

Nanoparticulate precursor route to synthesize nitrogen/fluorine-codoped TiO₂ as an oxygen evolution photocatalyst under visible light

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Mixed-anion compounds exhibit exceptional electronic structure and properties¹ that can be effectively tuned by changing their anionic features specially for energy conversion.² Oxynitrides are regarded as responsive photocatalysts with high activity for photocatalytic water oxidation, since nitridation makes the valence-band potential of the oxide semiconductor negative through the contribution of N 2p orbital.³ Here, F was utilized to compensate the unbalanced charge during the substitution ($2\text{O}_2^- \longleftrightarrow \text{N}_3^- + \text{F}^-$) thereby improving the nitrogen incorporation into a host oxide with a wide variety of compositions.⁴

Herein, rutile TiO₂ was prepared by a facile microwave-assisted solvothermal method. The as-prepared pristine TiO₂ showed uncommonly mesoporous monodispersed spherical morphology that consisted of numerous rod-like crystal. The as-prepared TiO₂ was mixed with different concentration of (NH₄)₂TiF₆ as the F source precursor and heated (the ratio of TiO₂ and (NH₄)₂TiF₆ refers as 100:0, 95:5, 85:15, 75:15, 65:35) under a NH₃ flow to obtain TiO₂:N,F. It turned out that 85:15 showed the highest activity among all the synthesized samples, with the average oxygen evolution rate of 10.5 μmol h⁻¹. The as-prepared TiO₂:N,F still remained the mesoporous structure after nitridation which may be beneficial for providing the active sites for water adsorption, and oxidation leading to 7 times higher photocatalytic activity after codoping with N and F, compared with the N and F codoped rutile TiO₂ (JRC-TIO-6), which was reported previously.⁴

The apparent quantum yields of the optimal sample were 55.4% at 365 nm and 2.3% at 400 nm, respectively. It was suggested that N and F played an important role in the absorption of light and the enhancement of photocatalytic activity under UV and visible light.

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