Supplementary Information (SI) for ChemComm.

Supplemental information

F/N co-doped $SrTiO_3$ for enhanced photocatalytic water oxidation under visible light

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Experimental Section

Synthesis of strontium titanate

Strontium titanate ($SrTiO_3$) was synthesised via a solid-state reaction. Strontium carbonate (1.5205 g) and titanium (IV) oxide (0.7987 g) were mixed and ground in an agate mortar for 30 minutes. The resulting powder blend was then transferred to an alumina crucible and heated in a muffle furnace in air. The temperature was raised to 1100°C at a rate of 10 °C/min, held for 10 hours, and subsequently cooled to room temperature naturally.

Synthesis of fluorine-doped strontium titanate

The doping process to produce fluorine-doped strontium ($SrTiO_3$-F) titanate was done by mixing powder materials strontium carbonate ($SrCO_3$), titanium (IV) oxide (anatase TiO_2) and strontium fluoride (SrF_2) based on required molar ratio. Take 12% fluorine-doped strontium titanate ($SrTiO_3$-12%F) as an example. $SrCO_3$ (1.4319 g), anatase TiO_2 (0.7987 g), SrF_2 (0.0754 g) were mixed and ground in an agate mortar for 30 minutes. The blended powder was then transferred to an alumina crucible and heated in a muffle furnace in air. The temperature was raised to 1100 °C at a rate of 10 °C/min, held for 10 hours, and subsequently cooled to room temperature naturally.

Nitridation of $SrTiO_3$ and F-doped $SrTiO_3$

0.2 g pristine or F-doped $SrTiO_3$ was placed in an alumina boat and loaded into a tube furnace. The sample was then heated at 800 °C for 2 hours under a flowing ammonia atmosphere (100 mL min^{-1}). After the heat treatment, the sample cooled to room temperature naturally. The nitride samples are denoted as $SrTiO_3$-N (from pristine $SrTiO_3$) and $SrTiO_3$-F-N (from $SrTiO_3$-F).

Cocatalyst deposition

The cocatalyst was loaded onto the photocatalyst as follows: 0.2 g of the photocatalyst was dispersed in 4 mL of an aqueous cobalt (II) nitrate solution with a Co concentration of 1 mg mL^{-1}. The slurry was then evaporated at 70 °C under magnetic stirring at 200 rpm. The resulting powder was finally calcined at 350 °C for 4 hours under a flowing argon atmosphere (100 mL min^{-1}).

Sample characterisations

The UV-Vis spectrophotometer (JASCO V770) was used to record the UV-visible light absorption spectra of samples. The Rigaku Miniflex benchtop X-ray diffractometer was used to collect the XRD patterns of sample powders. The surface photovoltage (SPV) analysed by using a stable surface photovoltage spectrometer (PL-SPV/IPCE1000). The transient photovoltage (TPV) was analysed by using a 355 nm excitation light coming from a lamp pumped solid state laser (Q-smart 450, Quentel Laser). X-ray photoelectron spectroscopy (XPS) was carried out using Thermo ESCALAB Xi+ analyzing system. Field-emission scanning electron microscopy (FESEM) images were obtained using a Verios G4 UC instrument (Thermo Scientific). Steady-state photoluminescence spectroscopy (PL) was carried out at 77 K with an excitation wavelength of 355 nm.

The electrochemical properties of sample powders were investigated by a three-electrode system. The Pt foil (1.5×1.5 cm), and Ag/AgCl electrode in saturated KCl solution were used as the counter, and reference electrode, respectively[1]. The electrode of samples was prepared by an electrophoretic method[2]

The electrochemical measurement was conducted using a Bio-Logic SAS VSP-300 potentiostat. The flat band potential of sample powders was determined by the Mott-Schottky (MS) analysis in a KH_2PO_4/K_2HPO_4 buffer solution (pH=6.73). The potentials were adjusted to the standard hydrogen electrode potential according to the Nerst relation (equation 1)[3]:

$$E_{SHE} = E_{Ag/AgCl} + 0.1976V \qquad \text{(equation 1)}$$

Photocatalytic evaluation

The performance photocatalytic water oxidation reaction was evaluated in a commercial photocatalytic testing system (Perfect Light Labsolar-6A, Beijing Perfectlight). 0.1 g of sample powder loaded with cobalt oxide (CoO_x), and 0.85 g silver nitrate ($AgNO_3$) powder were suspended into 100 mL deionised water. After thoroughly evacuating the air in the system, a 300 W Xenon lamp (Perfect Light PLS-SXE300, Beijing Perfectlight), was used for light illumination. The output light of the Xenon lamp was filtered through a cut-off or band-pass filter. The reaction temperature was maintained at 10 ℃ by a water jacket. The generated gas was analyzed periodically by a gas chromatograph (GC-2014, SHIMADZU). The AQY was calculated using the following equation (equation 2):

$$AQY = \frac{4 \times moles\ of\ O_2\ generated\ per\ hour}{moles\ of\ photon\ flux\ per\ hour} \times 100\% \qquad \text{(equation 2)}$$

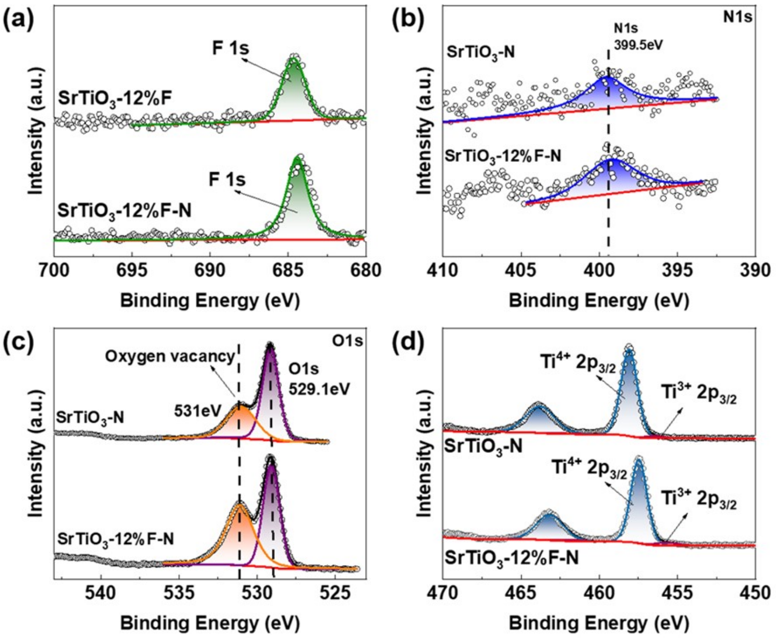

Figure S1. The XPS spectra of $SrTiO_3$-N and $SrTiO_3$-12%F-N: (a)F 1s; (b) N 1s; (c) O 1s; (d) Ti 2p.

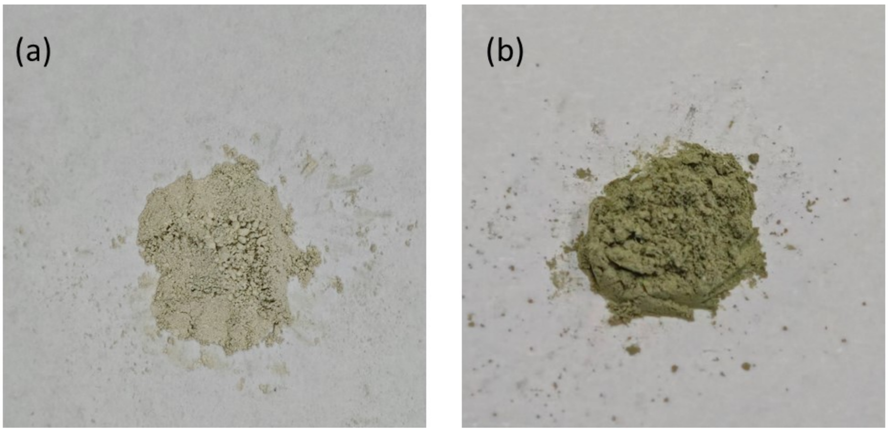

Figure S2. Photographs of (a) $SrTiO_3$-N and (b) $SrTiO_3$-12%F-N sample powders.

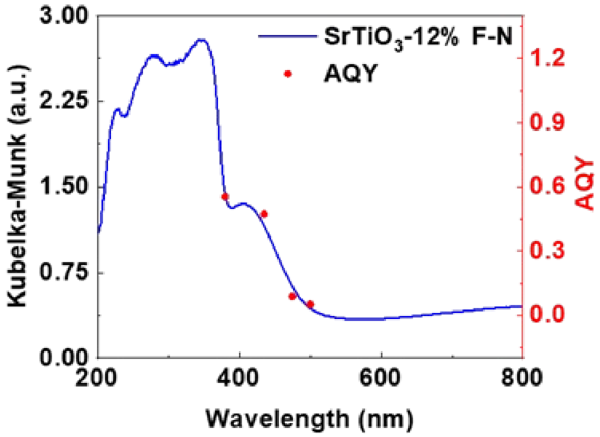

Figure S3. Correlation between optical absorption (Kubelka-Munk transform, left axis) and apparent quantum yield (AQY, right axis) for $SrTiO_3$-12%F-N.

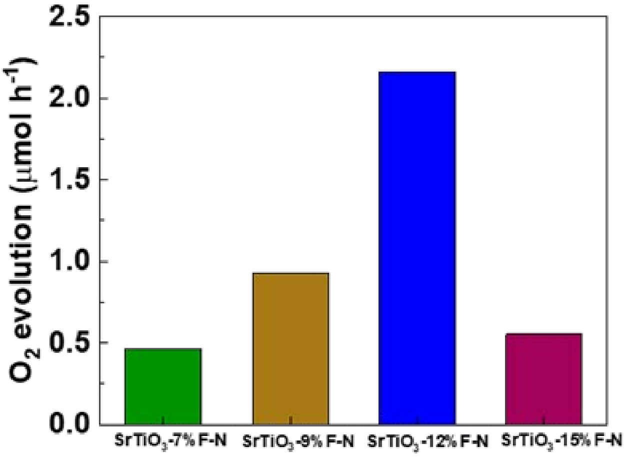

Figure S4. Comparison of photocatalytic oxygen evolution of F/N co-doped $SrTiO_3$ samples with different fluorine concentrations under visible-light irradiation.

Reference

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