

Effects of TiO₂ Surface Fluorination on Photocatalytic and Photoelectrochemical Behaviors

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The formation of surface fluorides on TiO₂ (F-TiO₂) uniquely affects both photocatalytic reactions and photoelectrochemical behaviors. The fluoride adsorption is favored at acidic pH and greatly reduces the positive charge on TiO₂ by replacing ≡Ti-OH by ≡Ti-F species. Effects of surface fluorination on the photocatalytic reactivities are very different depending on the kind of substrates to be degraded. The photocurrents collected in TiO₂ suspensions, which are mediated by electron shuttles, and short-circuit photocurrents are also markedly reduced in the presence of F⁻. It is proposed that fluorination enhances OH radical-mediated oxidation rate and inhibits hole-transfer mediated oxidation rate due to the hindered adsorption (or complexation) of substrates on F-TiO₂. In addition, ≡Ti-F group seems to act as an electron-trapping site and to reduce interfacial electron transfer rates by tightly holding trapped electrons due to the strong electronegativity of the fluorine. Finally, elementary charge transfer processes on F-TiO₂ and their implications to photocatalytic reaction pathways are discussed.