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Effects of fluorine modification on the photocatalytic hydrogen production performance of TiO₂

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As an efficient and environmentally friendly photocatalyst, TiO₂ has garnered significant interest among researchers. However, the rapid recombination of photogenerated carriers leads to the inhibition of its photocatalytic activity. Fluorine modification has been proven to be an effective method to improve the photocatalytic performance of TiO₂, leading to a multitude of research reports on this subject. Surface fluorine adsorption or lattice fluorine doping can deftly modulate the surface chemical attributes and electronic configuration of the TiO₂ photocatalyst, thereby amplifying its functional performance. The role of fluorine atoms coordinated with different number titanium atoms (terminal Ti₁-F, bridging Ti₂-F and Ti₃-F) are also discussed. This paper provides a minireview of various aspects of fluorine-modified TiO₂, including its classification (surface-adsorbed fluorination, lattice-doped fluorination and Ti_x-F) and characterization techniques (X-ray photoelectron spectroscopy and solid-state nuclear magnetic resonance). Finally, this treatise elucidates the mechanistic impact of fluorine modification on the photocatalytic hydrogen production performance of TiO₂.

KEYWORDS

surface-adsorbed fluorination, lattice-doped fluorination, TiO₂, Ti-F bonds, photocatalytic hydrogen production

1 Introduction

Titanium dioxide (TiO₂) is one of the most extensively utilized photocatalysts due to its excellent stability, cost-effectiveness and eco-friendliness (Nishiyama et al., 2021; Bhom and Isa, 2024; Wen et al., 2024). The low efficiency of photogenerated carrier separation and transport limits the wide application of TiO₂ (Cheng et al., 2024; Zhao et al., 2025). To enhance the photocatalytic activity of TiO₂, numerous modification studies have been undertaken, including noble metal deposition (Li et al., 2021), doping (Zhang et al., 2019) and heterojunction construction (Ma et al., 2019). A pivotal discovery made by Lai et al., in 1993 revealed that adjusting the ratio of hydrofluoric acid (HF) to fluoride ion in fluorinated reaction solutions could alter the band edge potential of TiO₂ (Lai et al., 1993). This finding established fluorine modification as an effective strategy to improve the photocatalytic performance of TiO₂ due to enhanced surface acidity, stronger adsorption of reactant molecules, additional Ti³⁺ self-doping, and stabilized {001} facets (Yang et al., 2008). After substituting O atoms or surface hydroxyl groups, fluorine introduced into TiO₂ is usually classified as surface-adsorbed fluorine or lattice-doped fluorine (Wu and Schmuki, 2023).

Moreover, according to the different number of titanium atoms coordinated with fluorine, Wang et al. and Hu et al. proposed that the F atoms doped in fluorinated TiO_2 system by a variety of chemical bonds: terminal $\text{Ti}_1\text{-F}$ bond (F1s), bridging fluorine F2c ($\text{Ti}_2\text{-F}$) and 3-coordinated fluorine F3c ($\text{Ti}_3\text{-F}$), where the x in $\text{Ti}_x\text{-F}$ represents the number of titanium atoms bonded to this fluorine atom (Wang et al., 2013). However, due to the complex types of Ti-F bonds in fluorinated TiO_2 , the mechanism of carrier separation and transport is unclear, the precise control of Ti-F bonds is difficult, the mechanism of fluorination reaction is not clear, and the understanding of the structure-property relationship is insufficient. There is an urgent need for follow-up and cooperation in related theoretical research. This minireview aims to summarize the impact of fluorine modification on the photocatalytic hydrogen production performance of TiO_2 through a comprehensive review of relevant literature. The discussion will encompass aspects such as classification of TiO_2 fluorination, characterization of fluorine species, and effect of fluorine on the photocatalytic hydrogen generation performance of TiO_2 .

2 Classification of TiO_2 fluorination

The fluorination route influences the physicochemical properties and photocatalytic performance of F- TiO_2 . Generally, the modification of TiO_2 with fluorine encompasses both surface-adsorbed fluorination and lattice-doped fluorination (Zulfikar et al., 2021). Surface-adsorbed fluorine is typically achieved through post-treatment fluorination via a ligand exchange between F^- ions and the surface functional groups of TiO_2 . The realization of fluorine doping in the internal phase lattice of materials often requires the introduction of fluorine in the preparation process of TiO_2 for *in-situ* synthesis. Herein, we will briefly describe the fluorination principle and fluorine species of these fluorination method, as well as the detailed structures and descriptions of corresponding examples.

2.1 Surface-adsorbed fluorination

Surface fluorinated TiO_2 material can be easily obtained by simple ligand exchange between F^- and the surface hydroxyl group (OH^-) through exposing TiO_2 photocatalyst to a mild aqueous solution containing F^- (NaF , NH_4F , ILs-F) (Park and Choi, 2004; Wang et al., 2008; Lin et al., 2020). After being immersed in NaF aqueous solution, the coordination unsaturated surface Ti^{4+} ions in TiO_2 will combine with water to form various hydrates, and the chemisorbed water molecules will dissociate to $\equiv\text{Ti-OH}$ to produce surface hydroxyl. Ligand exchange occurs between F^- and $\equiv\text{Ti-OH}$ to complete the adsorption of fluorine on the TiO_2 surface to form $\text{Ti}_1\text{-F}$ (Park and Choi, 2004). Compared with simple exchange $\equiv\text{Ti-OH}$, etching TiO_2 surface with HF can change the surface properties more strongly (Wang et al., 2008). When low concentration HF is etched, F^- not only replaces the end hydroxy-group on the surface but also the lattice oxygen. However, F^- does not penetrate into the interior of the TiO_2 lattice, and the substitution of lattice oxygen only occurs on the surface (Wang et al., 2008). Some studies also believe that during HF etching, HF dissociates and adsorbates on the

clean TiO_2 surface during surface fluorination. When the adsorption site on the surface is completely occupied by fluorine, the exposed hydroxyl group on the surface will be replaced by fluorine, and then a completely fluorinated surface covered by $-\text{TiOF}_2$ will be formed. Under the action of high concentration HF , These $-\text{TiOF}_2$ will further react with HF to produce oxygen vacancies, as shown in Figures 1a–d (Wang et al., 2011). Surface fluorinated TiO_2 prepared by post-treatment in liquid phase method often contains both surface adsorbing and inner surface phase doping fluorine. Researchers should comprehensively consider the fluorination effect and better understand the influence of inner surface phase doping fluorine in photocatalyst and distinguish it from the influence of surface adsorbing fluorine.

2.2 Lattice-doped fluorination

The radius of F^- (0.133 nm) is close to that of O^{2-} (0.132 nm), and F^- has a strong bonding ability with titanium atoms, so it is easier for F^- to stably dope TiO_2 than other elements (Wardman, 1989). As mentioned in the previous section, when TiO_2 is corroded by HF , lattice fluorine doping can be introduced while surface fluorine adsorption is achieved, but such lattice fluorine doping only exists in a few atomic layers on the surface and cannot enter the material phase. The realization of fluorine doping in the internal phase lattice of materials often requires the introduction of fluorine in the preparation process of TiO_2 for *in-situ* synthesis. As the commonly used synthesis method, sol-gel method usually involves the nucleophilic reaction of fluorine ions in the hydrolysis process of titanium salts, and then is included in the material phase.

As shown in Figures 1e,f, according to the different number of titanium atoms coordinated with fluorine, Wang et al. proposed that fluorine exists in F- TiO_2 in three forms: surface $\text{Ti}_1\text{-F}$ bond formed through replacing OH^- by F^- ; 2-bridged fluorine F2c ($\text{Ti}_2\text{-F}$) and 3-coordinated fluorine F3c ($\text{Ti}_3\text{-F}$) by substituting F atoms for O atoms (Wang et al., 2013). Due to possessing large number of lattice F atoms which could be converted into the lattice F3c atoms in the bulk TiO_2 phase during the preparation processes, TiOF_2 and HTiOF_3 are reported to be the promising intermediates to synthesis anatase TiO_2 (Liu et al., 2012). Hu et al. also reported the characterization of fluorine species such as $\text{Ti}_1\text{-F}$, $\text{Ti}_2\text{-F}$ and $\text{Ti}_3\text{-F}$ in $\text{TiOF}_2/\text{TiO}_2$ composites by solid-state nuclear magnetism (Hu et al., 2020a).

3 Characterization of fluorine in TiO_2

In general, X-ray photoelectron spectroscopy (XPS) and solid-state nuclear magnetic resonance (NMR) are used to characterize fluorine-modified TiO_2 to determine the presence of fluorine species.

3.1 Analysis of fluorine species by X-ray photoelectron spectroscopy (XPS)

There are usually two F_{1s} peaks in the XPS spectrum of fluorinated TiO_2 materials (Figure 1g), respectively in the range

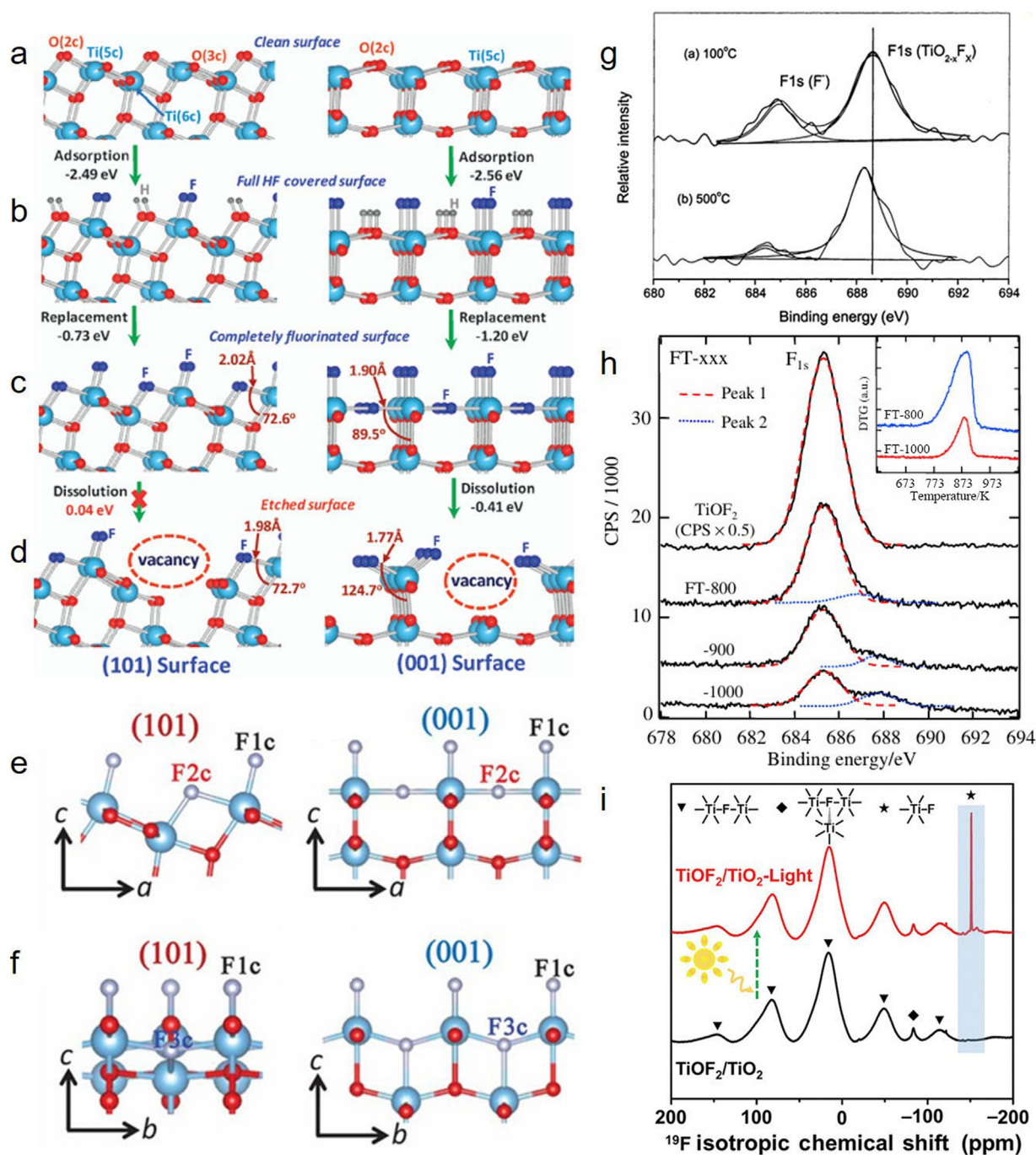


FIGURE 1 (density functional theory) calculated reaction energies and structures for different stages of HF interaction with single crystal anatase TiO₂(101) (left) and (001) (right) surfaces: (a) Clean surfaces; (b) full HF-covered surfaces; (c) complete fluorinated surfaces; (d) etched surfaces; (e) fluorinated surface with lattice F2c atoms; (f) fluorinated surface with lattice F3c atoms. All structures are optimized structures (Wang et al., 2011; Wang et al., 2013). XPS spectra of (g) F_{1s} spectra of F-doped TiO₂ (Yu et al., 2002) and (h) F_{1s} spectra of FT powder and pure TiOF₂ (Li et al., 2005); (i) ¹⁹F NMR spectra of TiOF₂/TiO₂ (Hu et al., 2020a).

of 684.4–685.3 eV (attributed to the physical adsorption of Ti₁-F or the presence of TiOF₂-like F (Ti₂-F) in the material). And in the 687.8–688.6 eV range (attributed to F⁻, which is substituted for O²⁻ into the lattice by either alone or co-doped with other elements (Yu et al., 2002)). As shown in Figure 1h, Li et al. observed in the F_{1s} XPS spectra of typical FT powder and pure TiOF₂ prepared by treating

TiO₂ with HF, that pure TiOF₂ had a symmetric peak at 685.3 eV, attributed to the Ti₂-F atoms in TiOF₂, and the peak at 687.8 eV was attributed to the doped fluorine atoms in TiO₂ (Li et al., 2005). Yang et al. also observed a symmetry peak at 684.5 eV on F_{1s} XPS spectra of anatase single crystal synthesized by TiF₄ and HF, which could not be accurately attributed to either TiOF₂ (Ti₂-F) or surface adsorbed

F ($\text{Ti}_1\text{-F}$) (Yang et al., 2008). Wang et al. believe that the binding energy of F_{1s} is related to the coordination state of F-Ti, and the peak near 687.6 eV on the XPS spectrum of F_{1s} can be attributed to the 3-coordination F ($\text{Ti}_3\text{-F}$). However, since the fluorinated surface of $\text{Ti}_2\text{-F}$ is more stable, and the test depth of XPS is generally about 5–10 nm, the binding energy of F_{1s} can be classified into 3 $\text{Ti}_3\text{-F}$. The surface of TiO_2 fluoride synthesized by hydrothermal or sol-gel method is often unable to detect the peak near 687.6 eV, but after $\text{Ti}_3\text{-F}$ is exposed to the sample surface by NaOH treatment, the signal of $\text{Ti}_3\text{-F}$ near 687.6 eV can be detected by XPS. Therefore, considering the fuzzy allocation of F_{1s} signals in XPS and the detection limit of XPS in the bulk phase, additional characterization techniques are needed to clearly distinguish fluorine species (Wang et al., 2013).

3.2 Nuclear magnetic resonance (NMR) to study the Ti-F coordination

Because of its high natural abundance, high sensitivity and wide chemical shift range, ^{19}F NMR is suitable for qualitative analysis of fluorine-containing compounds. Reyes-Garcia et al. studied the Ti-F coordination through solid-state ^{19}F NMR testing, and they found TiO_5F species in fluorine and boron co-doped TiO_2 (Reyes-Garcia et al., 2007). After this, ^{19}F NMR was used to study fluorine in F-doped TiO_2 (Hu et al., 2020a; Wang et al., 2022) and $\text{TiOF}_2/\text{TiO}_2$ mixtures (Hu et al., 2020a). Koketsu et al. tested solid ^{19}F NMR to show that in sample $\text{Ti}_{0.78}\text{O}_{0.22}\text{O}_{1.12}\text{F}_{0.4}(\text{OH})_{0.48}$, fluoride ions near the vacancy were in three different chemical environments according to the coordination relationship between titanium atoms and vacancy ($\square$): $\text{Ti}_3\text{-F}$, $\text{Ti}_{2\square}\text{-F}$ and $\text{Ti}_{1\square}\text{-F}$ (Koketsu et al., 2017). The coordination environment of fluorine in the bulk phase can significantly affect the photocatalytic performance of TiO_2 . Wang et al. reported that $\text{Ti}_3\text{-F}$ with high 1s binding energy contribute to the enhancement of visible light activity of TiO_2 fluoride. The introduction of such F leads to the formation of Ti^{3+} , shrinks the band gap, and the presence of $\text{Ti}_3\text{-F}$ enhances the adsorption of hydroxyl. The photocatalytic activity was further improved (Wang et al., 2013). Subsequently, Hu et al. used NMR to study the Ti-F coordination of the sample $\text{TiOF}_2/\text{TiO}_2$ (Hu et al., 2020a). As shown in Figure 1i, multiple resonance signals at $\sim 15\text{ppm}$ can be attributed to the $\text{Ti}_2\text{-F}$ environment in the TiOF_2 lattice, and the resonance at -84ppm can be attributed to the bulk phase $\text{Ti}_3\text{-F}$. It was further confirmed that F was successfully incorporated into TiO_2 . After light treatment, the formation of a new signal at -151ppm was attributed to the $\text{Ti}_1\text{-F}$ environment, indicating that the doped fluorine transformed from $\text{Ti}_2\text{-F}$ to $\text{Ti}_1\text{-F}$ and generated Ti^{3+} at the interface of TiOF_2 and TiO_2 , which significantly enhanced the charge transfer efficiency in $\text{TiOF}_2/\text{TiO}_2$, thereby improving the photocatalytic performance. Therefore, according to the solid ^{19}F NMR test results, fluorine atoms coordinate with different numbers of titanium atoms can be distinguished, but this research needs further exploration.

Furthermore, more comprehensive sample information can be provided by the combination of other technologies, such as electron paramagnetic resonance spectroscopy (Hu et al., 2020b) and electron energy loss spectroscopy (Wang et al., 2022).

4 Effect of fluorine on the photocatalytic hydrogen generation performance of TiO_2

In the past years, fluorine-modified TiO_2 has attracted attention in the field of photocatalytic hydrogen production (Wang et al., 2019; Bhom and Isa, 2024), which consists of the following steps: light absorption, charge separation and transport, and redox reactions at the photocatalyst's surface.

4.1 Light absorption

Fluorinated TiO_2 photocatalysts show stronger UV-visible light adsorption with a red shift (Figure 2a) were developed by Yu et al. through hydrolysis of titanium tetraisopropoxide in a mixed $\text{NH}_4\text{F-H}_2\text{O}$ solution (Yu et al., 2002; Chen et al., 2022; Hou et al., 2024). The reduction of Ti^{3+} from Ti^{4+} by charge compensation of F doping form a donor level between the band gaps of TiO_2 may benefit to the enhanced light absorption (Figure 2b). In addition, surface fluorination also produces some oxygen vacancies, resulting in visible-induced photocatalytic activity. Le et al. used the thermal shock method to fluorinate TiO_2 P25 powder at different temperatures, and the fluorinated sample produced oxygen vacancy at 400°C – 600°C , which was confirmed by XPS spectroscopy as the formation of TiO_2 surface fluorination (Khoa Le et al., 2012).

Zhao et al. concluded that the surface lattice F3c atoms ($\text{Ti}_3\text{-F}$) with higher 1s binding energy are identified to be the origin of visible light activity by analyzing the 1s CLSs of various types of F atoms in the fluorinated TiO_2 (Wang et al., 2013). Further analyzing the electronic structures of the fluorinated TiO_2 using semi-local density functional theory and non-local hybrid density functional theory calculations demonstrates that the introduction of the 3-coordinated surface F atoms leads to the formation of Ti^{3+} ions in the sub-surface, which is the cause for the bandgap shrinking, increasing the visible-light activity. However, the photocatalytic efficiency of fluorinated TiO_2 for water splitting is limited due to the limited absorption under visible light irradiation and the high recombination rate of photogenerated electron-hole pairs (Yu et al., 2010; Li et al., 2020). Developing a method to synthesize F- TiO_2 materials that with considerable visible-light photocatalytic activity is still a challenge.

4.2 Carriers separation and transport

Several investigations have been reported for increasing the efficiency of carriers separation/transport in TiO_2 based materials through fluorine modified. Surface fluorination of TiO_2 can significantly change the physicochemical properties and structure of the material surface: increasing the surface electronegativity, promoting the separation and transfer of surface charge, and inhibiting the recombination of electron hole pairs; promoting the formation of hydroxyl free radical and other active reactive substances (Yuan et al., 2025). The oxygen vacancy defects and Ti^{3+} centers formed on the surface of TiO_2 during fluorination process also favor the separation of charge carriers (electrons and holes) and can trap the holes (Wang et al., 2021).

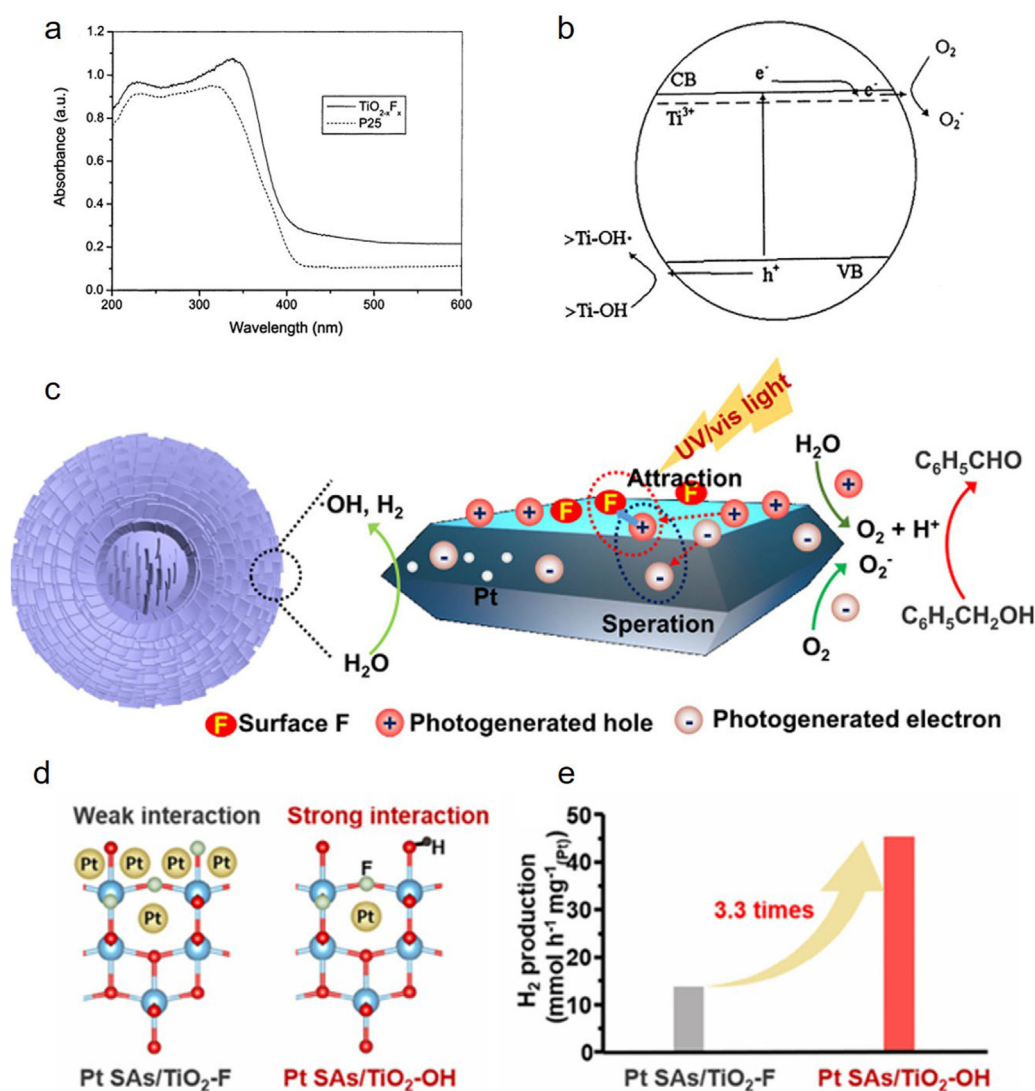


FIGURE 2

(a) UV-visible absorption spectra of Degussa P25 and the F-doped TiO₂; (b) schematic energy level diagram for Ti³⁺ and charge-carrier dynamics in F-doped TiO₂ (Yu et al., 2002); (c) proposed mechanism for the photocatalytic properties of TM-S (Hu et al., 2020b); (d) structure models and (e) normalized photocatalytic H₂ evolution rate of Pt SAs/TiO₂-F and Pt SAs/TiO₂-OH (Wu and Schmuki, 2023).

The surface charge separation can be further enhanced by loading Pt, Ag, Pd and other precious metals as cocatalyst on the fluorinated TiO₂ (Vaiano et al., 2018; Díaz-Sánchez et al., 2021). Yu et al. reported that the F ions on the surface of TiO₂ can greatly decrease the recombination rate of photogenerated carriers by acting as an electron-trapping sites to trap the photogenerated electrons due to its strong electronegativity and then transfer electrons to the Pt loaded (Yu et al., 2010). As shown in Figure 2c, our previous work further proved that the surface F anions with negative electric will attract the holes to migrate to the surface of TiO₂ and inhibit the migration of photogenerated electrons, which further prevents electron-hole recombination (Hu et al., 2020b). Besides, the introduction of surface fluorine provides anchoring sites for Pt nanoparticles and strengthens the interaction between Pt nanoparticles and the TiO₂ substrate resulting in significantly improved catalytic performance (Ji

et al., 2019). Many recent works focus on the loading of metal single atoms (SAs) on TiO₂ as cocatalyst for photocatalytic reactions (Hejazi et al., 2020; Cha et al., 2022). For example, Wu et al. reported that both surface and lattice Ti³⁺ suitable for Pt anchoring and charge compensation can be generated in pristine TiO₂-F nanosheets with surface terminal F species. After surface F species are removed by NaOH treatment, Pt single atoms (SAs) were stabilized by lattice F (Figure 2d), and shows much higher photocatalytic hydrogen generation efficiency than Pt SAs on TiO₂-F (Figure 2e (Wu et al., 2023; Wu and Schmuki, 2023)). Recently, combined with the surface stabilizing effect of the as-formed F-C/F-Ti bonds, single-atom catalysts (Pd, Ir, Pt) on TiO_xN_y nanorods surface via *in situ* fluoride ion etching for hydrogen evolution could be obtained (Zeng et al., 2025).

The crystallinity of fluorine-doped TiO₂ could be improved upon F⁻ doping and then benefit to the higher bulk electronic

conductivity, which is responsible for enhanced water splitting (Fang et al., 2014). Next, Hu et al. simulated the geometric structures and calculated the deformation density of the Ti₂-F, Ti₃-F, and Ti₁-F sites, respectively. The neighboring Ti atoms of Ti₁-F sites got more electrons, compared with those on the Ti₂-F or Ti₃-F sites. The generation of terminal Ti₁-F in TiOF₂/TiO₂ moved more electrons toward the terminal F atom resulting in the acceleration of the interfacial charge transfer (Hu et al., 2020b).

5 Conclusion

The current minireview focuses on the investigation of the surface-adsorbed fluorination and lattice-doped fluorination for F-TiO₂ nanomaterials, and the role of fluorine in photocatalytic water splitting. According to the different number of titanium atoms coordinated with fluorine, the F atoms introduced to fluorinated TiO₂ system are classified into terminal Ti₁-F, bridging Ti₂-F and Ti₃-F. In conclusion, both surface-adsorbed fluorination and lattice-doped fluorination are effective measures to improve the photocatalytic performance. Fluorine ions on the surface of TiO₂ can significantly change the physicochemical properties and structure of the material surface: increasing the surface electronegativity, promoting the separation and transfer of surface charge. Especially, the surface Ti₃-F is identified to be the origin of visible light activity. The surface lattice Ti₂-F are beneficial to stabilize Pt SAs and then bring high photocatalytic efficiency. Defects such as surface Ti³⁺ and oxygen vacancy defects formed during fluorination process could change the local electronic structure and improve the photocatalytic performance. Ti³⁺ defects introduced by lattice-doped fluorination can regulate the band structure of TiO₂ and inhibit photogenerated carrier recombination. The generation of terminal Ti₁-F moved more electrons toward the terminal F atom resulting in the acceleration of the interfacial charge transfer.

Although great progress has been made in the role of fluorine in photocatalysis, there are still many problems that need to be fully studied further. For example, due to the varied fluorine species in fluorine-modified TiO₂, there are challenges in the precise regulation of doped fluorine species, and the mechanism of action of various doped fluorine species on the improvement of photocatalytic performance at the atomic scale also needs to be improved.

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Author contributions

JH: Writing – original draft, Writing – review and editing. XS: Writing – review and editing. SWu: Writing – review and editing. PS: Writing – review and editing. ZG: Writing – review and editing. ZR: Writing – review and editing. XF: Writing – review and editing. SWa: Writing – review and editing.

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Conflict of interest

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