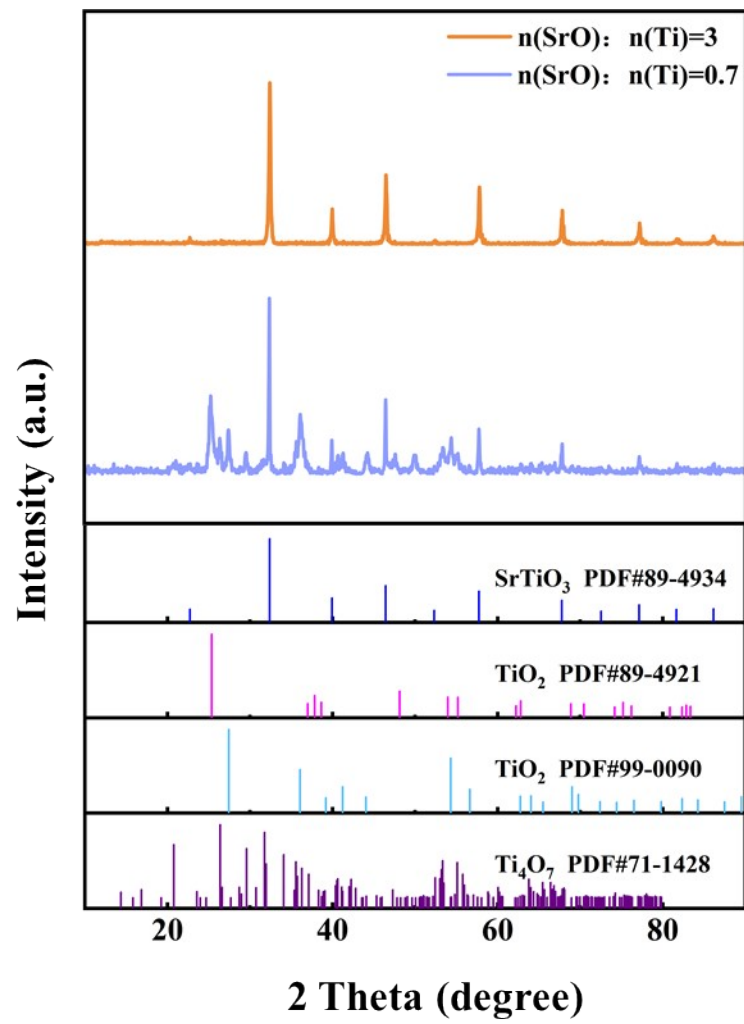


Fig.S1 XRD of samples was obtained by adding different stoichiometric ratios of SrO at an electrolytic voltage of 1.0 V.

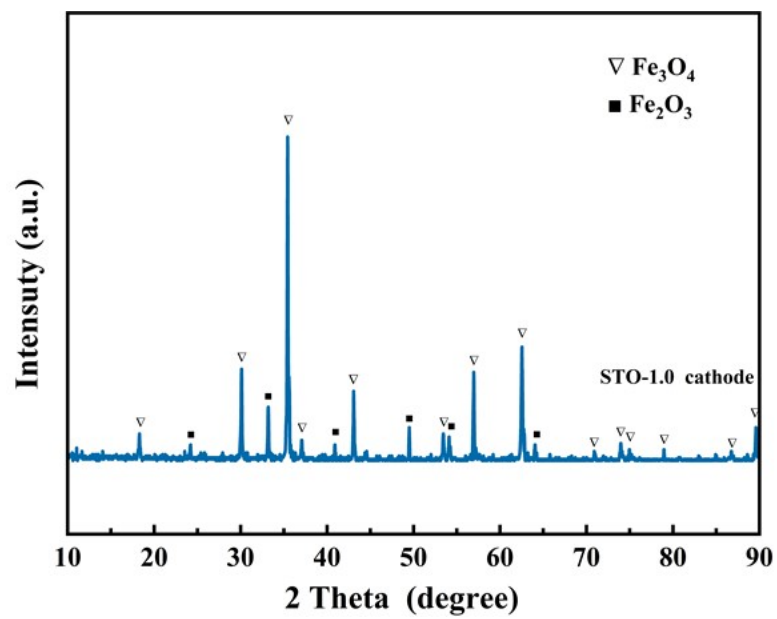


Fig.S2 XRD patterns of the auxiliary electrode after electrolysis at 1.0 V constant potential.

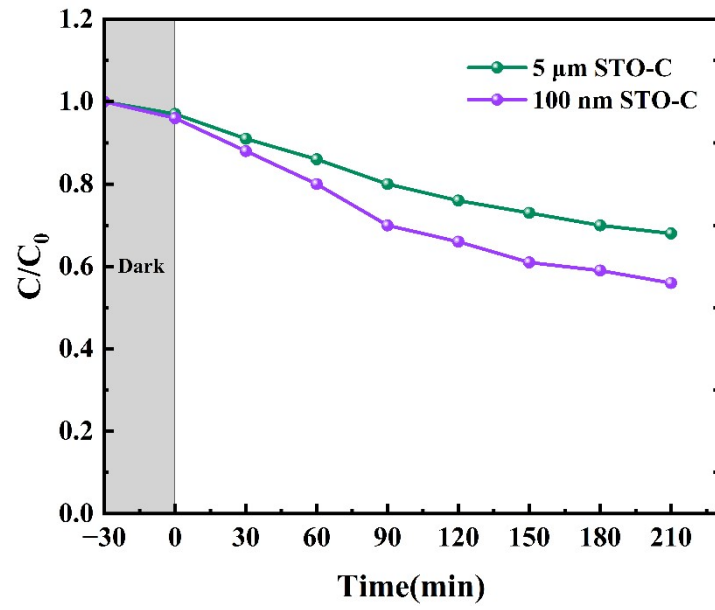


Fig.S3 Comparison of degradation rates of different sizes of commercial SrTiO₃.

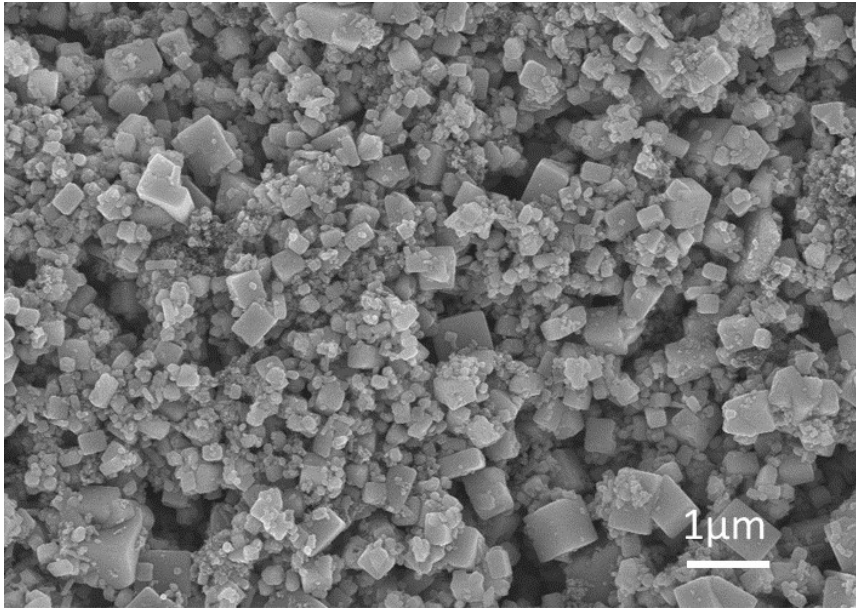


Fig.S4 The SEM of STO-1.8 after after 8 times cycling.

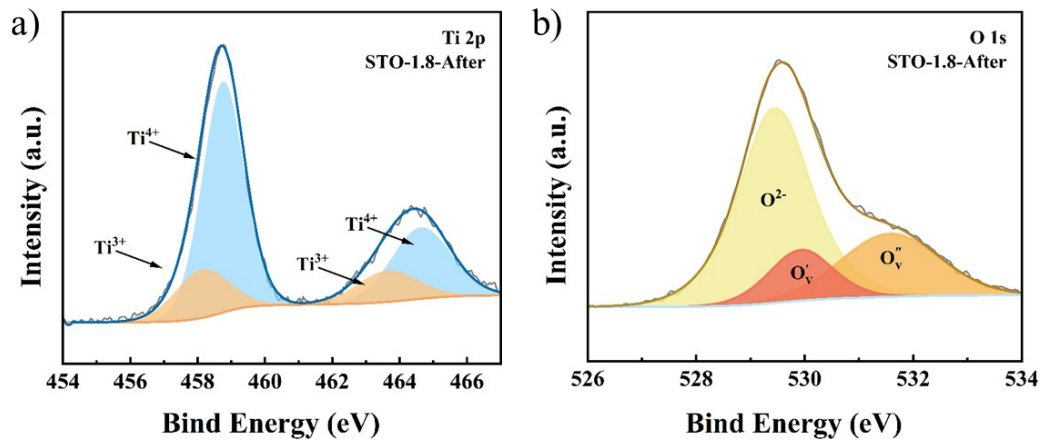


Fig.S5 High-resolution XPS spectra of the STO-1.8 after cycling:(a) Ti 2p;(b) O1s.