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A method for the preparation of anatase TiO<sub>2</sub>, which is stable to a temperature as high as 900 °C, without using any complex cationic dopants is presented. The synthetic procedure involves the reaction of titanium tetraisopropoxide (TTIP) with trifluoroacetic acid (TFA) followed by hydrolysis and sol–gel conversion to the xerogel and further calcination. The retention of the anatase phase to high temperatures can be attributed to the presence of small amounts of fluorine in the lattice, which is gradually removed between 500 and 900 °C as confirmed by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopic analysis. Samples prepared with a 1:16 TTIP/TFA composition calcined at 900 °C showed significantly higher photocatalytic activity compared to the *control* sample, standard commercial photocatalyst Degussa P25, and samples prepared using acetic acid and oxalic acid. The high-temperature anatase phase stability, determined by X-ray diffraction and Raman spectroscopy, coupled with its high crystallinity, microporosity, and minimal oxygen vacancy contributes to improved photocatalytic activity.

## Introduction

Titania (TiO<sub>2</sub>) is well-known for its applications in high-refractive optics,<sup>1</sup> oxide semiconductors,<sup>2</sup> oxygen sensors,<sup>3</sup> photovoltaics,<sup>4</sup> photocatalysis,<sup>5</sup> and pigments.<sup>6</sup> A particular

interest is in the development of TiO<sub>2</sub> anatase coatings for self-cleaning and hygienic applications,<sup>7</sup> where it is expected that the anatase form of TiO<sub>2</sub> should be most effective.<sup>8</sup> A recent commercial application has shown the effectiveness of such a photoactive silver-doped titania coating.<sup>9</sup> However, as the processing temperature required for this material was 900 °C, this coating contained 8% anatase and 92% rutile. The anatase-to-rutile transformation in synthetic titania usually occurs at temperatures in the range of 600–700 °C.<sup>10,11</sup> Therefore, there is a need for procedures which will produce anatase-phase TiO<sub>2</sub> which is stable at 900 °C. This challenge has been met in some cases by the addition of cationic dopants.<sup>12</sup> Except for a few cases,<sup>13</sup> however, the photoactivity of the cation-doped TiO<sub>2</sub> is decreased due to

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its thermal instability or an increase in charge carrier recombination centers.<sup>14</sup>

High crystallinity and suitable surface properties (accessible surface area, porosity, and pore volume) are the other key factors that contribute to the photocatalytic activity. A possible high temperature heat treatment may be useful to accomplish these features, provided the anatase phase is stable against heat treatment. In this context, the possibilities of sulfate-modified anatase TiO<sub>2</sub> systems have been explored.<sup>15</sup> Thus, Colon et al. have prepared a highly crystalline TiO<sub>2</sub> powder with good photocatalytic activity for the destruction of phenol at 700 °C by sulfating a hydrous titania gel.<sup>15a</sup> They attributed the activity to minimal crystal defects evolved after the elimination of sulfate species. Similarly, Zhang et al. extended the anatase phase stability of TiO<sub>2</sub> up to 600 °C (873 K) by adding a small amount of sulfate species into the hydrolysis product of TiCl<sub>4</sub>.<sup>15b</sup> As part of a program to develop high-temperature stable photoactive titania materials, we have recently prepared a nitrogen-doped titania which was stable up to 800 °C.<sup>16</sup> All these reports, however, involve a precipitate route synthesis which cannot be used for making thin films by dip-coating or spin-coating techniques. A sol–gel route should, on the other hand, be more effective in terms of the homogeneity of the sol, which is advantageous over the other techniques, and both powders and coatings can be prepared by a one-step sol–gel process. Here, we report a simple and effective sol–gel method to synthesize high-temperature stable (900 °C), photoactive anatase TiO<sub>2</sub>, which we believe should be useful in the preparation of smart coatings for ceramics in hygienic applications.

The preparation method involves the modification of a precursor, titanium tetraisopropoxide (TTIP), with trifluoroacetic acid (TFA) followed by hydrolysis, gelation, drying, and heat treatment to achieve nanosized TiO<sub>2</sub>. High-temperature heat treatment facilitates the preparation of highly crystalline anatase TiO<sub>2</sub> with minimal oxygen vacancy concentration. Methylene blue (MB) degradation experiments under UV light (365 nm) show its high activity, which is better than that of the commercial TiO<sub>2</sub>, Degussa P25. In order to compare and deduce the effectiveness of this preparative route, samples such as acetic acid (HOAc)-

modified TiO<sub>2</sub>,<sup>17</sup> oxalic acid (OxA)-modified TiO<sub>2</sub>,<sup>18</sup> and a control TiO<sub>2</sub> (prepared without any modifier) have also been produced by similar procedures. The factors influencing the photocatalytic activity are discussed.

## Experimental Section

In a typical synthesis {to prepare a sol (Ti-16TFA) with 1:16:4 (molar ratio) TTIP/TFA/H<sub>2</sub>O}, 2.5 mL of TTIP was added to 4.4 mL of a TFA solution in a glass beaker under stirring. Subsequently, 0.60 mL of Millipore water was added dropwise into the clear solution formed, and the beaker was sealed using a parafilm, and stirring was continued for a further 1 h. After 24 h of aging at room temperature (20 °C), the sol was dried at 90 °C in an air oven to obtain the gel. The gel was then calcined at different temperatures such as 300, 500, 600, 700, 800, 900, and 1000 °C at a heating rate of 5 °C per minute and held at these temperatures for 2 h (samples Ti-16TFA-300 to Ti-16TFA-1000). Sols with 1:1, 1:4, 1:8, 1:12, and 1:32 Ti/TFA ratios were also prepared and converted by a similar method to TiO<sub>2</sub> gels. Similar compositions of Ti/HOAc/H<sub>2</sub>O samples were also prepared for comparison. Ti/OxA/H<sub>2</sub>O samples were prepared by dissolving oxalic acid crystals in 125 mL of absolute ethanol before the addition of TTIP. A standard (control-TiO<sub>2</sub>) was prepared by adding 0.60 mL of Millipore water to 2.5 mL of a TTIP solution under stirring.

**Characterization Techniques.** Powder XRD patterns were recorded with a Siemens D 500 X-ray diffractometer in the 2θ range 20–70° using Cu Kα radiation. The anatase content in the sample was estimated using the Spurr equation:

$$F_A = 100 - \left( \frac{1}{1 + 0.8[I_A(101)/I_R(110)]} \right) 100 \quad (1)$$

where  $F_A$  is the mass fraction of anatase in the sample and  $I_A$  and  $I_R$  are the integrated intensities of the main peaks of anatase (101) and rutile (110), respectively. Crystallite sizes were calculated from the peak widths using the Scherrer equation  $\Phi = k\lambda/(\beta \cos \theta)$ , where  $\Phi$  is the crystallite size,  $k$  is the shape factor (a value of 0.9 was used in this study),  $\lambda$  is the X-ray radiation wavelength (1.546 Å for Cu Kα), and  $\beta$  is the line width at half-maximum height of the main intensity peak after subtraction of the equipment broadening. Room-temperature Raman spectra were recorded with a Renishaw 1000 micro-Raman system equipped with an Ar<sup>+</sup> ion laser (Laser Physics Reliant 150 Select Multi-Line) with a typical laser power of ~3 mW in order to avoid excessive heating. The 50×-magnifying objective of the Leica microscope focused the beam into a spot of about 1 μm in diameter. Fourier transform infrared spectroscopy (FTIR) spectra of the samples in KBr pellets were recorded using a Spectrum GX FTIR spectrometer in the range 4000–370 cm<sup>-1</sup>. The BET specific surface area was measured using Nova Station A surface area analyzer (Quantachrome Instruments version 2.1). The pore size distribution was obtained using the Horvath–Kawazoe method.<sup>19</sup>

Diffuse reflectance spectra (DRS) of the samples were recorded using a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer with an integrated sphere attachment. Sample pellets were prepared using

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135 a 4 mm die after thoroughly mixing the powder samples with KBr.<sup>20</sup>  
 136 The band gaps were calculated by extrapolating the lower wave-  
 137 length cutoff region.

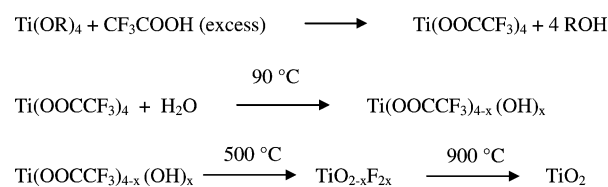
138 X-ray photoelectron spectroscopy (XPS) analyses were per-  
 139 formed on a Thermo VG Scientific (East Grinstead, U.K.) Sigma  
 140 Probe spectrometer. The instrument employs a monochromated Al  
 141 K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV), which was used at 140 W.  
 142 The area of analysis was approximately 500  $\mu\text{m}$  in diameter for  
 143 the samples analyzed. For survey spectra, a pass energy of 100 eV  
 144 and a 0.4 eV step size were employed. For C<sub>1s</sub> and Ti<sub>2p</sub> high-  
 145 resolution spectra, a pass energy of 20 eV and a 0.1 eV step size  
 146 were used. For O<sub>1s</sub> high-resolution spectra, a pass energy of 20 eV  
 147 and a 0.2 eV step size were used. For F<sub>1s</sub> and N<sub>1s</sub> high-resolution  
 148 spectra, a pass energy of 50 eV and a step size of 0.2 eV were  
 149 used. Charge compensation was achieved by using a low-energy  
 150 electron flood gun. Quantitative surface chemical analyses were  
 151 calculated from the high-resolution core-level spectra, following  
 152 the removal of a nonlinear Shirley background. The manufacturer's  
 153 Advantage software was used, which incorporates the appropriate  
 154 sensitivity factors and corrects for the electron energy analyzer  
 155 transmission function.

156 **Photoactivity Study.** Photoactivity experiments were conducted  
 157 by measuring the extent of degradation of an organic dye, methylene  
 158 blue, in the presence of TiO<sub>2</sub>. For this, 1.5 mg of TiO<sub>2</sub> powder  
 159 was first dispersed in 4 mL of Millipore water in a UV cell. The  
 160 suspension was then ultrasonicated for 10 min. A total of 0.1 mL  
 161 of  $2 \times 10^{-3}$  M MB was then added to the suspension. The samples  
 162 were irradiated under UV light using a Luzchem UV chamber  
 163 (Canada) consisting of 10 8-W Hitachi-II tubes (wavelength 365  
 164 nm). The absorbance maximum of MB (664 nm) was measured after  
 165 each interval of light irradiation from 0 min up to 85 min.  
 166 The kinetics of the MB degradation were analyzed as reported  
 167 previously.<sup>5a,16</sup> Photodegradation experiments had also been con-  
 168 ducted in Irish sunlight on the 24th of July, 2006.

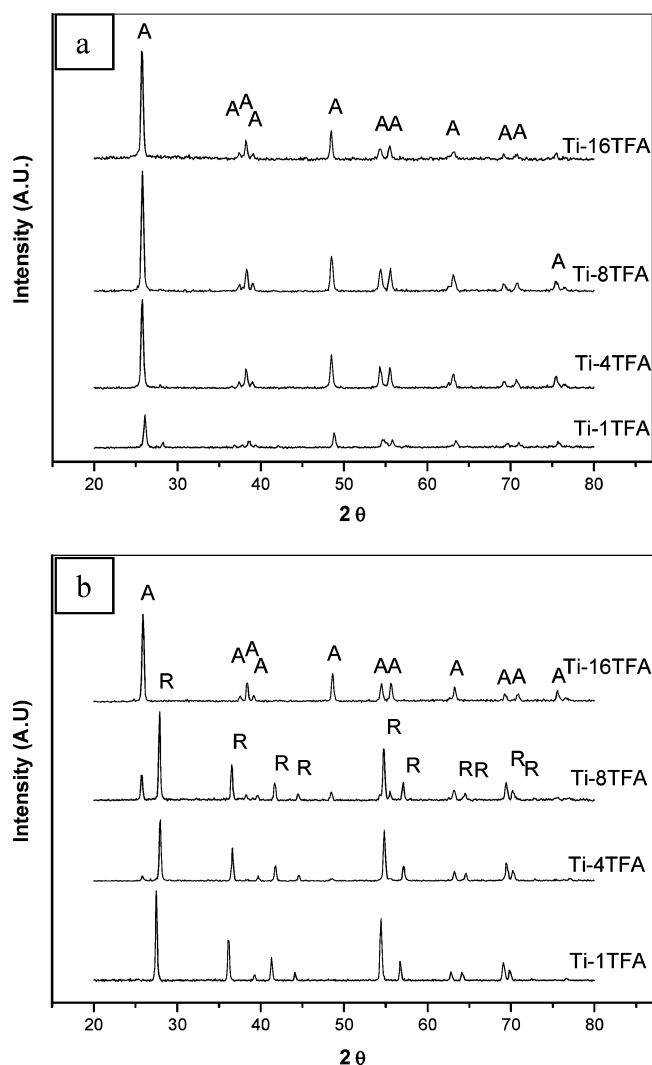
## Results

170 The preparation method involves the reaction of TTIP with  
 171 TFA followed by hydrolysis, gelation, drying at 90 °C, and  
 172 heating (500–900 °C) to give nanosized TiO<sub>2</sub>. The chemical  
 173 sequence may be represented as shown in Scheme 1.

### Scheme 1. Chemical Sequence of TFA Modified Sol–Gel Process



174 It is notable that, in contrast to the Ti-16HOAc system,  
 175 where gelation occurs immediately upon the addition of water  
 176 at room temperature (20 °C), the Ti-16TFA mixture (Sup-  
 177 porting Information 1) does not gel, indicating that the rate  
 178 of hydrolysis is considerably lower for the latter system.  
 179 Indeed, this is further evident from the longer shelf life of  
 180 the Ti-16TFA sol samples at room temperature (20 °C), and  
 181 the xerogel is only formed upon heating to 90 °C. These  
 182 materials have been found to be extremely robust in that  
 183 they have remained stable in their prepared form for in excess  
 184 of 1 year.



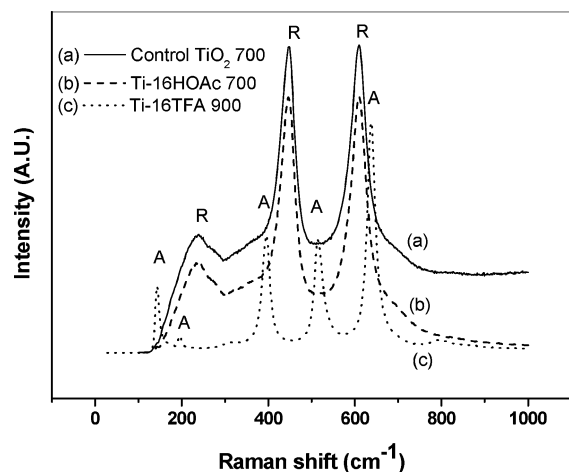
**Figure 1.** XRD patterns of various Ti-TFA samples (a) calcined at 700 °C and (b) calcined at 900 °C. (A, anatase; R, rutile).

**Table 1. Crystalline Phases and Weight Percentages of Anatase and Rutile (A:R) Determined from XRD**

sol used for preparation	% anatase (A):% rutile (R) at specified temperatures (error $\pm$ 5%)				
	600 °C	700 °C	800 °C	900 °C	1000 °C
Ti-32TFA	100:0	100:0	100:0	96:4	0:100
Ti-16TFA	100:0	100:0	100:0	100:0	0:100
Ti-12TFA	100:0	100:0	100:0	92:8	0:100
Ti-8TFA	100:0	100:0	90:10	43:57	0:100
Ti-4TFA	100:0	98:2	83:17	39:61	0:100
Ti-1TFA	100:0	82:18	25:75	0:100	0:100
Ti-16OxA	100:0	13:87	0:100	0:100	0:100
Ti-16HOAc	24:76	0:100	0:100	0:100	0:100
control TiO <sub>2</sub>	18:82	0:100	0:100	0:100	0:100

185 **X-ray Diffraction Analysis.** The phase evolution of the  
 186 samples has been followed by the powder X-ray diffraction  
 187 (XRD) technique. The XRD patterns of the samples calcined  
 188 at 700 and 900 °C are presented as Figure 1a and b,  
 189 respectively. The percentage anatase and rutile contents  
 190 calculated using the Spurr equation are presented in Table  
 191 1. It may be noted that a 100% anatase TiO<sub>2</sub> was observed  
 192 at a temperature as high as 900 °C for the sample prepared  
 193 from the Ti-16TFA sol. The intense anatase (101) peak is  
 194 indicative of its high crystallinity compared to the low-  
 195 temperature calcined samples. By contrast, even at 700 °C,  
 196 the control and HOAc-modified TiO<sub>2</sub> samples were 100%

(20) Gauglitz, G.; Vo-Dinh, T. *Handbook of Spectroscopy*; Wiley-VCH: New York, 2003; Vol. 1, p 97.



**Figure 2.** Raman spectra of (a) control TiO<sub>2</sub>-700, (b) Ti-16HOAc-700, and (c) Ti-16TFA-900 (A, anatase; R, rutile) registered at 514 nm excitation wavelength.

197 rutile, while the OxA-modified TiO<sub>2</sub> showed a mixed phase  
198 composition with 13% anatase and 87% rutile. For the  
199 samples prepared with lower molar ratios of TFA, the  
200 anatase-to-rutile transformation commences just below 700  
201 °C for the Ti-1TFA sample (Figure 1a) and is completely  
202 transformed to rutile at 900 °C. On the other hand, with the  
203 Ti-8TFA sample, the conversion to rutile only starts at ca.  
204 800 °C, and at 900 °C the sample contained ca. 57% rutile.  
205 All the samples show a 100% rutile phase at 1000 °C  
206 (Supporting Information 2).

207 Raman spectroscopy, being a more sensitive technique to  
208 detect even traces of a compound, was also employed for  
209 phase analysis (Figure 2). Ti-16TFA-500 (not shown here)  
210 and Ti-16TFA-900 gave spectral bands corresponding to  
211 anatase TiO<sub>2</sub> (144, 197, 395, 514, and 638 cm<sup>-1</sup>).<sup>21</sup> The  
212 control TiO<sub>2</sub> and Ti-16HOAc samples on the other hand were  
213 converted to rutile at 700 °C (bands at 143, 233, 447, and  
214 610 cm<sup>-1</sup>).<sup>22</sup>

215 N<sub>2</sub> adsorption studies were conducted to examine the effect  
216 of calcination on the textural properties. Ti-16TFA-900  
217 showed a surface area of 20 m<sup>2</sup> g<sup>-1</sup> compared to that of the  
218 control TiO<sub>2</sub> which was <1 m<sup>2</sup> g<sup>-1</sup> at 900 °C. The pore  
219 radius measured using the Horvath–Kawazoe method indi-  
220 cated the formation of a microporous network (9.273 Å) for  
221 Ti-16TFA-900, while the control TiO<sub>2</sub>-900 was almost  
222 nonporous. The adsorption isotherm of Ti-16TFA-900 (Sup-  
223 porting Information 3) also showed the presence of a  
224 predominantly microporous network. The dramatic change  
225 in the surface area and porosity values could be attributed  
226 to the incorporation of F atoms. It is reported that F

incorporation into the silica network creates nanovoids.<sup>23</sup> The  
evolution of microporosity in the present system is therefore  
ascribed to a similar effect.

Diffuse reflectance spectral analyses were performed to  
investigate the effect of calcination on the optical properties  
of different powder samples (Supporting Information 4).  
From such spectra, the band gap for the materials was  
calculated. A band gap of 3.02 eV is obtained for the control  
TiO<sub>2</sub>-700 and -900 samples, which corroborate with the  
reported data for rutile TiO<sub>2</sub>.<sup>2,5d</sup> The Ti-16TFA-700 and -900  
samples on the other hand showed a band gap of 3.28 eV.  
Furthermore, a steady decrease in the percent reflectance in  
the higher wavelength side of the spectrum demonstrates the  
oxygen vacancy concentration of samples.<sup>24</sup> Such a sloping  
baseline observed for Ti-16TFA-700 may be indicative of  
the presence of oxygen vacancies. Ti-16TFA-900, on the  
other hand, showed little change in baseline, consistent with  
a sample relatively free of this defect (with minimal oxygen  
vacancy).

To determine the role of TFA and especially whether any  
fluorine can be observed after calcination, XPS has been  
performed on the Ti-16TFA samples calcined at 500, 700,  
800, 900, and 1000 °C. Figure 3a and b present the XPS  
high-resolution spectra for F1s of Ti-16TFA-500 and Ti-  
16TFA-900 samples, respectively. The photoelectron peak  
located at 684.5 eV for Ti-16TFA-500 and Ti-16TFA-700  
(Supporting Information 5) is ascribed to the F1s species of  
F adsorbed on TiO<sub>2</sub>.<sup>25</sup> Concentrations of 0.5 atom % F and  
0.3 atom% F are determined for the Ti-16TFA-500 and Ti-  
16TFA-700 samples, respectively. Similar peaks are however  
absent in the Ti-16TFA-800 (Supporting Information 5) and  
Ti-16TFA-900 samples. However the TGA pattern obtained  
for the Ti-16TFA gel shows a small percent loss of mass up  
to 800 °C. By contrast, the weight loss appeared to be  
complete at ~400 °C for the Ti-16HOAc and the control  
TiO<sub>2</sub> gels (Supporting Information 6).

The presence of lattice F atoms is represented by a peak  
located at 688 eV in XPS.<sup>26</sup> Such a peak could be observed  
only for the Ti-16TFA-500 and Ti-16TFA-700 samples. XPS  
is a surface technique whose analysis depth is 4–5 nm, and  
therefore the presence of deep lattice F atoms (in Ti-16TFA-  
800 and Ti-16TFA-900 samples, where the surface and near-  
surface F atoms would be completely eliminated) may not  
be observable using this technique. By contrast, FTIR should  
be able to probe the presence of Ti–F bonds in the sample.  
Figure 4 presents the FTIR spectra of the control TiO<sub>2</sub>-500  
and the various Ti-16TFA samples. A weak band at 1080  
cm<sup>-1</sup> is observed for the Ti-16TFA-500 sample, consistent  
with the observation by Li et al. in the Mg–F system, but a  
similar band could not be detected in any other samples, and

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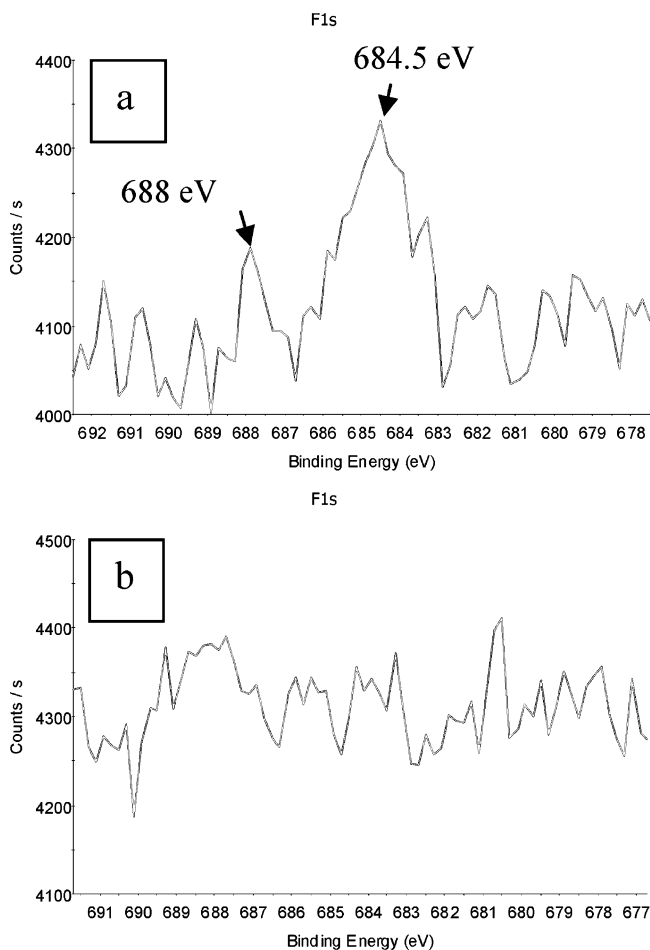


Figure 3. XPS spectra of (a) Ti-16TFA-500 and (b) Ti-16TFA-900.

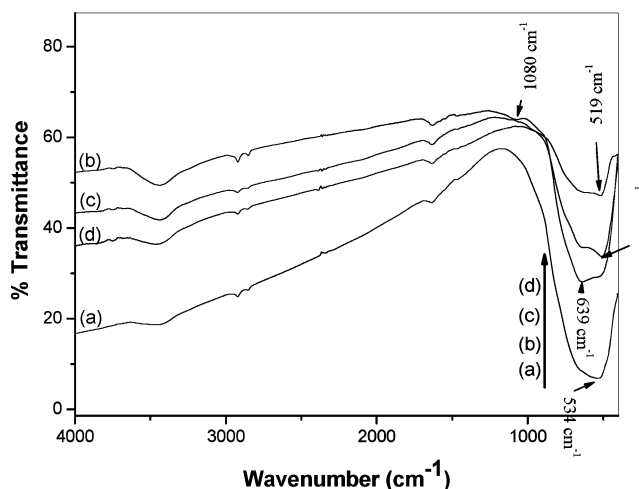


Figure 4. FTIR spectra of various TiO<sub>2</sub> samples [(a) control TiO<sub>2</sub>-500, (b) Ti-16TFA-500, (c) Ti-16TFA-700, and (d) Ti-16TFA-900].

277 this may be attributed to the surface-fluorinated Ti–F  
 278 species.<sup>27</sup> Further, in the lower-wave-number region, a sharp  
 279 band centered at 534 cm<sup>-1</sup> with a shoulder band at ~648  
 280 cm<sup>-1</sup> observed for the control TiO<sub>2</sub>-500 represents the Ti–

O–Ti phonon vibration.<sup>17a,27</sup> In comparison, main bands at 281  
 639, 510, and 519 cm<sup>-1</sup> can be observed for Ti-16TFA-500, 282  
 Ti-16TFA-700, and Ti-16TFA-900 samples, respectively. 283  
 The band at 639 cm<sup>-1</sup> is ascribed to the surface Ti–F 284  
 bonds,<sup>28</sup> whereas the bands at 510 and 519 cm<sup>-1</sup> are 285  
 consistent with a change in the chemical environment of the 286  
 titania matrix owing to the presence of a small amount of 287  
 lattice Ti–F bonds.<sup>27b</sup> The Ti-16TFA-800 sample showed a 288  
 similar pattern to Ti-16TFA-900 (Supporting Information 7). 289

In the sol–gel process, the hydrolysis (forced hydrolysis 290  
 in the present case) and polycondensation reactions occur 291  
 simultaneously as the sol was dried immediately after 24 292  
 hour aging. The drying process causes the formation of an 293  
 intimate gel of Ti(OOCCF<sub>3</sub>)<sub>4-x</sub>(OH)<sub>x</sub> (Supporting Information 294  
 1). The Ti–F bonds are only formed in the further condensa- 295  
 tion process (on calcination). This leads to the formation of 296  
 inlaid (deep) Ti–F bonds in the network structure. Those 297  
 Ti–F bonds, which are in the network structure, could not 298  
 be easily removed by heat treatment compared to the surface- 299  
 fluorinated ones. This explains the observations by TGA and 300  
 XPS. The mass loss shown by the Ti-16TFA gel up to 800 301  
 °C (above 400 °C) in TGA may be the mass loss of the 302  
 surface-fluorinated Ti–F species. The rest of the nominal 303  
 Ti–F bonds, which could not be quantified using XPS, may 304

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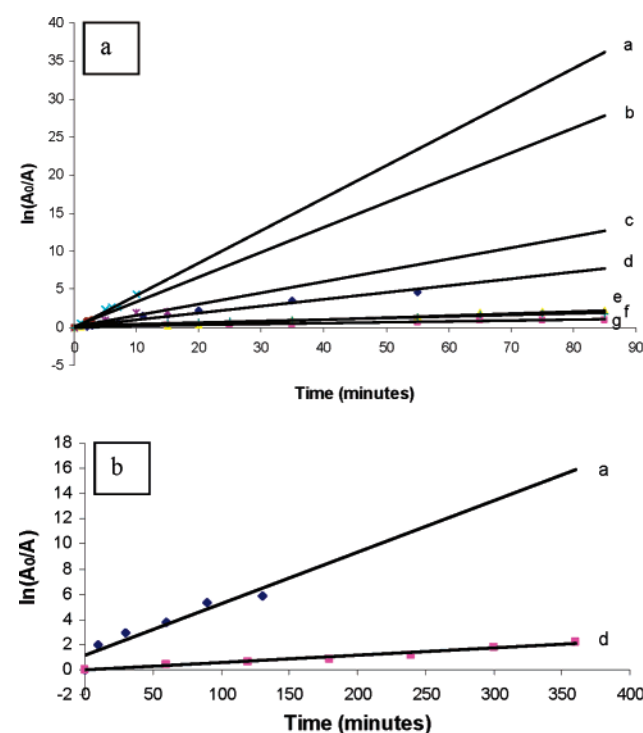


Table 2. Rate Constants of Various Degradation Reactions

sample	rate (min <sup>-1</sup> )
In UV light	
Degussa P25	0.327
control TiO <sub>2</sub> -700	0.089
control TiO <sub>2</sub> -900	0.021
Ti-12TFA-800	0.168
Ti-12TFA-900	0.200
Ti-32TFA-800	0.154
Ti-32TFA-900	0.246
Ti-16TFA-700	0.147
Ti-16TFA-800	0.197
Ti-16TFA-900	0.426
Ti-16HOAc-700	0.012
Ti-16OxA-700	0.028
In Sunlight	
Ti-16TFA-900	0.041
control TiO <sub>2</sub> -700	0.006

be the inlaid ones. The influence of such Ti–F bonds could however be detected using FTIR.

**Photoactivity.** Kinetic plots of various methylene blue degradation experiments are presented in Figure 5. The corresponding rate constants are presented in Table 2. A complete degradation of MB was observed within 10 min under UV light irradiation for the Ti-16TFA-900 sample. By contrast, the control TiO<sub>2</sub>-900, which was in a 100% rutile form, was found to be inactive up to a period of 6 h of UV irradiation. All the control samples took >2 h for complete methylene blue degradation. These results indicate that the TFA modification is highly effective in enhancing the photoactivity of TiO<sub>2</sub> at high temperatures. Furthermore, the activity for Ti-16TFA samples was in the order Ti-16TFA-900 > Ti-16TFA-800 > Ti-16TFA-700 > Ti-16TFA-600 > Ti-16TFA-500. These observations demonstrate the significant role of anatase crystallinity, surface properties, and the minimal oxygen vacancy concentration



**Figure 5.** Methylene blue degradation kinetics of various TiO<sub>2</sub> samples in the presence of UV light (a) and sunlight (b) [(a) Ti-16TFA-900, (b) Degussa P25, (c) Ti-16TFA-700, (d) control TiO<sub>2</sub>-700, (e) Ti-16OxA-700, (f) control TiO<sub>2</sub>-900, and (g) Ti-16HOAc-700; A, absorbance at 664 nm].

on the photoactivity of TiO<sub>2</sub>. Similar experiments have also been conducted in Dublin sunlight, where the Ti-16TFA-900 showed a complete degradation of MB in 90 min (Figure 5b). On the other hand, the control TiO<sub>2</sub>-700 could not degrade MB even after 10 h of solar light irradiation (Supporting Information 8).

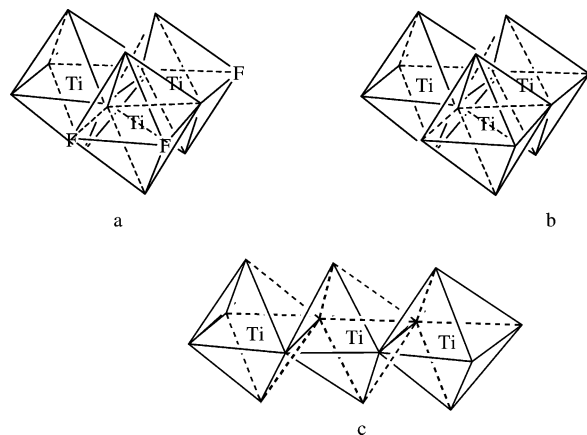
## Discussion

**Phase Evolution.** Among the samples, Ti-16TFA-900 shows the highest anatase-to-rutile phase transformation temperature (900 °C) compared to the low TFA samples and the samples prepared with HOAc, OxA, and control TiO<sub>2</sub>. An increase in the TFA concentration (Ti-32TFA), however, shows a similar effect on the phase transformation to that of Ti-16TFA. The structural evolution of the samples—phase formation and phase transformation—investigated by both Raman and XRD demonstrate the effect of different modifiers. The anatase-to-rutile transformation involves the rearrangement of the (TiO<sub>6</sub><sup>2-</sup>) octahedron.<sup>29</sup> The structure of anatase consists of zigzag chains of octahedra, linked to each other through shared edges, whereas in rutile, a linear chain of opposite edge-shared octahedra is found. Chains are further linked to each other by sharing corner oxygen atoms to form a 3D network. In our case, the metal cation (Ti<sup>4+</sup>) is expected to undergo a coordination expansion to six when chelated with TFA to form the independent Ti-(OOCF<sub>3</sub>)<sub>4</sub> octahedral complexes.<sup>30</sup> Further, when hydrolysis and condensation is initiated under the forced reaction conditions (temperature-dependent hydrolysis and condensation), initially, the independent octahedral complexes are hydrolyzed, forming Ti(OOCF<sub>3</sub>)<sub>4-x</sub>(OH)<sub>x</sub> species. The next step is the condensation of two octahedral complexes to form the vertex-shared octahedra.<sup>30</sup> Upon further heating, the condensation between the two vertex-shared octahedra leads to the formation of an edge-shared octahedra, which is followed by the linking up of a third octahedron. The spatial factors offered by the trifluoroacetate complex may cause the joining up of a third octahedron to the far corner of the dioctahedra, thereby reducing the electrostatic repulsion.<sup>31</sup> Subsequently, when the temperature is sufficiently high, the decomposition of the trifluoroacetate complex occurs. The faster thermal decomposition (cleavage of Ti–OOCF<sub>3</sub> bond) keeps up the rate of segregation (condensation), and under such a fast rate, the third octahedron will, preferentially, join to the existing dioctahedral complex to form a right-angled trioctahedral complex (anatase). This is perfectly in line with the previous reports, where it was suggested that the faster reaction rate promotes the formation of anatase rather than the thermodynamically favorable rutile structure.<sup>32,33</sup> The thermal

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**Scheme 2. Schematic Representation of Anatase and Rutile Crystallization Events<sup>a</sup>**



<sup>a</sup> (a) Anatase crystallization under the faster reaction conditions: the third octahedron, under the influence of fluorine, prefers to join to the existing dioctahedra by sharing an edge, forming a zigzag structure. (b) Anatase crystal structure after the removal of fluorine. (c) Rutile formation: the third octahedron preferably links up to the existing dioctahedra, forming a linear chain by sharing a pair of opposite edges, which is a thermodynamically favorable process. Under the high-temperature calcination process, the existing anatase clusters undergo a diffusional rearrangement to form the denser rutile crystals.

371 decomposition of trifluoroacetate species also causes the  
 372 fluorination of the remaining amorphous precipitate as well  
 373 as the existing anatase crystals (Scheme 2a). Under the  
 374 fluorinated condition, the crystallization as well as the crystal  
 375 growth can be a slow process due to the fact that the  
 376 fluorinated clusters may repel each other, slowing down the  
 377 reaction rate.<sup>32</sup> The inhibition of crystallization and crystal  
 378 growth in such cases can be observed from the limitation of  
 379 the X-ray peak intensity as well as the slower line-narrowing  
 380 of the X-ray diffraction lines under the increasing calcination  
 381 temperature. Upon further heating, the fluorine atoms are  
 382 being preferentially eliminated (Scheme 2b), causing a faster  
 383 atomic/ionic diffusion. Such faster diffusion conditions are  
 384 favorable for the formation of a denser rutile structure  
 385 (Scheme 2c).

386 The primary crystallite sizes calculated using the Scherrer  
 387 equation showed crystallite sizes of 26, 32, 33, 34 and 35  
 388 nm respectively for the Ti-16TFA-500, Ti-16TFA-600, Ti-  
 389 16TFA-700, Ti-16TFA-800, and Ti-12TFA-900 samples  
 390 (Supporting Information 9). In addition, a direct dependence  
 391 between the TFA concentration and rutile phase formation  
 392 can be noticed. The rutile phase formation occurs when the  
 393 anatase crystallite size was at 29, 31, 32, and 36 nm  
 394 respectively for the Ti-1TFA, Ti-4TFA, Ti-8TFA, and  
 395 Ti-12TFA samples, and for *control* TiO<sub>2</sub>, it was at 26 nm.  
 396 The shift in the phase transformation temperature with TFA  
 397 addition can therefore be attributed to the presence of fluorine  
 398 in the system. As the TFA concentration increases, there is  
 399 a greater chance of the F atoms being trapped in the titania  
 400 matrix. Upon further heating, fluorine is eliminated easily  
 401 from the sample with low fluorine content, whereas the  
 402 elimination could be very slow from the samples with high  
 403 fluorine content, consistent with the high amount of deep-

level trapped fluorine. As fluorine elimination and crystal  
 growth are simultaneous events, the crystallites have a chance  
 to grow to a greater extent in the high-TFA samples. Thus,  
 the critical size limit for the phase transformation of the  
 anatase crystals is shifted to higher crystallite size values  
 for high-TFA samples in the present case. By contrast, the  
 absence of fluorine in the *control* TiO<sub>2</sub> system caused a faster  
 temperature-dependent diffusional rearrangement, after the  
 initial anatase clustering, leading to the formation of a denser  
 rutile structure at a comparatively lower temperature of 700  
 °C. Essentially, the fluorine substituted in the oxygen atomic  
 site inhibits the extensive Ti–O–Ti bridging (Scheme 2a).  
 These defect centers will also act as a barrier for oxygen  
 ion diffusion necessary for the grain growth and assisted  
 phase transformation.<sup>34</sup> This clearly suggests the inhibiting  
 role of fluorine on the rutile phase nucleation, which may  
 only be commenced after the elimination of F atoms from  
 the structure. The higher bond enthalpy of Ti–O bonds (672  
 ± 9 kJ mol<sup>-1</sup>) compared to the Ti–F bonds (569 ± 33 kJ  
 mol<sup>-1</sup>) may account for the preferential F elimination.<sup>35</sup>

It should be stated here that, even though the optimum  
 amount of fluorine necessary for the inhibition of rutile phase  
 nucleation cannot be calculated quantitatively, the present  
 studies indicate that an initial concentration of 16 mol %  
 TFA is sufficient to retain the anatase phase up to 900 °C.  
 This is further ascertained from the fact that a higher TFA  
 concentration (32 mol %) shows a similar effect as 16 mol  
 % TFA and a lower concentration (12 mol %) could not  
 prevent the phase transformation up to 900 °C. It should  
 also be noted that a ±5% error can be expected in  
 determining the phase content.

**Photocatalytic Activity.** MB degradation experiments and  
 the corresponding kinetic analyses data show the highest  
 activity for the Ti-16TFA-900 sample compared to the other  
 TFA samples (both lower temperature and various concen-  
 tration TFA samples) and those prepared with HOAc, OxA,  
 and *control* TiO<sub>2</sub>. Semiconductor photocatalytic reactions are  
 known to occur through (i) direct valence band hole (h<sub>VB</sub>)  
 oxidation,<sup>36</sup> (ii) reactive oxygen species (namely, OH<sup>•</sup>, O<sup>2-</sup>,  
 and H<sub>2</sub>O<sub>2</sub>)<sup>36–37</sup> assisted oxidation, and (iii) direct conduction  
 band electron (e<sub>CB</sub>) reduction. The enhanced photocatalytic  
 activity<sup>36,38</sup> and photoinduced hydrophilicity<sup>39</sup> of surface-  
 fluorinated TiO<sub>2</sub> systems have been reported recently.

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447 Recently, Mauro et al. reported that the fluorinated TiO<sub>2</sub> 491  
 448 systems increase the generation of adsorbed and free OH• 492  
 449 radicals.<sup>39</sup> Such an enrichment in the reactive species 493  
 450 concentration in suspension was associated with a consider- 494  
 451 able enhancement in the photocatalytic activity.<sup>39</sup> In addition, 495  
 452 F doping was also found to enhance the photocatalytic 496  
 453 activity of TiO<sub>2</sub>.<sup>25a,39,40</sup> Despite many studies, the exact 497  
 454 mechanism of the photocatalytic reaction and the role of 498  
 455 influencing parameters in such systems is still not clear. The 499  
 456 influence of F atoms in different systems is reported 500  
 457 differently.<sup>25a,39,40</sup> The present sol-gel method enabled the 501  
 458 preparation of both surface-fluorinated and F-doped TiO<sub>2</sub> 502  
 459 systems from a single process, allowing a direct and 503  
 460 straightforward comparison of their activity. High-temper- 504  
 461 ature heat treatment (900 °C) enabled the preparation of 505  
 462 F-doped TiO<sub>2</sub> (small amount of F) with high crystallinity 506  
 463 and microporosity, whereas the low-temperature heat treat- 507  
 464 ment (500–700 °C) produced surface-fluorinated TiO<sub>2</sub>. The 508  
 465 Ti-16TFA-900 sample showed a higher photocatalytic activ- 509  
 466 ity compared to the surface-fluorinated TiO<sub>2</sub> in the present 510  
 467 study. 511

468 The photocatalytic activity of titania is mainly dependent 512  
 469 on factors such as accessible surface area, crystallinity, and 513  
 470 particle size.<sup>41</sup> The microporous nature of Ti-16TFA-900 514  
 471 increases the accessibility of MB molecules to have maxi- 515  
 472 mum surface coverage by direct adsorption, which effectively 516  
 473 enhances its reaction efficiency.<sup>25b</sup> The lower activity of the 517  
 474 low-temperature Ti-16TFA samples (activities in the order 518  
 475 Ti-16TFA-500 < Ti-16TFA-600 < Ti-16TFA-700 < 519  
 476 Ti-16TFA-800 < Ti-16TFA-900), in comparison, despite 520  
 477 their high surface accessibility (high surface areas), is 521  
 478 ascribed to the high electronegativity of fluorine, which 522  
 479 inhibits the interfacial charge transfer. In other words, the 523  
 480 steady increase in activity with an increase in calcination 524  
 481 temperature up to 900 °C may be attributed to the gradual 525  
 482 elimination of the fluorine incorporated in the titania matrix. 526  
 483 In addition, fluorine when incorporated into the titania matrix 527  
 484 increases the oxygen vacancy concentration. Subbarao et al. 528  
 485 reported the facilitating effect of oxygen vacancy on charge 529  
 486 carrier recombination.<sup>42</sup> The present observations are con- 530  
 487 sistent with the report by Subbarao et al., where the high 531  
 488 photoactivity is obtained for the sample with a high crystal- 532  
 489 linity, microporosity, and minimal oxygen vacancy concen- 533  
 490 tration. The hydroxyl-radical-generating ability of the F

atoms,<sup>39</sup> in the case of the low-temperature samples, has been 491  
 nullified by the increase in oxygen vacancies. Therefore, the 492  
 presence of fluorine can be assumed to be detrimental to 493  
 the activity as it (i) reduces the rate of interfacial charge 494  
 transfer and (ii) creates more oxygen vacancies. 495

Three factors have been identified which enhance the 496  
 activity of the Ti-16TFA-900 sample compared to the 497  
 surface-fluorinated TiO<sub>2</sub> samples in the present study. First 498  
 is the high anatase crystallinity of Ti-16TFA-900 compared 499  
 to the low-temperature calcined samples. Second is the 500  
 presence of minimal F content (minimal oxygen vacancy) 501  
 that reduces the charge carrier recombination process in 502  
 Ti-16TFA-900 compared to the low-temperature calcined Ti- 503  
 16TFA samples. The presence of these nominal inlaid F 504  
 atoms increases the surface –OH groups, adsorbed OH• 505  
 radicals, and free OH• radicals (in solution). In case of the 506  
 low-temperature Ti-16TFA samples, the higher electrone- 507  
 gativity of the surface-fluorinated F atoms will have more 508  
 influence in reducing the interfacial charge transfer compared 509  
 to the generation of such reactive species. The relatively high 510  
 adsorbing ability of surface F atoms (water and organic 511  
 adsorption, especially MB) in such systems is nullified by 512  
 the poor interfacial charge transfer to the adsorbed molecules. 513  
 Finally, this material shows far more suitable surface 514  
 properties, that is, a microporous nature of the Ti-16TFA- 515  
 900 sample with an enhanced probability of interfacial charge 516  
 transfer. Despite having high surface area values, the low- 517  
 temperature Ti-16TFA samples are less active due to the 518  
 factors described above. The hindering effect on rutile phase 519  
 nucleation by fluorine up to a temperature as high as 900 520  
 °C was therefore helpful in attaining a highly crystalline and 521  
 microporous anatase TiO<sub>2</sub>. The high photoactivity of the 522  
 Ti-16TFA-900 sample is therefore ascribed to the synergistic 523  
 effect of high crystallinity, microporosity, and minimum 524  
 oxygen vacancy concentration, which could well be achieved 525  
 by the high-temperature heat treatment. On the other hand, 526  
 the *control* TiO<sub>2</sub> samples are in the pure rutile form with 527  
 low porosity at these temperatures (700 and 900 °C) and 528  
 are therefore less active. It should be noted here that the 529  
 red-shifting of the band gap absorption of *control* TiO<sub>2</sub> 530  
 samples, which could have been favorable for the photoac- 531  
 tivity, has been nullified by the nonporous and noncatalytic 532  
 nature of the rutile phase. 533

## Summary

534

In summary, a simple and highly efficient procedure for 535  
 the preparation of high-temperature stable anatase (100% at 536  
 900 °C) titania with a high photocatalytic activity is 537  
 presented. Fluorine-assisted inhibition of rutile phase nucle- 538  
 ation followed by the elimination of fluorine and subsequent 539  
 commencement of rutile phase nucleation explains the high- 540  
 temperature stability for the Ti-16TFA samples. The 541  
 Ti-16TFA-900 sample shows the highest photocatalytic 542  
 activity in the presence of both UV light ( $\lambda$  365 nm) and 543  
 sunlight, which is attributed to a synergistic effect of the 544  
 high crystallinity, microporosity, and a minimal oxygen 545  
 vacancy concentration of anatase TiO<sub>2</sub>. This intrinsic doping 546  
 approach is therefore proposed to be an effective methodol- 547  
 ogy for replacing the conventional use of extrinsic cationic 548  
 dopants to obtain a high-temperature stable anatase phase. 549  
 The present sol-gel process to produce highly crystalline 550

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551 anatase TiO<sub>2</sub> stable up to a temperature as high as 900 °C  
552 therefore has fundamental as well as technological impor-  
553 tance.

554 **Abbreviations.** TTIP, titanium tetraisopropoxide; TFA,  
555 trifluoroacetic acid; HOAc, acetic acid; OxA, oxalic acid;  
556 MB, methylene blue.

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**Supporting Information Available:** FTIR data showing the 566  
chelation of TFA (Supporting Information 1), XRD patterns of Ti- 567  
12TFA and Ti-32TFA samples calcined at 900 °C (Supporting 568  
Information 2), N<sub>2</sub> adsorption and desorption isotherms of a 569  
Ti-16TFA-900 sample (Supporting Information 3), diffuse reflec- 570  
tance spectra (Supporting Information 4), high-resolution XPS 571  
spectra of Ti-TFA-800 and Ti-16TFA-900 (Supporting Information 572  
5), TGA analysis graphs (Supporting Information 6), FTIR spectra 573  
(Supporting Information 7), extensive UV–vis spectral character- 574  
ization data (Supporting Information 8), and a table showing the 575  
crystallite sizes of samples (Supporting Information 9). This material 576  
is available free of charge via the Internet at <http://pubs.acs.org>. 577

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