Photocatalytic Properties and Photoinduced Hydrophilicity of Surface-Fluorinated TiO_2

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Surface-fluorinated TiO_2 was prepared with the help of anhydrous hydrogen fluoride (AHF) via vapor-phase fluorination at 473 K for 2 h and characterized by XRD, SEM, UV−visible diffuse reflectance, Raman, XPS, and ATR−FTIR, respectively. XRD and UV−visible diffuse reflectance show that fluorination does not change the bulk crystal structure and optical absorption of TiO_2 under the above-mentioned preparation condition. However, the photoinduced hydrophilicity, photocatalytic H_2 evolution, and organic contaminant decomposition are greatly improved by the insertion of fluorine. XPS, ATR−FTIR, and Raman measurements of TiO_2 and surface-fluorinated TiO_2 reveal that fluorination remarkably increases the adsorption of polar molecules, including water and some organics, which is mainly attributed to the enhancement of surface acidity, and the formation of the surface hydroxyl radicals, which is beneficial for both photocatalytic oxidation reaction and hydrophilicity. Therefore, as expected, H_2 evolution from water, aldehyde decomposition, and methylene blue degradation increase, and water contact angle decreases, on the surface-fluorinated TiO_2 under UV light irradiation.

Introduction

TiO_2 has been widely studied as a photocatalytic material because of its potential applications, such as in water and air purification and H_2 evolution from water.[1,2] Recently, Hashimoto et al. reported another new application of TiO_2 in photochemistry, self-cleaning, and antifogging based on the photoinduced hydrophilicity.[3,4] All the properties abide by a similar photochemical pathway. Namely, after light illuminates the photocatalyst, electrons and hole pairs are generated in the photocatalyst. Subsequently, the photogenerated charge carriers transfer to the surface of the photocatalyst and induce the relevant chemical reactions with the adsorbed substances.[5] In addition to the potentially wide applications, TiO_2 is considered to be one of the ideal photochemical materials because of its low cost, stability, and environmentally benign features.[2] Therefore, it is undoubted that further increasing the reactivity of TiO_2 will be of great interest to those looking to realize and extend the practical application of the material.

The possible approaches to increasing the reactivity of TiO_2 involve (1) extending the optical absorption from UV to the visible light region;[6,7] (2) decreasing the recombination of photogenerated charge carriers;[2] and (3) improving the adsorption and subsequent reaction of the reactants on the surface of TiO_2. The former two have been extensively proved to be effective. For example, N doping[6,7] or C doping[8] can extend the optical absorption of TiO_2 and noble metals loading, such as Pt or Ag, can decrease the recombination of photogenerated holes and electrons and promotes interfacial electron transfer.[2,9−11] Because chemical reactions take place only on the surface of a catalyst, the surface modification can greatly affect the adsorption of all reactants and reaction efficiency.[12] The factors relevant to surface properties of TiO_2 include surface acidity, defects, hydroxyl groups, crystalline phase, and so on. Among them, the surface acidity, defects, and OH groups can give rise to a great influence on the chemical properties of TiO_2.[13−15] It has been reported that the surface acidization of TiO_2 can improve the

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adsorption and reaction of polar molecules.[13-15] Fluorination is a very effective way to increase the surface acidity of a material because of the strongest electronegativity of fluorine.[13] Furthermore, fluorine-doped TiO_2 is more stable against photocorrosion and can increase the surface OH radicals that are beneficial for the photocatalytic reactions.[7,16-18] Therefore, surface fluorination of TiO_2 ($F-TiO_2$) is investigated here.

$F-TiO_2$ is an exchange between surface oxygen atoms or hydroxyl groups and fluorine atoms. Recently, it was reported that $F-TiO_2$ improves the photocatalytic oxidation of phenol,[12,17] Acid Orange 7,[12] tetramethylammonium,[18] benzene,[19] and so on. However, few have investigated gaseous organic decomposition using $F-TiO_2$.[12,20] In addition, photoinduced hydrophilicity and photocatalytic H_2 evolution from water are closely related to the adsorption of water, a polar molecule. From this viewpoint, the influence of $F-TiO_2$ on photoinduced hydrophilicity and photocatalytic H_2 evolution is also an interesting topic. In the study, we first investigated the effect of $F-TiO_2$ on photoinduced hydrophilicity, polar organic gas decomposition, and photocatalytic H_2 evolution. In addition, we also observed the degradation of methylene blue (MB), a positively charged dye, on $F-TiO_2$, a negatively charged surface. The possible mechanisms were also discussed on the basis of a series of characterization.

Experimental Section

Materials. To investigate the effect of fluorination alone on the photophysical and photochemical properties of TiO_2, we used single crystals of TiO_2 with the rutile phase (Shinkosha Co., Ltd, Japan) in this research. They were cut into small plates along the (100) plane with a size of $10 \times 10 \times 0.5$ mm^3. The single side of the plates was polished and the polished side was used in all investigations.

The apparatus for the preparation of $F-TiO_2$ consist of two mass flow controllers (one is for N_2 and the other for anhydrous hydrogen fluoride (AHF)) and an electrically heated tubular Inconel reactor (14 mm in diameter and 300 mm in length). In a typical process, the TiO_2 plates were placed into the reactor, dried at 473 K for 4 h under a N_2 atmosphere, and then kept at 473 K for 2 h in a 100% HF steam. Finally, the remaining AHF on the sample surface was removed by N_2 at 473 K for 2 h and cooled in nitrogen to room temperature. The sample was nominated as $F-TiO_2$. As a comparison, the other sample only without fluorination was also used and is referred as TiO_2.

Characterization. The crystal structures of the samples were determined by the X-ray diffraction method using Cu Kα radiation (JEOL JDX-3500, Tokyo, Japan) and their transmittance was measured using a UV−visible spectrometer (UV-2500, Shimadzu, Japan) equipped with an integrating sphere attachment. The morphology of the samples was observed with a field emission scanning electron microscope (FE-SEM; JSM 6500, JEOL, Japan) operated at 15 kV. ATR−FTIR (attenuated total reflection−Fourier transform infrared) spectra of all samples were obtained with an IRPrestige-21 spectrometer (Shimadzu, Japan) equipped with a Hg−Cd−Te detector operating at 77 K. The background and sample spectra in the region from 4000 to 1000 cm^{-1} were recorded and the final absorption spectra were obtained by deducting the background spectra from the sample spectra to eliminate the influence of water vapor and carbonates in air on the measurements. The Raman spectra of the samples were measured at room temperature on an NRS-1000 Laser Raman spectrophotometer (JASCO, Japan) using a frequency-doubled, diode-pumped Nd:YVO_4 laser with 532 nm exciting line, 10 mW power, and 2 s exposure time. The surface of the samples was analyzed with X-ray photoelectron spectroscopy (XPS, a VG ESCALAB MkII spectrometer) using a Mg Kα line (1254 eV) and a Al Kα line (1487 eV) as an excitation source in an ultrahigh-vacuum chamber (1×10^{-10} Torr) at room temperature. The power was set to 200 W. No flood gun was used for charge compensation. The binding energies of all peaks were referenced against the C 1s line (284.6 eV) originating from surface adsorption carbons.

Photochemical Properties. Photocatalytic H_2 evolution was conducted in aqueous CH_3OH/H_2O solution (50 mL CH_3OH, 270 mL H_2O) with cocatalyst Pt under a 400 W high-pressure mercury lamp irradiation, where Pt was deposited on the photocatalyst using a photoplatinization method: suitable H_2PtCl_6 was dissolved in a CH_3OH/H_2O solution and H_2PtCl_6 was then in situ photoreduced to Pt on the TiO_2 surface for 1 h while methanol was photooxidized with UV light irradiation. The deposited Pt is about 0.02 wt %. An internal irradiation quartz reactor was used in the work. Gas evolution was determined by a gas chromatograph with a TCD detector (GC-8A, Shimadzu, Japan), which was connected to the reaction system with a circulating line. Photocatalytic acetaldehyde decomposition was performed with the sample placed at the bottom of a Pyrex glass cell under 300 W Xe lamp irradiation (for light power intensity and spectra, please see ref 5) at room temperature, as reported previously.[5] The reaction gas was a 0.5 atm gaseous mixture consisting of 837 ppm CH_3CHO, 21% O_2, and Ar balance gas. The photocatalytic MB degradation was carried out with the sample covered by MB dye under black lamp bulb irradiation (365 ± 20 nm, 0.1 mW/cm^2) at ambient condition, where the sample covered by MB was prepared by dropping MB solution onto the sample and then drying the sample. MB degradation was determined by the method described by Miyauchi et al.[4] with a UV−visible spectrometer (UV-2500, Shimadzu, Japan) and evaluated using the peak absorbance ranging from 600 to 650 nm. A photoinduced change of water contact angle (CA) was measured by a commercial contact angle meter (DropMaster 300, Kyowa Interface Science, Japan) at ambient condition, where UV irradiation was produced by a black lamp bulb. To subtly observe the CA difference between $F-TiO_2$ and TiO_2, we placed the samples in a weak UV irradiation region (20 μW/cm^2). In this work, all light intensities were measured by a UV spectroradiometer (USR-40D, USHIO, Japan)

Results and Discussion

Structure and Photophysical Properties. Figure 1 shows the X-ray diffraction patterns of $F-TiO_2$ (100) and TiO_2 (100). It is clear that fluorination does not change the bulk crystal structure of TiO_2. The morphology of the sample often influences its chemical properties as well. The morphology of $F-TiO_2$ and TiO_2 was observed by FE-SEM (not shown here). Similarly, the fluorination basically does not yet

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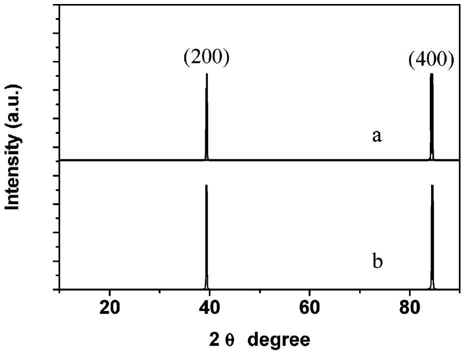

Figure 1. XRD patterns of (a) TiO_2 and (b) F−TiO_2.

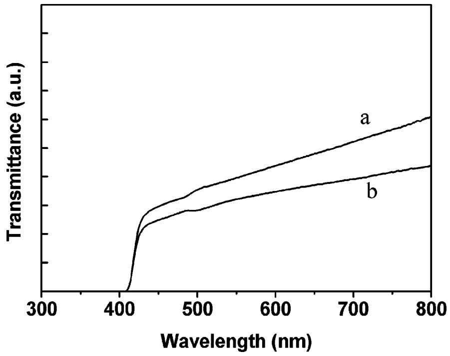

Figure 2. Transmittance of (a) TiO_2 and (b) F−TiO_2.

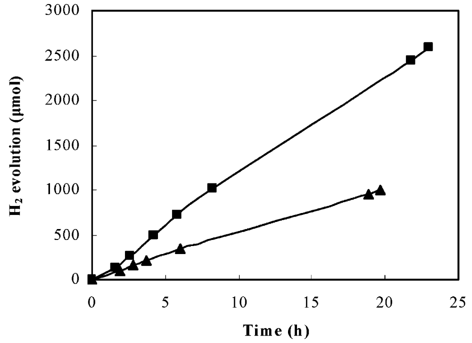

Figure 3. Photocatalytic H_2 evolution with Pt cocatalyst from a methanol/water solution on TiO_2 (▲) and F−TiO_2 (■) under UV light irradiation (400 W high-pressure Hg lamp).

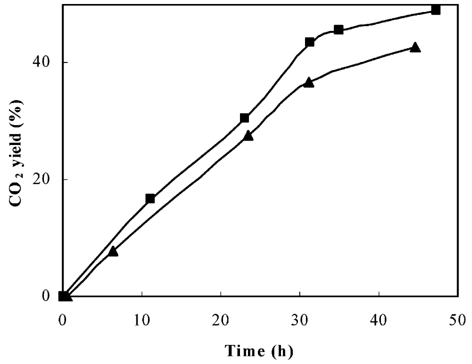

Figure 4. Photocatalytic decomposition of acetaldehyde under a 300 W Xe lamp irradiation on TiO_2 (▲) and F−TiO_2 (■).

change the morphology of the sample. The optical absorption is a key factor to the photochemical properties of every sample. Yu et al. reported that F-doped TiO_2 exhibited higher UV absorbance and a red shift in the band gap compared with pure TiO_2,[22] whereas Park et al. found that the fluorinated process did not affect the optical absorption edge of TiO_2.[12] Figure 2 represents the optical transmittance of the present two samples. F−TiO_2 shows the an optical absorption similar to that of TiO_2 and the band gap is about 410 nm, in agreement with the result of the reported rutile TiO_2.[2] This is also consistent with the theoretical calculation results, which reveals that fluorine doping does not influence the optical absorption of TiO_2.[23] The transmittance of the sample decreases when the light wavelength is longer than 410 nm, which is attributed to a decrease in the surface regularity due to surface fluorination, resulting in a reflection increase. However, the light irradiation in this region does not contribute to the photochemical properties of the samples because the two materials do not intrinsically absorb this part of the irradiation.

Photocatalytic Properties. Figure 3 shows the photocatalytic H_2 evolution on F−TiO_2 and TiO_2 from methanol/water solution under UV light irradiation. The average evolution rate is 113.1 μmol/h on F−TiO_2, whereas it is 51.2 μmol/h on TiO_2. From XRD and the optical absorption spectra, it is obvious that fluorination does not change the absorption or bulk crystal structure of TiO_2, so the increase of the reaction rate on F−TiO_2 is probably due to surface influence, including surface morphology change, defect and roughness increase, reactant (water and methanol) adsorption improvement, etc. FE-SEM measurement shows that the surface morphology hardly changes and the defects are often considered to be a recombination center of the photogenerated charge carriers so as to decrease the reaction rate;[2,24] so the possible causes for the increase in the reaction rate are the reactant adsorption improvement, surface roughness increase, and so on, which will be further discussed later. Figure 4 shows the photocatalytic decomposition of a polar organic contaminant, acetaldehyde, under 300 W Xe lamp illumination. F−TiO_2 also represents higher activity compared with pure TiO_2.

F−TiO_2 reveals the high photocatalytic activity for polar molecules' conversion, involving H_2 evolution from water and acetaldehyde decomposition. Next, we investigated the MB degradation on F−TiO_2 and TiO_2 in air at room temperature. MB is a representative dye in wastewater, where MB exists as MB^+ ion in aqueous solution. Surface fluorination of TiO_2 is an exchange between fluorine ions (F^-) and surface hydroxyl groups or oxygen atoms, and therefore, the surface of F−TiO_2 is negatively charged.[12] Figure 5 compares the MB absorption change on F−TiO_2 and TiO_2 under UV light irradiation. F−TiO_2 shows better performance than TiO_2, which is mainly attributed to stronger MB adsorption because of electrostatic attraction. This result indicates that the adsorptive ability of the material influences its photocatalytic properties.

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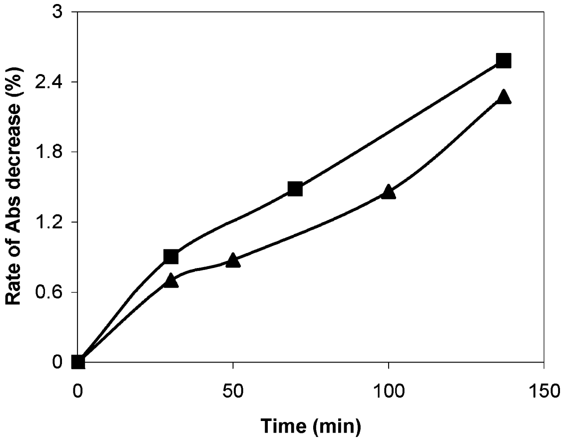

Figure 5. Rate of absorbance (Abs) decrease in methylene blue adsorbed on the surface of TiO_2 (▲) and $F-TiO_2$ (■) under UV light irradiation (black light bulb, light intensity = 0.1 mW/cm^2).

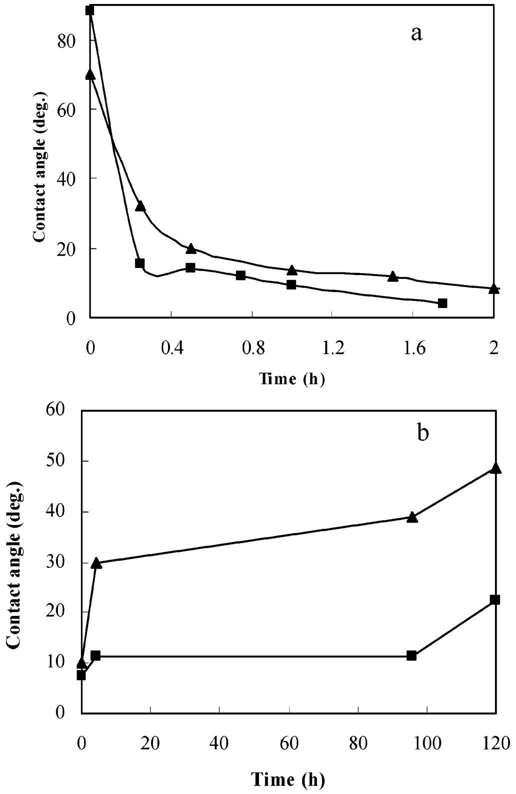

Figure 6. (a) Change of water contact angle under weak UV light irradiation (black light bulb, light intensity = 20 μW/cm^2) on TiO_2 (▲) and $F-TiO_2$ (■); (b) change of water contact angle vs time after turning off the black lamp on TiO_2 (▲) and $F-TiO_2$ (■).

Photoinduced Hydrophilicity. The variation of the CA under weak UV light irradiation was investigated on $F-TiO_2$ and TiO_2 at ambient condition. Figure 6 shows the detailed results, where Figure 6a represents the change in the CA after the black light bulb is turned on and Figure 6b the change in the CA after the black light bulb is turned off. Before UV light irradiation, the original CA is about 90° for $F-TiO_2$ and 70° for TiO_2. With UV light irradiation, both materials show photoinduced hydrophilicity, whereas the CA decreases quicker on $F-TiO_2$ than on TiO_2, indicating that the former has a better property. In particular, the CA increase is much slower on $F-TiO_2$ than on TiO_2 after the light is turned off. This suggests that fluorination greatly improves the duration of hydrophilicity of the material, which can extend the self-cleaning action of the material to unideal conditions, such as night, cloudy season, and so on.

The surface of $F-TiO_2$ was reported to be hydrophobic.[19] Therefore, the original CA on $F-TiO_2$ is bigger than that on TiO_2 without UV light irradiation. Hashimoto et al. found that photoinduced hydrophilicity is due to structural changes of the material surface, completely different from the conventional photocatalytic reaction.[4] The key is the hydroxyl groups' reconstruction and that their amount increases on the sample surface under UV light irradiation. In detail, photogenerated holes are trapped by surface lattice oxygen atoms, resulting in a breaking of the bonds between oxygen with titanium atoms. Subsequently, water molecules dissociatively adsorb at these sites (hydroxyl formation). So the bond strength between oxygen and titanium is important to photoinduced hydrophilicity. It has been found that fluorination can increase the hydroxyl amount of the surface in the aqueous solution.[17,18] Meanwhile, because the fluorine atoms have a much stronger affinity for electrons compared with oxygen, the electronic cloud will deviate from the original position in a titanium−oxygen polyhedral containing fluorine and the bonds between titanium and oxygen can be weakened in $F-TiO_2$. Therefore, plenty of oxygen vacancies are easily produced with the illumination of UV light in $F-TiO_2$. This can undoubtedly improve the photoinduced hydrophilicity. In addition, fluorinated process can also probably increase defects, including oxygen defects, which is considered to be beneficial to the decrease in the water CA. However, the original CA on $F-TiO_2$ is not smaller than that on TiO_2. This indicates that the number of the oxygen defects generated during the fluorination process is not enough to improve the photoinduced hydrophilicity in the present work. On the contrary, the number of oxygen vacancies produced under UV light irradiation is enough to do it. It is known that the CA increase is due to the dissociation of the adsorbed water from the material surface and readsorption of oxygen molecule. Because the fluorinated surface increases the polar molecule adsorption and hydroxyls produced by fluorination can strengthen the dissociated water adsorption, the desorption of the water molecules adsorbed on the surface of $F-TiO_2$ becomes difficult, resulting into the slow increase in the CA on $F-TiO_2$ after UV light irradiation is turned off.

Raman, XPS, and ATR−FTIR Characterization. From the above XRD patterns, it was found that fluorination does not change the bulk crystal structure of TiO_2. However, XRD usually reveals the long-range order of materials and gives average structural information within several unit cells. Raman scatting as a local probe is very sensitive to crystallinity and microstructures of materials.[25] Rutile crystal belongs to the centrosymmetry group with D_{4h}^{14} and two formula units per unit cell, so only surface effects can be observed.[26,27] The present fluorinated process just involves the surface modification. The Raman spectra of $F-TiO_2$ and TiO_2 were observed and are exhibited in Figure 7.

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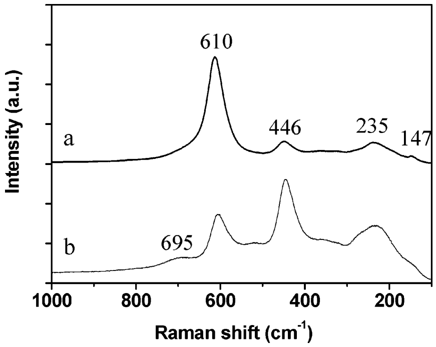

Figure 7. Raman spectra of (a) TiO_2 (rutile) and (b) $F-TiO_2$ under ambient condition.

For rutile, factor group analysis at $k = 0$ gives the following modes after subtracting the acoustic ones[27]

$$T = A_{1g}(R) + A_{2g} + A_{2u}(IR) + B_{1g}(R) + B_{2g}(R) + 2B_{1u} + E_g(R) + 3E_u(IR).$$

The centrosymmetric group gives four infrared-active vibrations ($A_{2u} + 3E_u$) and four Raman-active vibrations ($A_{1g} + B_{1g} + B_{2g} + E_g$). In the Raman modes, only the oxygen atoms are allowed to move during the vibrations.[26,27] Among them, the bands of 610, 446, and 147 cm^{-1} are attributed to the A_{1g}, E_g, and B_{1g} modes, respectively. The B_{2g} mode at 826 cm^{-1} is often too weak to be recorded.[26−28] The broad Raman band at 235 cm^{-1} is also present in these figures and originates from the second-order scattering as identified by Port et al.[28] From the Raman scattering spectra, it can be seen that fluorination does not changes the position of the Raman bands besides the intensity variation. The indicates that fluorination does not destroy the microstructures of TiO_2. However, a new band at 694 cm^{-1} was observed. Because the Raman spectra of rutile involve only the movement of oxygen ions and corresponding stretching and bending of the Ti−O bonds where the titanium ions are anchored in place,[26,27] the new band is possibly attributed to oxygen ion change, such as oxygen atom replacement by fluorine atom or surface oxygen defects. Because the series TiO_xF_y ($x = 0-1$, $y = 1-4$) is not stable at ambient condition, the Raman spectra of Ti−F vibrations have not been reported so far. we prepared several surface-fluorinated samples and found that the band at 695 cm^{-1} changed regularly. So the new bands is possibly caused by the movement of fluorine. Further evidence is being investigated. In addition, the intensity and width of the other bands change after the fluorinated process, which is attributed to slightly defect-induced disorder or surface irregularity.[25,26]

XPS is a sensitive way to investigate the surface state of a material, which was used to determine the elements' state and concentration at the surface of $F-TiO_2$. Figure 8 shows the XPS survey spectra of $F-TiO_2$ and TiO_2. Obviously, Ti, O, and C elements exist at the surface of the two samples, whereas the peak intensity is different. The fluorine concentration is too low to be detected by one scan at the surface of $F-TiO_2$. Plots a and b of Figure 9 exhibit XPS spectra in the selected region. Fluorine, as expected, is detected only in $F-TiO_2$ with 40 scans. Generally, the F 1s binding energy of 684 eV corresponds to the fluorine ions adsorbed on TiO_2 and that of 688 eV to the fluorine ions in the lattice.[21,22] So herein the fluorine atoms coordinate with titanium in $F-TiO_2$, rather than simply being adsorbed on the surface. In the above Raman spectra, the new band at 695 cm^{-1} is possibly attributed to the fluorine vibration. The present XPS result of F 1s indicates that the attribution is feasible.

The amount of titanium is considered to be invariable in the two samples. The area ratios of the F 1s, O 1s, and C 1s region (these spectra are not shown here) to the Ti 2p region are used to calculate the atomic ratios of fluorine, oxygen, and carbon to titanium on the basis of the approximation that the region is homogeneous. The apparent F/Ti ratio is 0 in TiO_2 and 0.05 in $F-TiO_2$; the apparent O/Ti ratio is 4 in TiO_2 and 7 in $F-TiO_2$; the apparent C/Ti ratio is 4 in TiO_2 and 16 in $F-TiO_2$. The fluorine concentration is very low, so it could not be observed in the XRD pattern of the sample. The ratio of O/Ti is more than 2 at the surface of TiO_2. This is due to the adsorbed water (including hydroxyl radicals) and other molecules containing oxygen on the surface. However, the ratio of O/Ti at the surface of $F-TiO_2$ is 7, 1.75 times higher than that at the surface of TiO_2. The ratio of C/Ti at the surface of $F-TiO_2$ is 4 times higher than that at the surface of TiO_2. These results indicate that many more organics and molecules containing oxygen (such as water) are adsorbed on the surface of $F-TiO_2$ compared with that of TiO_2, suggesting that fluorination increases the polar molecule adsorption. Namely, $F-TiO_2$ has a more active surface for adsorption than TiO_2 because of the presence of the electronegative fluorine atoms on the surface.

The photocatalytic properties are closely relevant to the surface hydroxyl radicals. The more the surface hydroxyl radicals, the higher the photooxidation ability of the sample. ATR−FTIR was further utilized to detect the water adsorption and dissociation on the surface of the samples, as shown in Figure 10. The peaks in the 1800−1600 cm^{-1} region are often assigned to molecularly physisorbed water and the multiple peaks in the 3800−3500 cm^{-1} region to the O−H stretching of different types of isolated surface Ti−OH groups.[4,29−31] The frequency of the OH groups is sensitive to their electronic states.[32] Szczepankiweicz et al. found that even the electronic fields generated by photoexcited charge carriers in TiO_2 produced Stark intensity effect and wavelength shifts for surface O−H stretching vibrations,[33] so the present peaks are assigned to physisorbed water and surface OH groups. Because the surface area of the single crystals is too small, the observed peaks of the adsorbed molecules are not strong. These spectra suggest the coexistence of

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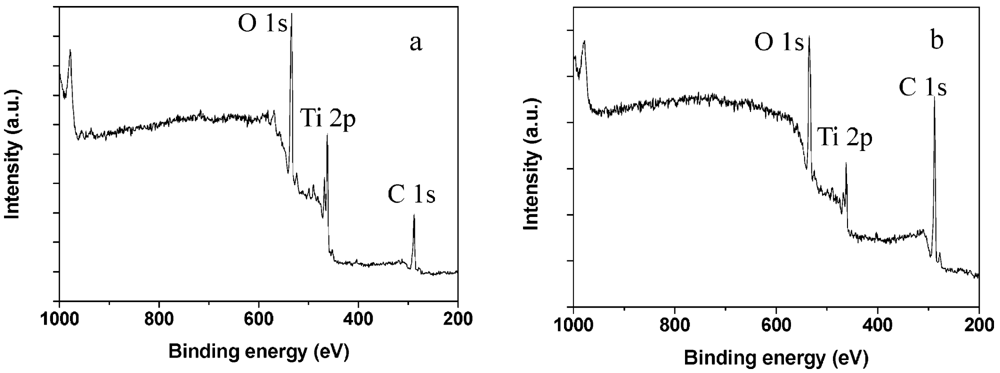

Figure 8. XPS survey spectra of (a) TiO_2 and (b) $F-TiO_2$.

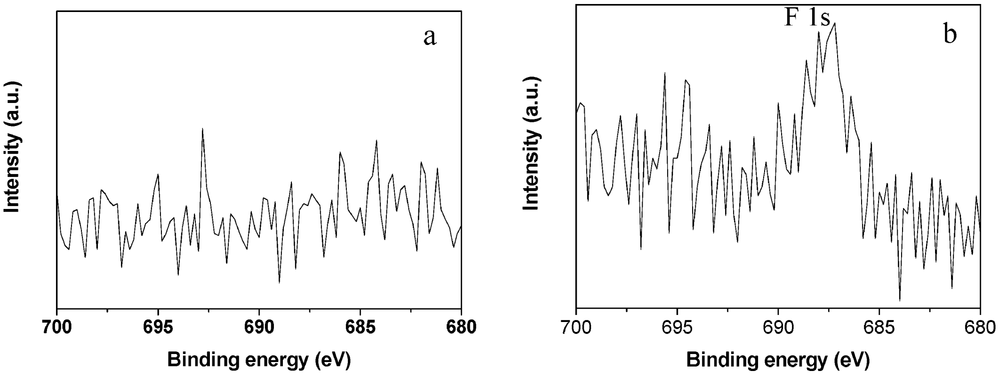

Figure 9. XPS spectra of F in (a) TiO_2 and (b) $F-TiO_2$ with 40 scans

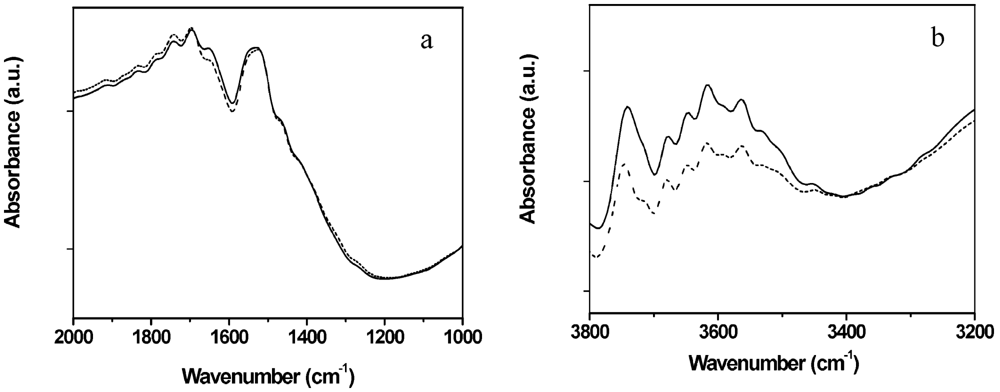

Figure 10. ATR-FTIR spectra of TiO_2 (dotted line) and $F-TiO_2$ (solid line) with FFT smoothing in two regions of interest: (a) 1000−2000 cm^{-1} and (b) 3200−3800 cm^{-1}.

dissociated and molecular water on the surface of the two samples. However, it is obvious that the two samples exhibit a similar ability to adsorb molecular water and quite different ability to adsorb the dissociated water. $F-TiO_2$ shows the stronger ability to adsorb dissociated water and yields OH radicals. In addition, the peaks in the 3400−3000 cm^{-1} region are assigned to molecularly chemisorbed water,[4,29,30] which are often adsorbed on the defect sites. On the present samples with single-crystal structure, these peaks are not observed because of a lack of plentiful defects.

As depicted above, the surface acidity of a material can heavily affect the adsorption of the polar molecules.[13−15] The fluorinating process is one of the most effective ways to increase the surface acidity of the material, proved by many studies.[13] Therefore, it is expected that fluorination can greatly improve the photocatalytic reaction relevant to the polar molecules, such as water and many organics, because of strongly adsorptive ability. This is proved by XPS characterization. In addition, Li et al.[13] and Minero et al.[17] claimed that fluorination of TiO_2 created new active sites for hydroxyl radicals formation and increased the photoelectron mobility, which was also certificated by the strong photocurrent of a single-crystal rutile electrode treated by HF.[34] Our ATR−FTIR characterization shows that dissociated water, namely surface hydroxyl radicals, really increases on $F-TiO_2$. $F-TiO_2$ is also characterized by a better charge-carrier separation because of the absence of surface Ti−OH groups, resulting in more active species existing on the fluorinated surface. Therefore, it is understandable that the fluorinated process greatly increases the photochemical properties of TiO_2 involving photocatalytic properties and

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photoinduced hydrophilicity. In addition, fluorination also possibly increases the surface defects and the surface roughness. The former is possibly beneficial for photocatalytically oxidative reaction. However, surface defects have been proved to be the recombination center of photoelectrons and photoholes, leading to a decrease in photocatalytic H_2 evolution.[2,24] The present research reveals that fluorination increases not only photocatalytic organic oxidation but also photocatalytic H_2 evolution, so either the number of the formed defects is too low to affect H_2 evolution or the negative action of the defects is offset by the positive effect of fluorination in photocatalytic H_2 evolution, although it probably plays a role for organic decomposition. Furthermore, ATR−FTIR characterization shows that the molecularly chemisorptive water is not observed, indicating that the surface defects are not much on the surface of F−TiO_2. Subbarao et al.[34] and Hattori et al.[35] also reported that fluorination could decrease the anion vacancy of TiO_2. So the action of the formed defects on the photocatalysis is not predominated in the present sample. Meanwhile, the effect of the roughness on hydrophilicity of TiO_2 film has been observed largely. Song et al. reported that the hydrophilicity of TiO_2 film was governed by the special surface properties rather than the surface-area change caused by roughness.[36] Takeuchi et al. also investigated the photoinduced hydrophilicity of the TiO_2 thin film under weak UV light in an indoor environment and found that the improvement of photoinduced hydrophilicity of the film was independent of the surface area of the film.[37] Furthermore, Sirghi et al. investigated the effect of both TiO_2 film roughness and thickness on the hydrophilicity.[38] They found that the roughness and thickness do not affect the hydrophilicity of the film if the TiO_2 film is thicker than 12 nm. It is obvious that the influence of surface roughness on TiO_2 hydrophilicity can be neglected. Therefore, the improvements of all photochemical properties of F−TiO_2 are attributed to the comprehensive factors, mainly including surface acidity, adsorption, hydroxyl radicals, and probably surface defects and roughness. In addition, the concentration of fluorine is undoubtedly a sensitive factor with influence on its photochemical properties. The relevant work is underway. Altogether, the fluorinated process is an effective and convenient pathway to improving the photochemical properties of a photocatalytic material.

Conclusions

Surface fluorination of TiO_2 was conducted at low temperature by HF. The fluorinated process does not change the bulk crystal structure and optical absorption of TiO_2. However, for the first time, the photocatalysis, including acetaldehyde oxidation decomposition, methylene blue dye degradation, and H_2 evolution from water, is found to increase by fluorination action. Furthermore, the photoinduced hydrophilicity is greatly improved and the duration of hydrophilicity also increases by surface fluorination. Raman, ATR−FTIR, and XPS characterization show that fluorine coordinates with titanium rather than simply being adsorbed on the surface, that surface fluorination increases the adsorption of polar molecules, such as water and some organics, and that water is dissociatively adsorbed to form more hydroxyl radicals. In addition, a better photoinduced charge carriers separation probably exists on the fluorinated sample because of the absence of surface Ti−OH groups. Therefore, the improvements of all photochemical properties of F−TiO_2 are attributed to the above-mentioned comprehensive factors. Altogether, the investigation provides a feasible and easy way to improve the photocatalytic properties of a photocatalytic material.

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