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Nature of visible-light responsive fluorinated titanium dioxides

Yun Wang,^a Haimin Zhang,^a Porun Liu,^a Tao Sun,^a Yibing Li,^a Huagui Yang,^{a,b} Xiangdong Yao,^c Huijun Zhao^{*a,d}

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The origin of visible-light activity of fluorinated TiO₂ has been systematically investigated via comprehensive theoretical studies. The 3-coordinated surface F atoms with higher 1s binding energy are identified to be the origin of the visible light activity for the fluorinated TiO₂ by systematic analysing 1s core-level shifts of various types of F atoms in fluorinated TiO₂. Further analysing the electronic structures of the fluorinated TiO₂ using semi-local density functional theory and non-local hybrid density functional theory calculations demonstrate that the introduction of the surface 3-coordinated F atoms leads to the formation of Ti³⁺ ions in the sub-surface, which is the cause for the bandgap shrinking, giving a rise for visible-light activity. The results also reveal that the presence of 3-coordinated surface F atoms strengthens the adsorption of hydroxyl groups on their vicinity to enhance the photocatalytic activity. The findings of this work address a long-standing scientific question, providing useful guidance for design and development of high performance VL photocatalysts.

1. Introduction

Titanium dioxides (TiO₂) are prominent photocatalysts for applications in the clean environment and energy fields.¹⁻² However, as a wide bandgap semiconductor, the large-scale applications of TiO₂-based photocatalysts have been limited by their poor sunlight utilization capability.³ Doping methods are normally employed to reduce their bandgap to achieve visible-light (VL) activities. Among all doping techniques, the fluorination approach is unique since it does not introduce any intermediate energy band, enabling the retention of high photocatalytic activity without compromising the superior stability of TiO₂.⁴ The fluorination method has been widely accepted as an effective means to enhance the photocatalytic activity of TiO₂-based photocatalysts.⁵ The fluorinated TiO₂ with enhanced photoactivity was firstly reported by Minero and co-workers in 2000.⁶ Fluorinated TiO₂ photocatalysts with VL activities were subsequently demonstrated by different research groups.⁷⁻¹⁴ Although a noticeable progress has been achieved on experimental fronts, little mechanistic insight is known regarding the origin of VL activity and bandgap shrinking of the fluorinated TiO₂. In fact, the precise mechanistic understanding of the intrinsic relationship between the atomistic arrangement and the bandgap shrinking that creates the VL activity remains as a mystery. This could be partially attributed to the controversial experimental observations as not all fabricated fluorinated TiO₂ photocatalysts are VL active. For example, hydrofluoric acid (HF) been used to synthesize {001} facets dominated anatase TiO₂ photocatalysts with no VL activity but highly active under UV illumination.¹⁵⁻²⁰ Hence, the precise theoretical understanding of the nature of the VL activity of the fluorinated TiO₂

photocatalysts would pave a way for future design and development of high performance VL photocatalysts.

Previous experimental studies have revealed that the fluorinated TiO₂ photocatalysts with VL activity often consist of F atoms with 1s X-ray photoelectron spectroscopic (XPS) binding energy around 687.8-688.6 eV (denoted as F_I).^{8-10, 13} The bandgap of the fluorinated TiO₂ with F_I atoms was found to reduce to 2.9 eV.¹⁰ However, some fluorinated TiO₂ surfaces with F_I atoms show no bandgap shrinking, but possess VL activities for photocatalytic degradation of organic compounds.⁸⁻⁹ The 1s binding energy of other F atoms are around 684.4-685.0 eV (denoted as F_{II}).¹⁰ F_{II} atoms are once ascribed to the surface adsorbed F atoms, that can be found in all fluorinated TiO₂ surfaces, while F_I atoms are proposed to be the lattice F atoms by substituting the lattice O atoms on TiO₂ surfaces.¹⁰ It should be noted that previous studies have revealed that not all lattice F atoms are F_I type.²¹⁻²² The TiOF₂ crystal is one of the typical examples for which the observed F 1s peak is around 685.3 eV rather than 688 eV, although all F atoms are located in the lattice sites.²¹ In this study, the relationship between the VL activities and the existence of F_I atoms is also confirmed experimentally. Hence, important questions raised are what is the nature of the lattice F_I atoms and their inherent relationship with the origin of VL activity?

2. Experimental and theoretical details

Material. Anatase TiO₂ single crystals were synthesized through a facile low temperature hydrothermal method. In a typical synthesis, 0.035 g metal titanium (Ti) powder (100 mesh, 99.7 purity, Aldrich), 57 mL of deionized water (Millipore Corp., 18 MΩ cm), 3.0 mL of hydrogen peroxide (H₂O₂, 30 wt. % in water,

Sigma-Aldrich), and 0.3 mL of hydrofluoric acid (HF, 48 wt. % in H₂O, Sigma-Aldrich) were added into a Teflon-lined autoclave with an overall volume of 100 mL, and kept at 180 °C for 15 h. After hydrothermal reaction, the autoclave was cooled to room temperature naturally, and then the powder product was collected by centrifugation and adequately washed with deionized water. Finally, the obtained products were dried in a N₂ stream for further characterization and use. The TiO₂ washed by NaOH was reported to be visible-light active previously.⁹ To this end, some collected products were washed using 1.0 M NaOH solution for several times. And the NaOH washed samples were calcinated at 450 °C for 2 hours.

Characterization. The obtained products were comprehensively characterized by scanning electron microscopy (SEM, JSM-6300F), field-emission transmission electron microscopy (TEM Tecnai F20) with an accelerating voltage of 200 kV, tunneling X-ray diffraction (XRD, Shimadzu XRD-6000 diffractometer, equipped with a graphite monochromatic copper radiation (Cu K α) system operated at 40 kV and 30 mA.), and X-ray photoelectron spectra (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). For XPS analysis, all binding energies were carefully aligned by referenced to the C 1s peak (284.5 eV) arising from surface hydrocarbons or possible adventitious hydrocarbon. UV-vis diffuse reflectance spectra of the samples were recorded on a Varian Cary 5E UV-vis-NIR spectrophotometer.

Calculation Method. The fluorinated (101) and (001) anatase TiO₂ surfaces were theoretically studied using the Vienna Ab initio Simulation Package (VASP) based on the density functional theory (DFT) with the all-electron projected augmented wave (PAW) method in this study.²³⁻²⁴ The electron-ion interactions were described using the ultrasoft pseudopotentials with a kinetic energy cut-off of 500.0 eV.²⁵ For the electron-electron exchanges and correlation interactions, the functional of Perdew, Burke and Ernzerhof (PBE),²⁶ a form of the general gradient approximation (GGA), was used to optimize structures and calculate the systems' stabilities. Since GGA/DFT calculations often underestimate the bandgap energies of semiconductors due to the limit of its approximation,²⁷ the non-local screened hybrid DFT method with the HSE06 functional was used to recalculate the electronic structures of some systems.²⁸⁻²⁹ According to the previous theoretical results, 20% exact exchange with 80% PBE exchange were employed with the screening parameter as 0.2 Å⁻¹ for exchange of the HSE06 functional.³⁰ We performed Brillouin-zone integrations using Monkhorst-Pack grids of special points. (2 $\times$ 4 $\times$ 1) and (4 $\times$ 4 $\times$ 1) k-point meshes were employed for the (101) (1 $\times$ 1) surface cell and (001) (1 $\times$ 1) surface cells, respectively. Our selected kinetic energy cut-off and density of k-point mesh were similar as the previous theoretical studies.^{15, 31-35} The anatase (001) surface was modeled by a slab with the (1 $\times$ 1) surface cell comprising an 18 atomic layers separated by a vacuum region of 10 Å. The anatase (101) surface was modeled by a slab with the (1 $\times$ 1) surface cell comprising a 24 atomic layers. The molecules adsorbed on both surfaces of the slabs. When the geometry was optimized, the adsorbates and all the atoms were allowed to relax. For the

Fig. 1 (a) XRD of as-synthesized anatase TiO₂ nanocrystals before (black) and after (blue) NaOH washing; (b) SEM and (c) SAED pattern(left) and HRTEM (right) images of as-synthesized anatase TiO₂ nanocrystals; (d) high-resolution F 1s XPS of the as-synthesized anatase TiO₂ nanocrystals before NaOH washing; (e) high-resolution F 1s XPS of the as-synthesized anatase TiO₂ nanocrystals after NaOH washing; (f) UV-vis diffuse reflectance spectra of fluorinated anatase TiO₂ before (black) and after (blue) NaOH washing.

isolated molecules, a cubic unit cell with the lattice constant as 15.0 Å was used to accommodate one molecule in the calculations.

Fig. 2 Atomic structures of fluorinated anatase TiO₂ (101) and (001) surfaces: (a) fluorinated anatase (101) surface with lattice F2c atoms; (b) fluorinated anatase (001) surface with lattice F2c atoms; (c) fluorinated anatase (101) surface with lattice F3c atoms; and (d) fluorinated anatase (001) surface with lattice F3c atoms. Key: big blue- Ti, red- O, and small grey- F.

Table 1. $1s$ core-level shifts (CLSs) between F2c and F1c or between F3c and F1c in anatase (101) and (001) surfaces in the initial state (IS) approximations or final state (FS) approximation with the PBE or HSE06 functional.

Functional	Anatase (101) surface		Anatase (101) surface	
	CLS _{F2c-F1c} (eV)	CLS _{F3c-F1c} (eV)	CLS _{F2c-F1c} (eV)	CLS _{F3c-F1c} (eV)
PBE(IS)	0.4	1.8	1.1	1.9
HSE06 (IS)	0.6	2.3	1.8	2.7
PBE(FS)	1.0	2.5	1.5	2.8
HSE06 (FS)	1.1	2.4	1.4	2.8

3. Results and discussions

The characterization results with XRD, SEM and TEM images (Figs. 1a-c) confirm that our synthesized nanocrystals are anatase TiO₂ exposed with {101} and {001} facets. Figs. 1d-e show the high-resolution F $1s$ XPS images of products before and after NaOH washing and 450 °C calcinations. It can be found that the F $1s$ peak around 688 eV is emerged after the NaOH washing and calcinations. The UV-vis diffuse reflectance spectra for both products are shown in Fig. 1f. The bandgap energies of the fluorinated TiO₂ with F₁ atoms red-shift to 2.9 eV, which matches the outcomes of previous experiments greatly and demonstrates the existence of F₁ atoms can cause the VL activities.^{8-10, 13}

According to our previous DFT studies, both the anatase (101) and (001) surfaces can be readily fluorinated,¹⁵ which means that partial lattice O atoms on the surface can be thermodynamically substituted by F atoms. The atomistic structures of the fluorinated anatase (101) and (001) surfaces are shown in Figs. 2a-d. In our previous studies on the fluorinated anatase (101) and (001) surfaces, the coordination number of the lattice F atoms is two (denoted as F2c, see Figs. 2a-b).¹⁵ The systems with the lattice F2c atoms are found to be 1.40 or 0.84 eV more stable than those with the three-folded lattice F atoms (denoted as F3c, see Figs. 2c-d) on (101) and (001) surfaces, respectively. To clarify whether the $1s$ binding energy of lattice F2c atoms shifted to a lower energy level, as proposed by Yu et al.,¹⁰ the F $1s$ core-level shifts (CLSs) of the adsorbed F atoms (marked as F1c, see Figs. 2a-d) and the lattice F2c atoms in the fluorinated TiO₂ surfaces are calculated with the PBE and HSE06 functionals. The F $1s$ CLSs are calculated in both initial and final state approximations, as listed in Table 1. Our results show that the choice of the DFT functionals has insignificant impact on the CLSs. Since the final state approximation considers the electron relaxation after the core electrons have been removed, the data in the final state approximation offer results that are better correlated to the experimental observations.³⁶ It can be found from Table 1 that $1s$ CLSs between the F2c and F1c atoms are 1.0-1.5 eV, much less than that of experimentally observed values of 2.8 – 4.2 eV.^{8, 10} This confirms that the lattice F2c atoms are not F₁ type atoms. Indeed, the F $1s$ XPS peaks of surface F2c atoms (~1.2 eV larger than that of F1c atoms) were recently observed by Czoska.³⁷ Therefore, there must be another type of surface F atoms responsible for the VL activity.

Recently, TiOF₂ and HTiOF₃ are reported to be the intermediates to produce anatase TiO₂.^{22, 38-39} These intermediates possess a large number of lattice F atoms that could be change to the lattice F3c atoms in the bulk TiO₂ phase during the formation

Fig. 3 Charge density difference plots (the total density is subtracted the superposition of atomic charge densities) for anatase TiO₂ (001) surface with lattice F2c (left) or F3c (right) atoms. The blue and yellow isosurfaces show negative and positive electron densities difference, respectively. Key: big blue- Ti, red- O, and small grey- F.

processes. The F3c atoms in the bulk TiO₂ phase have been confirmed by the electron paramagnetic resonance (EPR) results.³⁷ The recent experimental results have also demonstrated that the anatase (001) surface can be selectively etched.^{15, 22, 40} Under such circumstances, the F3c atoms once in the bulk phase can be turned into surface atoms through the etching of the (001) facets, which can then be detected by the XPS. The calculated CLSs data of surface F3c atoms both in the (001) and (101) surfaces (as shown in Table 1) indicate that the $1s$ binding energy of F3c atoms shifts to the higher binding energy by 2.8 eV when compared with F1c in the final state approximation, which are close to the experimental value of 2.9 eV (see Fig. 1e). This agreement, thus, suggests that the F3c atoms could be the F₁ type of atoms, responsible for the VL activity.

The binding energy shift of electrons is determined by the electrostatic shielding of charge densities around the nucleus. A less valence electron charge results in an increased binding energy of the inner core electrons because there is a stronger attractive force from the nucleus and vice versa. Hence, the Badar charges of F1c, F2c and F3c atoms are analyzed. Surprisingly, the F3c atoms possess higher charges (-0.82) than that of F1c (-0.66) or F2c (-0.79). This is contrary to the deduction principle described above. To explain this discrepancy, the charge density differences (obtained by subtracting the superposition of lattice F2c or F3c and the rest atoms from the total density) are calculated to better understand the bonding mechanisms between surface Ti atoms and the neighboring F atoms (Fig. 3). The iso-value for the charge difference plot is ± 0.015 electrons/Å³. The charge depletion around surface Ti atoms and charge accumulation around F atoms are observed. At the same time, there is charge accumulation around the locations between the F and Ti atoms, as highlighted within the dashed ovals in Fig. 3. These plots of charge density differences suggest that both the covalent and ionic interactions synergistically contribute to the Ti-F bonds. The covalent characteristics indicate higher charge densities distribute at the locations between Ti and F, leading to decreased total charge densities around F nuclei with an increase in their coordination number from 2 to 3. Overall, the reduced charge densities around F3c nuclei enhance their $1s$ binding energy.

Our PBE/GGA calculations show that the average energies per unit with one lattice F3c atom are 1.40 and 0.84 eV weaker than that with F2c in anatase (101) and (001) surfaces, respectively. The instability of fluorinated anatase surfaces with F3c atoms explains why no F₁ $1s$ XPS peaks are observed in the fluorinated TiO₂ nanocrystals synthesized by the hydrothermal

Fig. 4 (a)TDOS images of fluorinated anatase TiO₂ (001) surfaces; (b) frequency-dependent averaged optical response function of fluorinated surfaces; (c) PDOS images of F3c, surface Ti, and sub-surface Ti atoms in the (001) surface; (d) PDOS images of surface F2c, surface Ti, and sub-surface Ti atoms in the (001) surface; and (e) side view and (f) top view of the partial charge densities of the (001) surface with F3c atoms in the 1.5 eV < $E-E_{Fermi}$ < 2.0 eV energy range.

and sol-gel synthesis.^{37,41} However, the bulk F3c atoms can change into the surface atoms because of the selective etching occur in the anatase (001) facets in the TiO₂ nanocrystals.¹⁵ While the surfaces with F2c atoms are more stable, the rearrangement to change F3c atoms into F2c atoms is kinetically prohibited (the energy barrier is larger than 3.0 eV in our calculations). Consequently, the surface F3c atoms can be retained after the etching and be detected by XPS.

To validate whether the lattice F3c atoms in the surface are responsible for the VL activity of the fluorinated TiO₂, their bandgap energies are calculated using the HSE06 functional on the basis of their total density of states (TDOS) of fluorinated anatase (001) surface with lattice F2c or F3c atoms (see Fig. 4a). The bandgap energy for the surface with lattice F2c atoms is 3.3 eV, which is same as that of anatase TiO₂ bulk. This matches the experimental observations that the stable fluorinated TiO₂ nanocrystals can only absorb ultraviolet (UV) light.⁴¹ In a strong contrast, the bandgap for the surface with lattice F3c atoms is 2.8 eV according to the analysis of the TDOS, which is close to the experimentally determined value of 2.9 eV for the VL active fluorinated TiO₂.¹⁰ The VL activities of F3c doped anatase (001) surfaces are further demonstrated by the simulated optical spectrum obtained from the averaged imaginary part of the dielectric function. Since the calculations for the optical properties needs denser k-point meshes (a (8×8×1) mesh is used) and larger number of unoccupied bands (the number of unoccupied bands is twice as that of the occupied bands), the PBE functional with acceptable calculation costs is used to compare the different optical properties of fluorinated surface, as

Fig. 5 Illustration of the reactions between NaOH and fluorinated TiO₂ (001) surface with (a) surface F2c atoms; and (b) surface F3c atoms. Key: big blue- Ti, red- O, small grey- F, yellow-Na, and pink- H.

shown in Fig. 4b. Since the theoretical bandgap energies obtained using the PBE functional is much lower than the experimental values, the light with longer wavelengths are absorbed in the simulated spectrum. Fig. 4b demonstrates the absorption capability of the F3c doped surface is stronger at the larger wavelength range, which indicates the red-shift of the bandgap energies. Thus, the simulated optical properties are in agreement with the conclusion from UV-vis diffuse reflectance spectra (see Fig. 1f) and TDOS analysis qualitatively.

To understand the origin of the bandgap shrink, the PDOS images of the anatase (001) surface with F2c or F3c atoms are analysed using the PBE functional, as shown in Figs. 4c-d. It can be found that for the surface with F3c atoms, some 3d PDOS peaks of the sub-surface Ti atoms shift toward the Fermi energy level (1.5 eV < $E-E_{Fermi}$ < 2.0 eV, as indicated by blue area in Fig. 4c), which causes the reduction of the bandgap energy, enabling VL absorption. The partial charge densities in the 1.5 eV < $E-E_{Fermi}$ < 2.0 eV energy range are shown in the Figs. 4e-f. The partial charge densities locate at one of the 3d t_{2g} orbitals of the sub-surface Ti atoms. This can be explained by considering that the introduction of the surface lattice F3c atoms leads to the formation of reduced Ti³⁺ ions in the second layer that demand extra electrons for charge compensation. Our results are in agreement the previous theoretical studies that the VL activities of fluorinated anatase TiO₂ bulk are ascribed to the formation of Ti³⁺ ions.⁴²⁻⁴⁴ Figs. 4e-f also reveal that the influence of the surface F3c on the electronic structures of the sub-surface Ti atoms is long-range. The non-localised (long-ranged) effects of the surface F3c atoms to the electronic structures of the sub-surface Ti atoms obtained in this work are similar to previous theoretical calculation results obtained from the defective TiO₂ surfaces.³⁴ As a comparison, there is no direct interaction between the surface F2c atoms with the Ti atoms in the second layer. Consequently, the electronic structures of the sub-surface Ti cations change little in the (001) surface with the F2c atoms. The above evidence confirm that the bandgap shrinking mechanism of the fluorinated TiO₂ with surface F3c atoms differs remarkably from those anion doped (e.g., N) TiO₂, where the reduced bandgap is caused by the introduced intermediate energy levels.⁴ This unique bandgap shrinking mechanism provides the fluorinated TiO₂ containing surface F3c atoms with VL

photocatalytic activity and superior stability, as demonstrated by experimental data.⁵

It has been experimentally demonstrated that the F_{II} atoms can be washed off by NaOH solution,⁹ suggesting that the hydroxyl groups can replace the adsorbed F_{Ic} atoms around the lattice F on surface.⁹ To this end, the systems with adsorbed hydroxyl groups and different surface lattice F atoms are investigated via the reactions at anatase (001) surfaces, as shown in Fig. 5. The calculated energies for both reactions are negative, implying that these reactions are exothermic. Thus, the substitutions of the adsorbed F_{Ic} atoms by hydroxyl groups are thermodynamically preferable for (001) surfaces containing F_{2c} or F_{3c} atoms. Moreover, the F_{Ic} atoms close to F_{3c} atoms can be more readily replaced by hydroxyl groups. Since the adsorbed hydroxyl groups can be further oxidized into hydroxyl radicals by photo-holes in photocatalysis, which have been previously demonstrated to be the active intermediate for the photocatalytic degradation of organic compounds,⁴⁵⁻⁴⁶ the function of the surface F_{3c} atoms to enhance the photocatalytic performance of TiO₂ nanocrystals is explained.

4. Conclusions

In summary, the insight of the VL activity origin for fluorinated TiO₂ has been revealed via comprehensive theoretical studies. The results confirm that the proper fluorination approaches can tune TiO₂-based photocatalysts to possess VL activities. The surface lattice F_{3c} atoms with higher *I*_s binding energy are identified to be the origin of VL activity by analysing the *I*_s CLSs of various types of F atoms in the fluorinated TiO₂. The VL activity is originated from the bandgap shrinking, caused by the presence of F_{3c} atoms that facilitate the formation of the Ti³⁺ ions in the sub-surface. The surface F_{3c} atoms possess stronger adsorption ability toward hydroxyl groups in their vicinity, enhancing the photocatalytic activity. The findings of this work suggest that fabricating TiO₂ nanocrystals with high content of lattice F_{3c} atoms and then converting into surface F_{3c} atoms could be an effective and practical approach to synthesise VL active TiO₂-based photocatalysts with improved photocatalytic efficiency. Such a generically applicable synthetic strategy may pave a way for development of high performance VL photocatalysts and facilitate their practical applications in clean environment and energy fields.

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Notes and references

^a Centre for Clean Environment and Energy, and Griffith School of Environment, Griffith University, Gold Coast Campus, QLD 4222, Australia. E-mail: h.zhao@griffith.edu.au

^b Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

^c QLD Micro- and Nanotechnology Centre, Griffith University, Nathan Campus, QLD 4111, Australia

^d Key Laboratory of Materials Physics, Hefei Key Laboratory of Nanomaterials and Nanotechnology, Institutes of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China

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