Nitrogen/fluorine-codoped rutile titania as a stable oxygen-evolution photocatalyst for solar-driven Z-scheme water splitting

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**Fig. S1.** SEM images of R-TiO$_2$:N,F with different $C$ values.

**Fig. S2.** SEM image and EDX elemental mapping of fluorine rich particle in R-TiO$_2$:N,F ($C = 50$).

**Fig. S3.** N-K edge XANES of R-TiO$_2$:N,F with various $C$ values.
**Fig. S4.** Mott-Schottky plots of R-TiO$_2$:N,F ($C = 15$) recorded at different pH values. Impedance frequency was 100 Hz.

**Fig. S5.** Cyclic voltammograms of R-TiO$_2$:N,F ($C = 15$)/FTO electrode measured in Na$_2$SO$_4$ aqueous electrolyte solution at different pH values in the dark. The shape of CV profiles at each pH became constant with increasing the scan times (after the second scan), indicating that the electrode is electrochemically stable at the pH range examined.

**Fig. S6.** Time courses of O$_2$ evolution on R-TiO$_2$:N,F with different $C$ values under visible light irradiation in AgNO$_3$ aqueous solution. Reaction conditions: catalyst, 50 mg; La$_2$O$_3$ 200 mg; 10 mM AgNO$_3$ aqueous solution, 140 mL; light source, 300 W Xe lamp fitted with CM-1 mirror and L42 cutoff filter ($\lambda > 420$ nm).
Fig. S7. Photocatalytic activity of R-TiO$_2$:N,F for O$_2$ evolution under visible light irradiation with various wavelength in AgNO$_3$ aqueous solution. Reaction conditions: catalyst, 50 mg; La$_2$O$_3$ 200 mg; 10 mM AgNO$_3$ aqueous solution, 140 mL; light source, 300 W Xe lamp fitted with CM-1 mirror and various cutoff filters (L42, Y44, O54, O58). Output current of the Xe lamp was 10 A.

Fig. S8. SEM image of RuO$_2$-loaded R-TiO$_2$:N,F (C = 15).

Fig. S9. (A) XRD and (B) DRS of RuO$_2$/R-TiO$_2$:N,F before and after the oxygen evolution reaction from NaIO$_3$ aqueous solution.
**Electronic Supplementary Information**

**Fig. S10.** Time course of O$_2$ evolution during photocatalytic reaction of RuO$_2$/R-TiO$_2$:N,F (C = 15) under visible light irradiation in FeCl$_3$ aqueous solution. Reaction conditions: catalyst, 50 mg; 10 mM FeCl$_3$ aqueous solution (pH 2.3), 140 mL; light source, 300 W xenon lamp fitted with CM-1 mirror and L42 cutoff filter (λ > 420 nm).

**Fig. S11.** (A) XRD pattern and (B) UV-visible diffuse reflectance spectrum of the as-prepared SrTiO$_3$:Rh.

**Fig. S12.** Time course of H$_2$ and O$_2$ evolution from mixtures of RuO$_2$/R-TiO$_2$:N,F (C = 15) (50 mg) and Ru/SrTiO$_3$:Rh (25 mg) dispersed in an aqueous solution (120 mL) containing tris(2,2’-bipyridyl)cobalt(II) sulfate (0.5 mM) under AM1.5G irradiation (0.1 W cm$^{-2}$).
Fig. S13. Time course of H₂ and O₂ evolution from mixtures of RuO₂/R-TiO₂:N,F (C = 15) (50 mg) and Ru/SrTiO₃:Rh (25 mg) dispersed in pure water (120 mL) under visible-light irradiation (λ > 420 nm).

Fig. S14. Amounts of H₂ and O₂ evolved from mixtures of RuO₂/R-TiO₂ (50 mg) and Ru/SrTiO₃:Rh (25 mg) dispersed in an aqueous solution (120 mL) containing tris(2,2'-bipyridyl)cobalt(II) sulfate (0.5 mM) under visible-light irradiation (λ > 440 nm) after 10 h. Here a Y44 cutoff filter was employed. Data for the RuO₂/R-TiO₂:N,F-based system is also shown for comparison.

Fig. S15. Transient absorption spectra for R-TiO₂:N,F with different C values excited with 480 nm laser pulses under N₂ atmosphere. Transmittance and reflectance were measured below and above 6000 cm⁻¹, respectively.

Table S1. Surface atomic ratios of R-TiO₂:N,F (C = 15) determined by XPS analysis.

<table>
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