

2006

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### Recommended Citation

Pillai, S.C. et al. (2006) Synthesis of High-Temperature Stable Anatase TiO<sub>2</sub> Photocatalyst, *Journal of Physical Chemistry. C*, vol. 111 no. 4, 2007, 1605–1611. doi:10.1021/jp065933h

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# Synthesis of High-Temperature Stable Anatase TiO<sub>2</sub> Photocatalyst

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*Received: September 12, 2006; In Final Form: November 9, 2006*

In the absence of a dopant or precursor modification, anatase to rutile transformation in synthetic TiO<sub>2</sub> usually occurs at a temperature of 600–700 °C. Conventionally, metal oxide dopants (e.g., Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) are used to tune the anatase to rutile transformation. A simple methodology is reported here to extend the anatase to rutile transformation by employing various concentrations of urea. XRD and Raman spectroscopy were used to characterize various phases formed during thermal treatment. A significantly higher anatase phase (97%) has been obtained at 800 °C with use of a 1:1 Ti(OPr)<sub>4</sub>:urea composition and 11% anatase composition is retained even after calcining the powder at 900 °C. On comparison a sample that has been prepared without urea showed that rutile phases started to form at a temperature as low as 600 °C. The effect of smaller amounts of urea such as 1:0.25 and 1:0.5 Ti(OPr)<sub>4</sub>:urea has also been studied and compared. The investigation concluded that the stoichiometric modification by urea 1:1 Ti(OPr)<sub>4</sub>:urea composition is most effective in extending the anatase to rutile phase transformation by 200 °C compared to the unmodified sample. In addition, BET analysis carried out on samples calcined at 500 °C showed that the addition of urea up to 1:1 Ti(OPr)<sub>4</sub>:urea increased the total pore volume (from 0.108 to 0.224 cm<sup>3</sup>/g) and average pore diameter (11 to 30 nm) compared to the standard sample. Samples prepared with 1:1 Ti(OPr)<sub>4</sub>:urea composition calcined at 900 °C show significantly higher photocatalytic activity compared to the standard sample prepared under similar conditions. Kinetic analysis shows a marked increase in the photocatalytic degradation of rhodamine 6G on going from the standard sample (0.27 min<sup>-1</sup>, decoloration in 120 min) to the urea-modified sample (0.73 min<sup>-1</sup>, decoloration in 50 min).

## 1. Introduction

Nanocrystalline titania (TiO<sub>2</sub>) has received significant attention in the last few decades due to the photoinduced electron-transfer properties associated with the anatase metastable phase.<sup>1–3</sup> Titania usually exists in three different forms: anatase (tetragonal,  $a = b = 3.78$  Å;  $c = 9.50$  Å), rutile (tetragonal,  $a = b = 4.58$  Å;  $c = 2.95$  Å), and brookite (rhombohedral,  $a = 5.43$  Å;  $b = 9.16$  Å;  $c = 5.13$  Å). These crystalline structures consist of [TiO<sub>6</sub>]<sup>2-</sup> octahedra, which share edges and corners in different manners while keeping the overall stoichiometry as TiO<sub>2</sub>.<sup>4–7</sup> Even though anatase has more edge sharing octahedra, the interstitial spaces between octahedra are larger, which makes rutile denser than anatase (the density of anatase is 3.84 g/cm<sup>3</sup> and that of rutile is 4.26 g/cm<sup>3</sup>).<sup>4–7</sup> Among the various phases of titania reported, anatase shows a better photocatalytic activity and antibacterial performance.<sup>8–12</sup> A stable anatase phase up to the sintering temperature of the ceramic substrates is most desirable for applications on antibacterial self-cleaning building materials (e.g., bathroom tile, sanitary ware, etc.).<sup>13–15</sup> These applications require high-purity

titania with a definite phase composition.<sup>13–15</sup> The production of high-photoactivity material with high-temperature anatase phase stability is one of the key challenges in smart coating technology. Anatase-to-rutile transformation in pure titania usually occurs at 600 to 700 °C.<sup>16–18</sup> Phase transition to rutile is nonreversible due to the greater thermodynamic stability of rutile phase.<sup>19–20</sup> Researchers at Toto Ltd. recently reported<sup>21</sup> a method to produce photoactive titania-Ag coatings on ceramic materials. The composition contains up to 7% anatase present at 900 °C.<sup>21</sup> Any improvement in the anatase phase composition at these high temperatures is expected to show a higher photocatalytic activity.<sup>21</sup> Conventionally metal oxide doping is used to extend the anatase-to-rutile transformation temperature above 700 °C.<sup>22–26</sup> Various metal oxide dopants such as Al<sub>2</sub>O<sub>3</sub>, NiO, SiO<sub>2</sub>, ZrO<sub>2</sub>, ZnO, and Sb<sub>2</sub>O<sub>5</sub> have already been studied to assess the effect on both anatase-to-rutile transformation and alteration of modification on textural properties of titania.<sup>22–26</sup> Formation of secondary impurity phases (e.g., Al<sub>2</sub>TiO<sub>5</sub>, NiTiO<sub>3</sub>) at high temperature is the main disadvantages of this technique. Modifying the precursor characteristics by employing chelating agents is another approach attempted earlier to obtain titania having specific properties.<sup>27–28</sup> Recent research showed that urea has little effect on the phase formation in titania.<sup>29</sup> Previously, urea has been employed to improve the pore parameters and morphology by utilizing it as a pore-forming agent.<sup>29–31</sup> Zheng et al. reported preparation of mesoporous titania via sol-gel

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reactions by using urea as a template.<sup>32</sup> Bakardjieva et al. showed the formation of TiO<sub>2</sub> nanocrystals from titanyleoxy chloride by using urea as a precipitating agent.<sup>33</sup> Also there are recent reports published which explain the visible light activity of titania by doping with nitrogen where urea or thiourea is used as a precursor.<sup>34–37</sup> However, there is no systematic study available in the literature on the effect of various concentrations of urea on high-temperature stability of anatase. Here in our study the titania precursor gel has been prepared by hydrolysis and condensation reaction of titanium isopropoxide (Ti(OPr)<sub>4</sub>) with various mole ratios of urea. The phase transformation during heat treatment was investigated by X-ray powder diffraction (XRD). The current study showed that a major anatase phase (up to 97%) can be retained at 800 °C by modifying titanium isopropoxide with urea. On the other hand, the standard titania showed the presence of rutile at a temperature as low as 600 °C. This method has therefore been found to be effective in extending the anatase-to-rutile phase transformation by at least 200 °C without using any metal oxide additives. Titania composition prepared by 1:1 Ti(OPr)<sub>4</sub>:urea molar ratio calcined at 900 °C shows significantly higher photocatalytic activity compared to the standard sample. Degradation kinetics on a model dye, rhodamine 6G, demonstrate that the urea-modified sample is more than three times as efficient as the standard sample, a fact attributed to the increased amount of anatase in the urea-modified sample.

## 2. Experimental Methods

The reagents used in this study were titanium isopropoxide (Aldrich) and urea (Aldrich). In a typical experiment to synthesize 1:1 titania precursor:urea solution, 46.80 mL of titanium isopropoxide (Ti(OPr)<sub>4</sub>) was added into 412 mL of isopropanol. To the above solution, 10 g of urea dissolved in 70 mL of water was added. The solution was then stirred for 5 min and aged for 2 h at room temperature. It was then dried at 80 °C for 24 h. The dried powder was calcined at a constant heating rate of 5 deg/min at 500, 600, 700, 800, 900, and 1000 °C and held at these temperatures for 2 h.

The same procedure is adopted to synthesize 1:0.25 and 1:0.5 Ti(OPr)<sub>4</sub>:urea samples. A standard sample without urea was also prepared to compare the results. XRD patterns of the calcined gels were obtained with a Siemens D 500 X-ray diffractometer in the diffraction angle range  $2\theta = 20\text{--}70^\circ$ , using Cu K $\alpha$  radiation. The amount of anatase in the sample was estimated by using the Spurr equation (eq 1)<sup>38</sup>

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

where  $F_A$  is the mass fraction of anatase in the sample and  $I_A(101)$  and  $I_R(110)$  are the integrated main peak intensities of anatase and rutile, respectively.

The BET (Brunauer, Emmett, and Teller) surface area measurements and pore analysis were carried out by nitrogen adsorption with use of a Micromeritics Gemini 2375 surface area analyzer. The measurements were carried out at liquid nitrogen temperature after degassing the powder samples for 1 h 30 min at 200 °C.

Differential Scanning Calorimetry (DSC) measurements were carried out with a Rheometric Scientific DSC QC. A small amount of the dried sample (less than 3 mg) was heated from room temperature (25 °C) to 400 °C at a constant heating rate of 10 deg/min.

The FTIR spectra of the gel dried at 80 °C was measured by using a Spectrum GX-FTIR spectrophotometer in the wave number range 4000–400 cm<sup>-1</sup>, using 70 scans per sample.

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

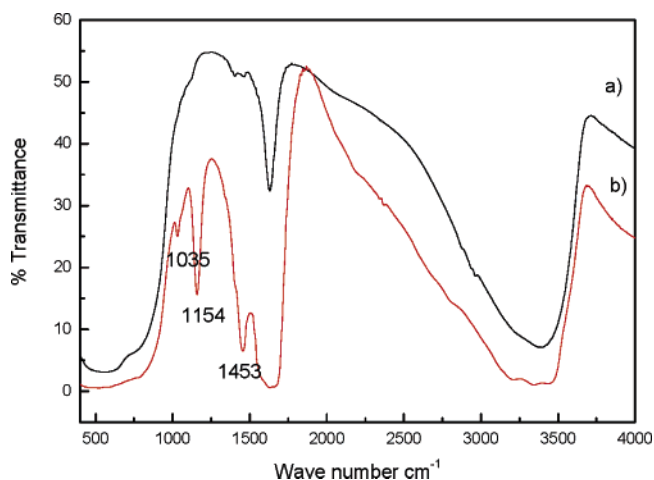
**Photocatalysis Studies.** In a typical experiment, a 0.06 g standard sample calcined at 900 °C was dispersed in 50 mL of Rhodamine 6G solutions having a concentration of  $5 \times 10^{-6}$  M. The above suspension was irradiated in a Q-Sun Xenon solar simulator chamber (0.68 W/m<sup>2</sup> at 340 nm) with stirring. Degradation was monitored by taking aliquots at increasing time intervals. These aliquots were centrifuged and absorption spectra of the samples were recorded. Similar experiments were carried out for urea modified sample calcined at 900 °C. The rate of degradation was assumed to obey pseudo-first-order kinetics and hence the rate constant for degradation,  $k$ , was obtained from the first-order plot according to eq 2

$$\ln\left(\frac{A_0}{A}\right) = kt \quad (2)$$

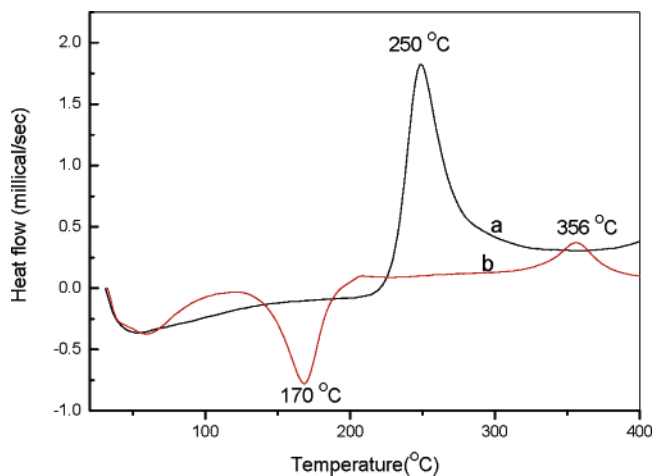
where  $A_0$  is the initial absorbance,  $A$  is the absorbance after a time ( $t$ ) of the rhodamine dye degradation, and  $k$  is the first-order rate constant.

## 3. Results

**3.1. FTIR Spectroscopy.** FTIR spectra of the precursor samples dried at 80 °C have been recorded. The absorption band at 3500–3000 and 1600 cm<sup>-1</sup> in all spectra indicate hydroxyl group stretching vibrations.<sup>29</sup> The broad peak at 500 cm<sup>-1</sup> found in the standard and urea modified samples indicates the Ti–O–Ti stretching vibrations.<sup>29</sup> The peak observed at 1035 cm<sup>-1</sup> corresponds to the Ti–O–C bond. The Ti–O–C bond is predicted to be the result of the interaction between the Ti–O network and the C=O in the urea.<sup>29</sup> The peaks corresponding to Ti–O–C bond increase in intensity when the urea concentration increases (Supporting Information Figure 1). This is a good indication that there is a great degree of interaction between the inorganic and organic components by the condensation reaction. The peak obtained at 1154 cm<sup>-1</sup> is assigned to the stretching vibration of C–N.<sup>29</sup> The peak obtained at 1453 cm<sup>-1</sup> is due to the deformation mode of ammonium ions formed by the decomposition of excess urea.<sup>40</sup> FTIR results thus show a strong chelation of urea molecules to the titania precursor. It has been observed that the peaks at 1035 (which is assigned for the Ti–O–C bond) and 1154 cm<sup>-1</sup> (C–N) were absent above a calcination temperature of 200 °C and all additional peaks except Ti–O stretching are absent above 300 °C.



**Figure 1.** FTIR spectra of the 80 °C dried titania precursor: (a) standard sample and (b) sample of 1:1 Ti(OPr)<sub>4</sub>:urea composition.



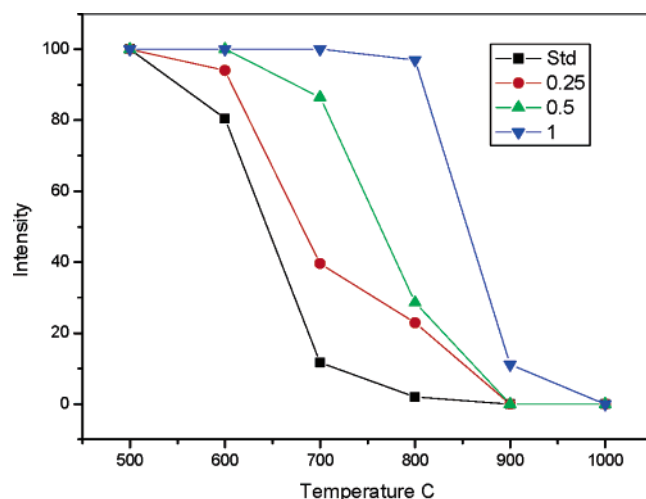
**Figure 2.** Differential scanning calorimetry of (a) standard and (b) sample of 1:1 Ti(OPr)<sub>4</sub>:urea composition.

**TABLE 1: BET Surface Area Analysis at 500 °C**

material	surface area (m <sup>2</sup> /g)	total pore vol (cm <sup>3</sup> /g)	av pore diameter (nm) ±10%
standard TiO <sub>2</sub> sample	38	0.108	11
1:1 Ti(OPr) <sub>4</sub> :urea composition	30	0.224	30

191 **3.2. Differential Scanning Calorimetry (DSC).** Differential  
 192 Scanning Calorimetry (DSC) studies have been carried out  
 193 (Figure 2) to investigate the amorphous-to-crystalline transition  
 194 of the titania precursor. An endothermic peak at 170 °C has  
 195 been observed for the 1:1 Ti(OPr)<sub>4</sub>:urea sample and this peak  
 196 has been assigned as the thermal decomposition of the titania-  
 197 urea precursor. The exothermic peaks (Figure 2a,b) at 250 and  
 198 356 °C respectively for the standard and 1:1 Ti(OPr)<sub>4</sub>:urea  
 199 samples indicate the amorphous-to-crystalline formation.<sup>27</sup> It  
 200 is therefore evident from Figure 2 that the amorphous-to-crystalline  
 201 formation is delayed in the case of the urea-modified sample.  
 202 XRD analysis has been conducted to confirm the crystallization  
 203 characteristics at 250 °C. An amorphous phase was obtained  
 204 for the 1:1 Ti(OPr)<sub>4</sub>:urea samples while a crystalline anatase  
 205 phase was observed for the standard sample (Supporting  
 206 Information Figure 2).

207 **3.3. Surface Area Measurements.** BET surface area and total  
 208 pore volume are calculated at  $p/p_0 = 0.99$  by the BET method



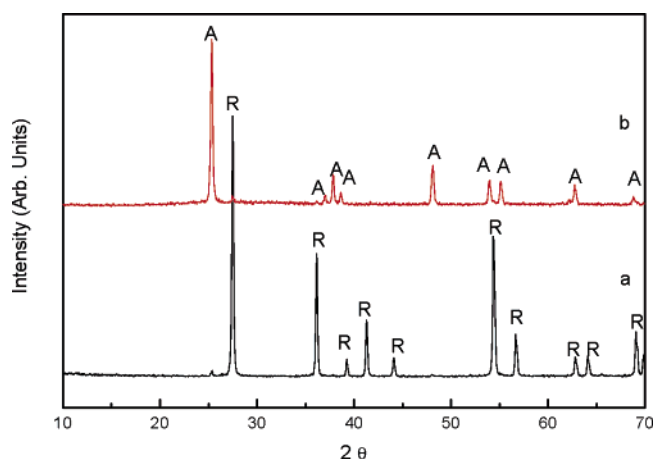
**Figure 3.** Anatase content in the samples calcined at various temperatures.

209 for the samples calcined at 500 °C. The results are shown in  
 210 Table 1. Both isotherms for the standard and urea added samples  
 211 are type IV-like in their behavior (Supporting Information Figure  
 212 3). An earlier report<sup>32</sup> shows that the urea is a good pore forming  
 213 agent so that it will help in the generation of mesoporosity in  
 214 the titania framework. The current study also confirms that the  
 215 addition of urea (1:1) increases the pore diameter to 30 nm  
 216 compared to the 11 nm pore diameter of the standard sample  
 217 (Table 1). BET analysis of the samples calcined at higher  
 218 temperatures showed that the 1:1 Ti(OPr)<sub>4</sub>:urea sample possesses  
 219 a higher surface area (15 m<sup>2</sup>/g) at 800 °C compared to the  
 220 standard sample calcined (5 m<sup>2</sup>/g) at the same temperature. The  
 221 surface area of both the 1:1 Ti(OPr)<sub>4</sub>:urea sample and the  
 222 standard sample at 900 °C showed surface areas of 5 and 4  
 223 m<sup>2</sup>/g, respectively.

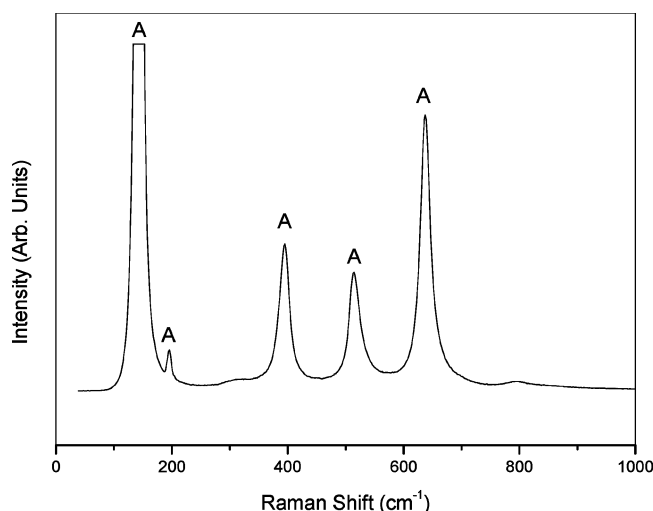
224 **3.4. XRD Analysis.** Titania precursor samples prepared with  
 225 urea indicated a significant rise in transformation temperature of  
 226 anatase to rutile. As the amount of urea increased, the  
 227 transformation temperature is also raised to higher temperatures  
 228 (Figure 3).

229 The weight fraction of the anatase found in the sample was  
 230 calculated by comparing the XRD integrated intensities of (101)  
 231 reflection of anatase and (110) reflection of rutile. All the  
 232 samples heated to 500 °C show only anatase phase (Figure 3).  
 233 The standard sample showed the formation of rutile at a  
 234 temperature as low as 600 °C (the anatase content was calculated  
 235 as 80%). However, all the urea-modified samples except the  
 236 1:0.25 (only 6% rutile; 94% anatase) calcined at 600 °C show  
 237 a complete anatase phase, indicating that a lower percentage of  
 238 urea has little effect on the anatase rutile transformation  
 239 (Supporting Information Figure 4).

240 At 700 °C the standard sample showed rutile as the major  
 241 phase with 12% anatase (Figure 3) while the samples with 1:0.25  
 242 and 1:0.5 Ti(OPr)<sub>4</sub>:urea composition showed the presence of  
 243 40% and 86% anatase, respectively (Supporting Information  
 244 Figure 5). At 800 °C standard (Figures 3 and 4, and Supporting  
 245 Information Figure 6), 1:0.25 and 1:0.5 Ti(OPr)<sub>4</sub>:urea composi-  
 246 tion showed a lower anatase content (0%, 23%, and 27%,  
 247 respectively). A significantly high anatase content (97%) was  
 248 obtained for sample with the highest urea content, i.e., 1:1 Ti-  
 249 (OPr)<sub>4</sub>:urea, up to a temperature of 800 °C (Figures 3 and 4).  
 250 All the samples except a sample with the composition of 1:1  
 251 Ti(OPr)<sub>4</sub>:urea turned to fully rutile at 900 °C. The sample with



**Figure 4.** XRD of the samples calcined at 800 °C (A = anatase; R = rutile) of (a) standard sample and (b) sample prepared by 1:1 Ti(OPr)<sub>4</sub>:urea composition.



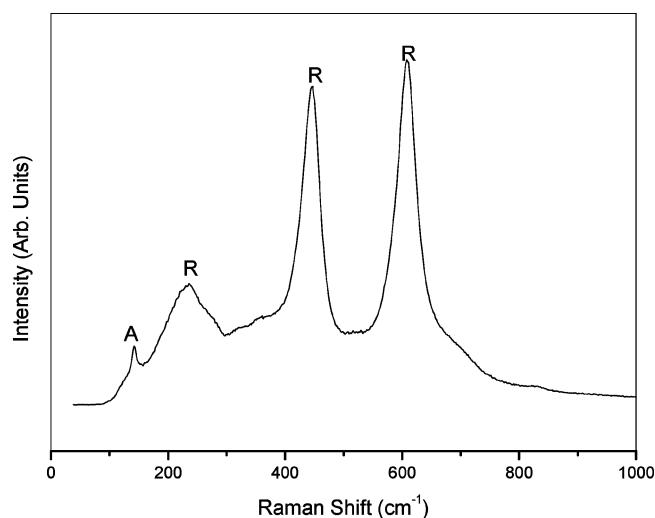
**Figure 5.** Raman spectra of titania sample with 1:1 Ti(OPr)<sub>4</sub>:urea calcined at 800 °C (A = anatase).

a composition of 1:1 Ti(OPr)<sub>4</sub>:urea showed 11% anatase at 900 °C (Supporting Information Figure 7).

XRD studies concluded that the modification by urea 1:1 Ti(OPr)<sub>4</sub>:urea has been effective in increasing the anatase-to-rutile transformation to high temperature.

**3.5. Raman Studies.** Raman spectroscopy was applied as an additional tool to probe the phase formation of standard (Supporting Information Figures 8 and 9) and 1:1 Ti(OPr)<sub>4</sub>:urea titania samples. Figures 5 and 6 show Raman spectra obtained with samples of composition 1:1 Ti(OPr)<sub>4</sub>:urea calcined at 800 and 900 °C. According to factor group analysis the anatase phase consists of six and the rutile phase consists of five Raman active modes (i.e., anatase—144, 197, 399, 513, and 639 cm<sup>-1</sup>; rutile—144, 446, 612, and 827 cm<sup>-1</sup>). Figure 5 shows a strong peak at 197 cm<sup>-1</sup>, which is the characteristic peak of the anatase phase. The peak at 197 cm<sup>-1</sup> appears along with other characteristic rutile phases in Figure 6 indicating the presence of the anatase phase in the 900 °C calcined sample. These two Raman spectra are consistent with the XRD results.

**3.6. X-ray Photoelectron Spectroscopy (XPS).** XPS measurements have been carried out to determine N or C incorporation above 500 °C (Figure 7; Supporting Information Figure 10). The presence of C (ca. 11%) and N (ca. 0.5%) was confirmed in the XPS analysis (Table 2). It was previously reported that the N<sub>1s</sub> peak will show a binding energy value of



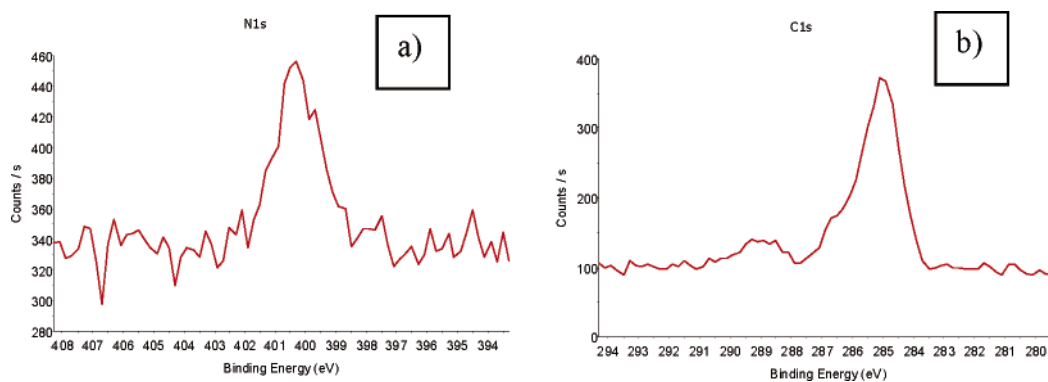
**Figure 6.** Raman spectra of titania sample with 1:1 Ti(OPr)<sub>4</sub>:urea calcined at 900 °C (A = anatase; R = rutile).

400–402 eV and C<sub>1s</sub> will show a binding energy of 281–287 eV.<sup>41</sup> The signal (Figure 7a) observed at 400 eV was explained previously as a result of the molecular chemisorbed nitrogen.<sup>42,43</sup> However, there was no indication of Ti–N bond formation (396 eV).<sup>42</sup>

Three forms of carbon have been identified previously which are surface adsorbed (287.5 eV), solid solution (285 eV), and the carbide Ti–C (281.5 eV).<sup>41</sup> It can be seen from the XPS spectra (Figure 7b) of C<sub>1s</sub> that the majority of the carbon present in the TiO<sub>2</sub> matrix exists as a solid solution (285 eV). A small surface adsorbed carbon peak is found in all the samples even though the intensity of this peak decreases at 800 °C. There is no indication of the formation of any Ti–C phase. Carbon can locate as a solid solution within the tetrahedral and octahedral interstices existing within the anatase crystal.<sup>41</sup>

**3.7. Photocatalytic Studies.** Photocatalytic studies have been carried out by studying the decomposition reaction of rhodamine dye in the presence of standard and the urea modified samples. The urea modified sample 1:1 Ti(OPr)<sub>4</sub>:urea shows more than three times the activity of the unmodified titania. The full decolorization of the rhodamine dye occurred within 50 min in the case of 1:1 Ti(OPr)<sub>4</sub>:urea sample calcined at 900 °C whereas the standard sample takes more than 120 min to complete the degradation process. This enhanced efficiency is reflected in a kinetic analysis of the results. The degradation process, involving hydroxyl radical formation and subsequent degradation of the dye by the hydroxyl radical, obeys pseudo-first-order kinetics. First-order degradation rate constants, obtained by plotting the natural logarithm of the absorbance against irradiation time, are 0.27 ± 0.02 min<sup>-1</sup> for the standard sample and 0.73 ± 0.06 min<sup>-1</sup> for the urea-modified sample. A similar trend is observed with the urea-modified sample calcined at 800 °C, which has more than three times the degradation rate of the standard (Supporting Information Figure 11). An initial lag is also observed with this sample. This lag time was about 10 min for both samples and may be due to a slower adsorption of the dye onto the urea-modified sample. Dark studies, where the above experiments were repeated in the absence of a light source, were studied to eliminate any adsorption effects on the studies. Sample left for up to 24 h showed little change in absorbance. The kinetic plots and the progress of the reactions are shown in Figure 8.

The calcination temperature of the sample affects the catalytic efficiency. Both standard and urea modified samples were


**Figure 7.** XPS plots of 1:1 Ti(OPr)<sub>4</sub>:urea sample calcined at 800 °C: (a) N<sub>1s</sub> and (b) C<sub>1s</sub>.

**TABLE 2: XPS Analysis of the 1:1 Ti(OPr)<sub>4</sub>:Urea Sample Calcined in the Range 500–800 °C**

O <sub>2</sub> sample Ti	C <sub>1s</sub> /at %	O1s/at %	Ti2p/At %	N1s/at %
S1 500 °C	12.2	63.0	24.4	0.4
S2 600 °C	12.5	63.2	23.9	0.5
S3 700 °C	11.3	63.8	24.4	0.5
S4 800 °C	11.1	64.0	24.3	0.5

321 calcined at 500, 600, 700, 800, and 900 °C. For the standard  
 322 samples, the most efficient photocatalyst was found to be the  
 323 sample calcined at 600 °C, whereas for the urea-modified sample  
 324 the most efficient temperature was found to be 900 °C  
 325 (Supporting Information Figure 12 and Table 1).

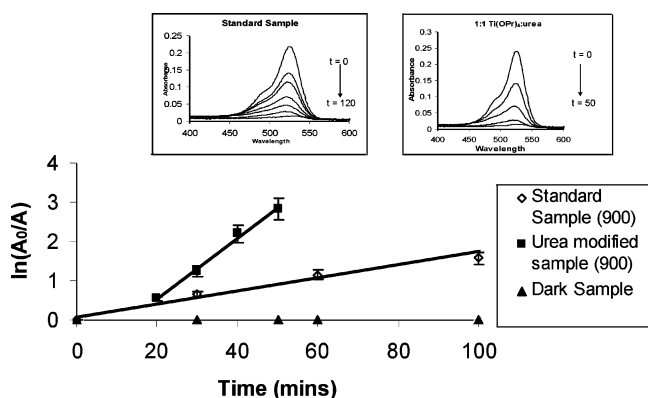
#### 326 4. Discussion

327 Titanium tetraisopropoxide hydrolyzes vigorously with water  
 328 and polycondensates of [Ti(OH)<sub>n</sub>X<sub>m</sub>]<sup>z-</sup> ions are initially formed.  
 329 (When the alkoxide reacts with water the metal ion increases  
 330 its coordination by employing its vacant d-orbitals to accept  
 331 oxygen lone pairs from ligands such as OH groups.) The linkage  
 332 between TiO<sub>6</sub><sup>2-</sup> octahedron is formed by the dehydration  
 333 reaction of [Ti(OH)<sub>n</sub>X<sub>m</sub>]<sup>z-</sup>. It was previously reported that the  
 334 anatase phase has an edge-shared TiO<sub>6</sub><sup>2-</sup> octahedra structure  
 335 while rutile has a corner-shared octahedra.<sup>4</sup> The condensation  
 336 reaction can also be catalyzed in acidic or basic conditions to  
 337 make TiO<sub>6</sub><sup>2-</sup> octahedral from [Ti(OH)<sub>n</sub>X<sub>m</sub>]<sup>z-</sup>. Urea is used here  
 338 to modify the condensation reaction since gel modifiers are  
 339 known to control the pore characteristics.<sup>27</sup> The current investigation  
 340 also showed that a modifier, urea, can extend the anatase

341 formation to higher temperatures without using any metal or  
 342 metal oxide dopants. It was previously proved that the precursor  
 343 processing conditions could influence significantly the high-  
 344 temperature properties of various nanocrystalline metal oxides  
 345 such as ZnO.<sup>44–46</sup> It should also be noted that the high-  
 346 temperature anatase phase stability has been achieved previously  
 347 by using copper sulfate as a dopant precursor.<sup>47</sup> However, when  
 348 a precursor without any metal ions (1:1 Ti(OPr)<sub>4</sub>:H<sub>2</sub>SO<sub>4</sub>) was  
 349 used a major rutile phase was (63%) formed at 800 °C  
 350 (Supporting Information Figure 12).

351 One of the major problems in the preparation of nanocrystalline  
 352 TiO<sub>2</sub> is the fast reactivity of inorganic precursor toward  
 353 hydrolysis and condensation.<sup>48–50</sup> Urea molecules chelated to  
 354 the Ti ions have amino groups with a high electronegativity  
 355 which retard the condensation reactions of titanium isopropoxide  
 356 by altering the reaction pathway.<sup>29</sup> The chelation is evidenced  
 357 from FTIR data which show a strong peak at 1035 cm<sup>-1</sup>  
 358 corresponding to the Ti–O–C bond formed by the interaction  
 359 between the Ti–O inorganic network and the C=O of urea  
 360 (Figure 1). As the urea content is increased the chelation  
 361 becomes stronger and this facilitates a stronger titania gel  
 362 network. This is clearly seen from the FTIR results where the  
 363 band at 1035 cm<sup>-1</sup> is weaker at lower urea concentration and  
 364 increases in intensity with an increase in urea concentration. It  
 365 has been previously reported that a gel network with little  
 366 branching and cross linking with a smaller void region is  
 367 morphologically weak and collapses easily on calcinations.<sup>39</sup>  
 368 Therefore strengthening the gel network with urea assists the  
 369 retention of the anatase phase to higher temperatures. Further-  
 370 more, the uniform distribution of titania precursor molecules  
 371 in a urea-stabilized gel network is considered to have caused  
 372 the reduction in the anatase/anatase contact points that possibly  
 373 reduces the growth process of anatase particles, and this  
 374 subsequently promotes pore growth.<sup>18</sup> Therefore the onset of  
 375 the nucleation process associated with rutile formation is  
 376 delayed.

377 The efficiency of electron–hole formation in a photocatalytic  
 378 reaction is dependent on the band gap and the frequency of  
 379 incident light, and how competitive electron–hole recombination  
 380 is with the parallel electron–oxygen and hole–water reactions.<sup>51–53</sup>  
 381 The anatase phase is found to be a better photocatalyst than  
 382 rutile in spite of the fact that the band gap of rutile (3.0 eV) is  
 383 smaller than that of anatase (3.2 eV). A faster electron–hole  
 384 recombination is feasible in rutile as the recombination prob-  
 385 ability is inversely proportional to the magnitude of the band  
 386 gap.<sup>52</sup> It has also been reported that a mixture of anatase and  
 387 rutile is more photoactive than 100% anatase.<sup>51,52</sup> The com-  
 388 mercial photocatalyst Degussa P-25 consisting of an anatase/  
 389 rutile proportion of 70/30 is more active than pure anatase or  
 390 pure rutile.<sup>51</sup> Various preparation methods of the sample which


**Figure 8.** Kinetic study of standard sample and 1:1 Ti(OPr)<sub>4</sub>:urea calcined sample at 900 °C. A<sub>0</sub> is the initial absorbance and A is the absorbance after a time of the rhodamine dye degradation. (Error bars ±10%.) The best fit for the urea-modified sample is shown excluding the lag time. Inset: Absorption spectra of rhodamine dye degradation, using standard sample (left inset) and sample with 1:1 Ti(OPr)<sub>4</sub>:urea (right inset).

391 result in different crystal structures or surface morphologies were  
 392 also found to produce different recombination lifetimes and  
 393 interfacial electron-transfer rate constants.<sup>53–55</sup> It has been  
 394 observed in the current study that an anatase/rutile proportion of  
 395 11/89 required less than half of the time to degrade rhodamine  
 396 dye compared to the 100% rutile sample. The larger amount of  
 397 the anatase phase is the most likely cause for higher activity of  
 398 the urea-modified sample toward the degradation of the  
 399 rhodamine dye.

## 400 5. Conclusions

401 A method for making the high-temperature stable anatase  
 402 phase without using any complex dopants has been reported.  
 403 Ninety-seven percent anatase phase has been obtained at 800  
 404 °C with use of a 1:1 Ti(OPr)<sub>4</sub>:urea composition and 11% of  
 405 anatase is retained even after calcining at 900 °C. The current  
 406 technique is, therefore, found to be effective in extending the  
 407 anatase-to-rutile phase transformation by at least 200 °C  
 408 compared to the standard samples. A significantly higher  
 409 photoactivity has been achieved for sample modified using urea,  
 410 calcined at 900 °C compared to the sample prepared without  
 411 using urea calcined under similar conditions. Kinetic analysis  
 412 shows that for the urea-modified sample at 900 °C, the  
 413 decomposition rate of rhodamine 6G is almost three times faster  
 414 due to the presence of the anatase phase at this temperature.  
 415 This methodology is therefore suitable for the high-temperature  
 416 photocatalytic application in building materials (e.g., ceramics,  
 417 glass, and bricks).<sup>21</sup> A high-temperature stable anatase phase,  
 418 good photocatalytic activity, and simplicity of processing are  
 419 the main advantages of this method. The characterization of  
 420 the materials has been supported by XRD, XPS, DSC, Raman,  
 421 FTIR, and surface area analysis. The investigation confirmed  
 422 the use of urea as a potential candidate, both as a pore-forming  
 423 agent to create mesoporosity in titania and also to obtain the  
 424 high-temperature stabilized anatase phase. This approach is very  
 425 effective and significant to a considerable extent in dispensing  
 426 with the conventional use of metal oxide dopants to retain the  
 427 anatase phase at high temperatures. The transformation tem-  
 428 perature is expected to increase at a much higher temperature  
 429 with the simultaneous use of precursor modification and metal  
 430 oxide dopant addition. More studies are underway in this  
 431 direction.

432 **Acknowledgment.** This work has been carried out as part  
 433 of the innovation partnership between NTERA Ltd. and Dublin  
 434 Institute of Technology. The authors gratefully acknowledge  
 435 the financial support of Enterprise Ireland and NTERA Ltd.,  
 436 Dublin, Ireland. P.P. and R.G. thank R&D Strand I award 2005.  
 437 The authors thank Dr. Anthony Betts for his valuable comments.

438 **Supporting Information Available:** Tables five BET  
 439 surface area analysis and XPS analysis of Ti(OPr)<sub>4</sub>:urea and  
 440 figures giving FTIR spectra, Raman spectra, XPS plots and  
 441 XRD. This material is available free of charge via the Internet  
 442 at <http://pubs.acs.org>.

## 443 References and Notes

444 (1) Gratzel, M. *Nature* **2001**, *414*, 338.  
 445 (2) Hagfeldt, A.; Gratzel, M. *Chem. Rev.* **1995**, *95*, 49.  
 446 (3) Mills, A.; Lee, S. K. *J. Photochem. Photobiol., A* **2002**, *152*, 233.  
 447 (4) Gopal, M.; Chan, W. J. M.; Jonghe, L. C. D. *J. Mater. Sci.* **1997**,  
 448 *32*, 6001.  
 449 (5) *Encyclopedia of Chemical Technology*; Mark, H. F., Othmer, D. F.,  
 450 Overberger, C. G., Seaberg, G. T., Eds.; John Wiley: New York, 1983;  
 451 Vol. 23, p 139.

(6) Weast, R. C. *Handbook of Chemistry and Physics*; CRC Press: 452  
 Boca Raton, FL, 1984; p B-154.  
 (7) Kostov, I. *Minerology*, 3rd ed.; Nauka, Izkustia, Sofia, 1973. 453  
 (8) Yang, S. W.; Gao, L. *J. Am. Ceram. Soc.* **2005**, *88*, 968. 454  
 (9) (a) Karakitsou, K. E.; Verykios, X. E. *J. Phys. Chem.* **1993**, *97*, 455  
 1184. (b) McLoughlin, O. A.; Kehoe, S. C.; McGuigan, K. G.; Duffy, E. 456  
 F.; Touati, F. A.; Gernjak, W.; Alberola, I. O.; Rodriguez, S. M.; Gill, L. 457  
 W. *Solar Energy* **2004**, *77*, 657. 458  
 (10) (a) Addamo, M.; Augugliaro, V.; Paola, D. A.; Lopez, G. E.; Loddò, 459  
 V.; Marci, G.; Molinari, R.; Palmisano, L.; Schiavello, M. *J. Phys. Chem.* 460  
*B* **2004**, *108*, 3303. (b) Lonnen, J.; Kilvington, S.; Kehoe, S. C.; Touati, F. 461  
 A.; McGuigan, K. G. *Water Res.* **2005**, *39*, 877. 462  
 (11) Hu, C.; Lan, Y.; Hu, X.; Wang, A. *J. Phys. Chem. B* **2006**, *110*, 463  
 4066. 464  
 (12) Sakatani, Y.; Grosso, D.; Nicole, L.; Boissiere, C.; Illia, S.; Sanchez, 465  
 C. *J. Mater. Chem.* **2006**, *16*, 77. 466  
 (13) Fujishima, A.; Rao, T. N.; Tryk, D. A. *J. Photochem. Photobiol.,* 467  
*C* **2001**, *1*, 1. 468  
 (14) Parkin, I. P.; Palgrave, R. G. *J. Mater. Chem.* **2005**, *15*, 1689. 469  
 (15) Mills, A.; Lee, S. K. *J. Photochem. Photobiol., A* **2006**, *182*, 470  
 181. 471  
 (16) Zzanderna, A. W.; Rao, C. N. R.; Honig, J. M. *Trans. Faraday* 472  
*Soc.* **1958**, *54*, 1069. 473  
 (17) Yoganarasimhan, S. R.; Rao, C. N. R. *Trans. Faraday Soc.* **1962**, 474  
*58*, 1579. 475  
 (18) Kumar, S. R.; Pillai, S. C.; Hareesh, U. S.; Mukundan, P.; Warri- 476  
 er, K. G. *Mater. Lett.* **2000**, *43*, 286. 477  
 (19) Reidy, D. J.; Holmes, J. D.; Morris, M. A. *J. Eur. Ceram. Soc.* 478  
**2006**, *26*, 1527. 479  
 (20) Navrotsky, A.; Kleppla, O. J. *J. Am. Ceram. Soc.* **1967**, *50*, 480  
 626. 481  
 (21) Machida, M.; Norimoto, W. K.; Kimura, T. *J. Am. Ceram. Soc.* 482  
**2005**, *88*, 95. 483  
 (22) Rao, C. N. R.; Turner, A.; Hanig, J. M. *J. Phys. Chem.* **1959**, *11*, 484  
 173. 485  
 (23) Ranjit, K. T.; Willner, I.; Bossmann, S. H.; Braun, A. M. *Environ.* 486  
*Sci. Technol.* **2001**, *35*, 154. 487  
 (24) Reidy, D. J.; Holmes, J. D.; Nagle, C.; Morris, M. A. *J. Mater.* 488  
*Chem.* **2005**, *15*, 3494. 489  
 (25) Kumar, K. N. P.; Kiezer, K.; Burggraaf, A. *J. Mater. Chem.* **1993**, 490  
*3*, 141. 491  
 (26) Baiju, K. V.; Sibin, C. P.; Rajesh, K.; Pillai, P. K.; Mukundan, P.; 492  
 Warri- 493  
 er, K. G. K.; Wunderlich, W. *Mater. Chem. Phys.* **2005**, *90*, 123. 494  
 (27) Suresh, C.; Biju, V.; Mukundan, P.; Warri- 495  
 er, K. G. K. *Polyhedron* 496  
**1998**, *17*, 3131. 497  
 (28) Khimich, N. N.; Venzel, B. I.; Drozdova, I. A.; Koptelova, L. A. 498  
*Russ. J. Appl. Chem.* **2002**, *75*, 1108. 499  
 (29) Cheng, P.; Qiu, J.; Gu, M.; Shangguan, W. *Mater. Lett.* **2004**, *58*, 500  
 3751. 501  
 (30) Yuan, J.; Chen, M.; Shi, J.; Shangguan, W. *Int. J. Hydrogen Energy* 502  
**2006**, *31*, 1326. 503  
 (31) Yin, S.; Ihara, K.; Aita, Y.; Komatsu, M.; Sato, T. *J. Photochem.* 504  
*Photobiol., A* **2006**, *179*, 105. 505  
 (32) Zheng, J. Y.; Pang, J. B.; Qiu, K. Y.; Wei, Y. *Microporous* 506  
*Mesoporous Mater.* **2001**, *49*, 189. 507  
 (33) Bakardjieva, S.; Subrt, J.; Stengl, V.; Dianez, M. J.; Dianez, M. J. 508  
 S.; Sayagues, M. J. *Appl. Catal., B* **2005**, *58*, 193. 509  
 (34) Yin, S.; Aita, Y.; Komatsu, M.; Sato, T. *J. Eur. Ceram. Soc.* **2006**, 510  
*26*, 2735. 511  
 (35) Sakthivel, S.; Janczarek, M.; Kisch, H. *J. Phys. Chem. B* **2004**, 512  
*108*, 19384. 513  
 (36) Yates, H. M.; Nolan, M. G.; Sheel, D. W.; Pemble, M. E. *J.* 514  
*Photochem. Photobiol., A* **2006**, *179*, 213. 515  
 (37) Yamamoto, Y.; Moribe, S.; Ikoma, T.; Akiyama, K.; Zhang, Q.; 516  
 Saito, F.; Kubota, S. T. *Mol. Phys.* **2006**, *104*, 1733. 517  
 (38) Spurr, R. A.; Myers, H. *Anal. Chem.* **1957**, *29*, 760. 518  
 (39) Kung, H. H.; Ko, E. I. *Chem. Eng. J.* **1996**, *64*, 203. 519  
 (40) Ren, L.; Huang, X.; Sun, F.; He, X. *Mater. Lett.* DOI: 10.1016/ 520  
 j.matlet.2006.04.097. 521  
 (41) Shi, Z. M.; Ye, X. Y.; Liang, K. M.; Gu, S. R.; Pan, F. *J. Mater.* 522  
*Sci.* **2003**, *22*, 1255. 523  
 (42) Irie, H.; Watanabe, Y.; Hashimoto, K. *J. Phys. Chem. B* **2003**, *107*, 524  
 5483. 525  
 (43) Cheng, X.; Lou, Y.; Samia, A. C. S.; Burda, C.; Gole, J. L. *Adv.* 526  
*Funt. Mater.* **2005**, *15*, 41. 527  
 (44) Pillai, S. C.; Kelly, J. M.; McCormack, D. E.; Ramesh, R. *J. Mater.* 528  
*Chem.* **2004**, *14*, 1572. 529  
 (45) Pillai, S. C.; Kelly, J. M.; McCormack, D. E.; O'Brien, P.; Ramesh, 530  
 R. *J. Mater. Chem.* **2003**, *13*, 2586. 531  
 (46) Pillai, S. C.; Kelly, J. M.; McCormack, D. E.; Ramesh, R. *Mater.* 532  
*Sci. Technol.* **2004**, *20*, 964. 533  
 (47) Bokhimi, X.; Morales, A.; Novaro, O.; López, T.; Chimal, O.; 534  
 Asomoza, M.; Gómez, R. *Chem. Mater.* **1997**, *9*, 2616. 535



- 535 (48) Pillai, S. C.; Boland, S. W.; Haile, S. M. *J. Am. Ceram. Soc.* **2004**,  
536 87, 1388.  
537 (49) Boland, S. W.; Pillai, S. C.; Yang, W. D.; Haile, S. M. *J. Mater.*  
538 *Res.* **2004**, 19, 1492.  
539 (50) Sibin, C. P.; Kumar, S. R.; Mukundan, P.; Warriar, K. G. K. *Chem.*  
540 *Mater.* **2002**, 14, 2876.  
541 (51) (a) Abe, R.; Sayama, K.; Domen, K.; Arakawa, H. *Chem. Phys.*  
542 *Lett.* **2001**, 344, 339. (b) Carp, O.; Huisman, C. L.; Reller, A. *Prog. Solid*  
543 *State Chem.* **2004**, 32, 33.
- (52) Gandhe, A. R.; Naik, S. P.; Fernandes, J. B. *Microporous Mesopo-* 544  
*rous Mater.* **2005**, 87, 103. 545
- (53) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. 546  
*Chem. Rev.* **1995**, 95, 69. 547
- (54) Acosta, D. R.; Martinez, A. I.; Lopez, A. A.; Magana, C. R. *J.* 548  
*Mol. Catal. A: Chem.* **2005**, 228, 183. 549
- (55) Baiju, K. V.; Periyat, P.; Pillai, P. K.; Mukundan, P.; Warriar, K. 550  
G. K.; Wunderlich, W. *Mater. Lett.* DOI: 10.1016/j.matlet.2006.07.124. 551