

# Preparation of water-dispersible TiO<sub>2</sub> nanoparticles from titanium tetrachloride using urea hydrogen peroxide as an oxygen donor†

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TiO<sub>2</sub> nanoparticles were prepared from titanium tetrachloride (TiCl<sub>4</sub>) in CH<sub>2</sub>Cl<sub>2</sub> at 80 °C for 30 h, 42 h and 70 h using urea hydrogen peroxide (UHP) as an oxygen donor with a TiCl<sub>4</sub>:UHP molar ratio of 1:2. The XRD patterns and Raman spectroscopy results showed that the products consisted of anatase TiO<sub>2</sub>. IR and solid-state <sup>13</sup>C NMR with cross polarization and magic angle spinning techniques revealed the presence of urea. TEM observation revealed that the products prepared by the reactions for 30 and 42 h consisted of water-dispersible spheroid nanoparticles with a long axis of ~5 nm, while an aggregation of nanoparticles was evident upon reaction for 70 h. Thermogravimetry, inductively-coupled plasma emission spectrometry and CHN analysis showed that the amount of urea increases in the following order: TiO<sub>2</sub>\_42h, TiO<sub>2</sub>\_70h, TiO<sub>2</sub>\_30h. The photocatalytic activity of the products dispersible in water (TiO<sub>2</sub>\_30h and TiO<sub>2</sub>\_42h) was estimated based on the degradation behaviour of methylene blue, and TiO<sub>2</sub>\_42h showed higher photocatalytic activity than TiO<sub>2</sub>\_30h. It is proposed that TiCl<sub>4</sub> was directly oxidized by UHP to form anatase TiO<sub>2</sub> in the early stage of the process.

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## Introduction

Nanochemistry has been developed for the preparation of nanostructures, which are of particular interest because of their interesting chemical, physical and biological behaviour.<sup>1</sup> Among nanostructures, nanoparticles (NPs) are attracting considerable attention since they can exhibit properties superior to those of large particles based on their large surface areas and quantum effect.<sup>2</sup> So far, a variety of applications have been developed using many kinds of NPs.<sup>3</sup> Titania (TiO<sub>2</sub>) is an attractive functional oxide since it exhibits interesting photochemical and optical properties, including photocatalytic activity and high refractive indices.<sup>4,5</sup> The preparation of TiO<sub>2</sub> NPs has consequently been achieved with many different techniques, such as hydrolytic

sol-gel, hydrothermal/solvothermal synthesis, and electrochemical deposition.<sup>6–8</sup>

Among the various preparation techniques for TiO<sub>2</sub> NPs, a non-hydrolytic sol-gel process has been employed for the preparation of TiO<sub>2</sub> NPs.<sup>9–12</sup> Titanium tetrahalides, typically titanium tetrachloride (TiCl<sub>4</sub>), have been utilized in this process. TiCl<sub>4</sub> was reacted with an oxygen donor, such as diisopropylether, or a titanium alkoxide, typically titanium tetraisopropoxide.<sup>13,14</sup> Since these reactions were conducted in organic solvents without the presence of H<sub>2</sub>O (which can also act as an oxygen donor), one of the advantages of this non-hydrolytic sol-gel process is the ability to control the amount of oxygen in the entire process, and this kind of control is extremely attractive for the size control of TiO<sub>2</sub> NPs.<sup>9,11</sup>

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), another oxygen donor, has been utilized in the preparation of limited types of metal oxides, such as ZnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>.<sup>15–18</sup> H<sub>2</sub>O<sub>2</sub> has also been utilized as a ligand in Ti complexes, and the resulting complexes can be water-soluble precursors for TiO<sub>2</sub>.<sup>19–23</sup> H<sub>2</sub>O<sub>2</sub> has also been utilized as an oxidizing reagent in organic synthesis.<sup>24–26</sup> H<sub>2</sub>O<sub>2</sub> is available only as aqueous solutions, which limits its usage in organic synthesis to a large extent. Urea-hydrogen peroxide (UHP; CO(NH<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O<sub>2</sub>) is a 1:1 adduct between urea and hydrogen peroxide.<sup>27</sup> It can be prepared easily from an aqueous solution of urea and H<sub>2</sub>O<sub>2</sub>, and it is also inexpensive and commercially available.<sup>28,29</sup> Since UHP is soluble in some organic solvents, such as

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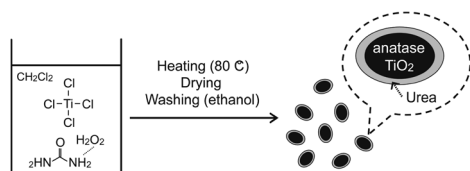
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**Fig. 1** Overview of the preparation of the water-dispersible anatase  $\text{TiO}_2$  nanoparticles.

alcohols and chloroform,<sup>29</sup> UHP has been utilized for oxidation reactions such as epoxidation and sulfide oxidation.<sup>29,30</sup>

Here, we report the first application of UHP for metal oxide preparation. UHP can possibly play multiple roles, as an oxidation reagent as well as a donor of water which can cause hydrolysis, and urea which can coordinate to Lewis acid sites. In the present study,  $\text{TiO}_2$  NPs have been prepared by a reaction of  $\text{TiCl}_4$  with UHP in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). The resulting products consist of water-dispersible  $\text{TiO}_2$  spheroid NPs with a long axis of ~5 nm. An overview of the preparation of water-dispersible anatase  $\text{TiO}_2$  NPs using UHP is illustrated in Fig. 1.

## Experimental

### General information

X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT-2500 diffractometer (Ni-filtered  $\text{CuK}\alpha$  radiation). Raman spectra were obtained with a Renishaw in Via Reflex spectrometer using a 532 nm laser. Infrared (IR) spectra were recorded on a JASCO FT/IR-460 Plus spectrometer using the KBr method. Samples were dried under reduced pressure before preparing KBr disks. Solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy was performed with a JEOL ECX-400 spectrometer at 99.55 MHz. Solid-state  $^{13}\text{C}$  NMR spectra were obtained with cross-polarization (CP) and magic angle spinning (MAS) techniques (pulse delay, 10 s; contact time, 5 ms; spinning rate, 8 kHz). Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-1011 microscope operating at 100 kV. TEM samples were prepared by evaporating a diluted aqueous dispersion of  $\text{TiO}_2$  NPs on carbon supported on a copper mesh TEM grid. Field-emission transmission electron microscopy (FE-TEM) images were obtained with a Hitachi HF-2200 microscope operating at 100 kV. The Brunauer–Emmett–Teller (BET) specific surface areas of the products were determined by the  $\text{N}_2$  adsorption–desorption method at  $-196^\circ\text{C}$  with a BELSORP-mini II instrument and preliminary drying at  $150^\circ\text{C}$  for 1 h. Thermogravimetry (TG) was performed with a Rigaku TG8120 Thermoplus EVO thermobalance in the range of 50 to  $1000^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$  under a nitrogen flow. Inductively coupled plasma (ICP) emission spectrometry was performed with a Varian Vista-MPX CCD Simultaneous ICP-OES instrument after dissolving the products (1.2 mg) in 12 mL of a mixed solution (prepared from 80 mL of  $\text{H}_2\text{SO}_4$  and 27 g of  $\text{SO}_4(\text{NH}_4)_2$ ) at  $150^\circ\text{C}$ . Elemental analysis (CHN) was performed with a

Perkin Elmer PE2400II instrument. Ion chromatography (IC) was performed with a Japan Dionex ICS-90 instrument after dissolving 5 mg of the product in 0.2 mL of  $\text{H}_2\text{SO}_4$  and subsequently diluting to 100 mL.  $\text{Cl}_2$  gas was detected with Gastec Passive Dositive No. 8D. The average concentration of  $\text{Cl}_2$  after 20 h was obtained by opening the autoclaves in a glovebag filled with nitrogen. Ultraviolet-visible (UV-Vis) spectra were obtained with Jasco V-630 and Shimadzu PC-2400 spectrometers.

### Materials

The  $\text{TiO}_2$  NPs were prepared using UHP (97%,  $\text{H}_2\text{O}_2$  35%, Aldrich) as an oxygen donor,  $\text{TiCl}_4$  (1.0 M, in dichloromethane) as the Ti source, and  $\text{CH}_2\text{Cl}_2$  as a solvent.  $\text{CH}_2\text{Cl}_2$  was distilled over  $\text{CaH}_2$ . Ethanol was used as a washing solvent without further purification. Urea,  $\text{CO}(\text{NH}_2)_2$  (99.0%), and aqueous hydrogen peroxide,  $\text{H}_2\text{O}_2$  (30.0%), were used in control experiments without further purification. Methylene blue was used for the measurements of the photocatalytic activity. Sulfuric acid ( $\text{H}_2\text{SO}_4$ , >96%) and  $\text{SO}_4(\text{NH}_4)_2$  (99.5%) were used without further purification.

### Preparation of the $\text{TiO}_2$ nanoparticles using UHP

All manipulations conducted before sealing the autoclave were carried out in a glovebox filled with nitrogen. The reaction was performed in a 20 mL Teflon-lined stainless autoclave. A  $\text{CH}_2\text{Cl}_2$  solution of  $\text{TiCl}_4$  (6.50 mL, corresponding to 6.50 mmol  $\text{TiCl}_4$ ) was added to UHP (1.22 g, 13.0 mmol) in the autoclaves ( $\text{TiCl}_4$ :UHP molar ratio of 1:2). The autoclave was then sealed following the addition of  $\text{CH}_2\text{Cl}_2$  (10.0 mL) to the mixture in the autoclave. The autoclave was heated in an oven at  $80^\circ\text{C}$  for 20, 30, 42, and 70 h. The resultant white solids were centrifuged, washed twice with ethanol, and dried under reduced pressure at ambient temperature. The 70 h product was washed four times. The products were labelled  $\text{TiO}_{2-x}\text{h}$ , where  $x$  is the reaction period.

### Photocatalytic activity of the $\text{TiO}_2$ nanoparticles dispersed in water

The photocatalytic activity of the products was evaluated by degrading methylene blue in an aqueous solution.  $\text{TiO}_{2-30\text{h}}$  or  $\text{TiO}_{2-42\text{h}}$  was dispersed in water (0.5 mass%) to obtain a highly transparent dispersion. The aqueous  $\text{TiO}_2$  dispersion, methylene blue and deionized water were then mixed. The mixture contained 0.0100 mass%  $\text{TiO}_2$  and 0.0100 mmol  $\text{L}^{-1}$  methylene blue. The mixture was transferred to a cylindrical glass beaker (inside diameter: 55.3 mm and height: 59.6 mm). Before the photocatalytic activity measurements, the aqueous  $\text{TiO}_2$  dispersion was sonicated for 10 min. The aqueous  $\text{TiO}_2$  dispersion was stirred continuously in an ice bath under a BLB lamp (FL15 BLB, TOSHIBA) ( $0.50\text{ mW cm}^{-2}$  at 365 nm). The maximum absorbance (664.5 nm) of methylene blue was measured after 15, 30, 45, 60, 90, 120, 150, and 180 min with a UV-Vis spectrometer.



### Control experiments: preparation of the TiO<sub>2</sub> nanoparticles without using UHP

Control experiments were conducted without using UHP. All manipulations conducted before sealing the autoclave were carried out in a glovebag filled with nitrogen.

TiCl<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O-urea-CH<sub>2</sub>Cl<sub>2</sub> system (TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>-urea): a CH<sub>2</sub>Cl<sub>2</sub> solution of TiCl<sub>4</sub> (6.50 mL, corresponding to 6.50 mmol TiCl<sub>4</sub>) was added to 30% aqueous H<sub>2</sub>O<sub>2</sub> (1.47 mL, 13.0 mmol H<sub>2</sub>O<sub>2</sub>) and urea (0.781 g, 13.0 mmol) in an autoclave (TiCl<sub>4</sub>:urea:H<sub>2</sub>O<sub>2</sub>:water = 1:2:2:9 in a molar ratio). The autoclave was then sealed following the addition of CH<sub>2</sub>Cl<sub>2</sub> (10.0 mL) to the mixture in the autoclave.

TiCl<sub>4</sub>-H<sub>2</sub>O-urea-CH<sub>2</sub>Cl<sub>2</sub> system (TiO<sub>2</sub>-water-urea): a CH<sub>2</sub>Cl<sub>2</sub> solution of TiCl<sub>4</sub> (6.50 mL, corresponding to 6.50 mmol TiCl<sub>4</sub>) was added to water (1.47 mL, 57.2 mmol) and urea (0.781 g, 13.0 mmol) in an autoclave (TiCl<sub>4</sub>:urea:water = 1:2:13 in a molar ratio). The autoclave was then sealed following the addition of CH<sub>2</sub>Cl<sub>2</sub> (10.0 mL) to the mixture in the autoclave.

TiCl<sub>4</sub>-H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O-CH<sub>2</sub>Cl<sub>2</sub> system (TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>): a CH<sub>2</sub>Cl<sub>2</sub> solution of TiCl<sub>4</sub> (6.50 mL, corresponding to 6.50 mmol TiCl<sub>4</sub>) was added to 30% aqueous H<sub>2</sub>O<sub>2</sub> (1.47 mL, 13.0 mmol H<sub>2</sub>O<sub>2</sub>) in an autoclave (TiCl<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:water = 1:2:9 in a molar ratio). The autoclave was then sealed following the addition of CH<sub>2</sub>Cl<sub>2</sub> (10.0 mL) to the mixture in the autoclave.

These autoclaves were heated in an oven at 80 °C for 30 h. The resultant solids were centrifuged, washed twice with ethanol, and dried under reduced pressure at ambient temperature.

## Results and discussion

### Preparation of the TiO<sub>2</sub> nanoparticles using UHP

White smoke was formed when the autoclave used for the preparation of TiO<sub>2</sub>-20h was opened, a result showing that TiCl<sub>4</sub> did not react completely and that a considerable number of Ti-Cl bonds remained upon reaction for 20 h. TiO<sub>2</sub>-30h, TiO<sub>2</sub>-42h and TiO<sub>2</sub>-70h were obtained as mixtures of transparent liquids and white solids, on the other hand, and fine white powders were obtained after these products were washed and dried. Thus, the characterization results of TiO<sub>2</sub>-30h, TiO<sub>2</sub>-42h and TiO<sub>2</sub>-70h are described hereafter. The Ti-based yields of TiO<sub>2</sub>-30h, TiO<sub>2</sub>-42h and TiO<sub>2</sub>-70h were 77, 71, and 77%, respectively.

Fig. 2 shows the XRD patterns of the products. TiO<sub>2</sub>-30h, TiO<sub>2</sub>-42h and TiO<sub>2</sub>-70h correspond to anatase TiO<sub>2</sub> (JCPDS no. 21-1272). It should be noted that the XRD profile does not change with variations in the reaction time. The XRD pattern of TiO<sub>2</sub>-70h also showed the presence of NH<sub>4</sub>Cl (JCPDS no. 7-8), however, when TiO<sub>2</sub>-70h was washed twice with ethanol (Fig. S1, ESI<sup>†</sup>), and TiO<sub>2</sub>-70h was thus washed four times. It should be noted that NH<sub>4</sub>Cl was also detected in unwashed TiO<sub>2</sub>-30h and TiO<sub>2</sub>-42h. NH<sub>4</sub>Cl seems to be formed from NH<sub>3</sub> and HCl because of the hydrolysis of urea and TiCl<sub>4</sub>.<sup>31,32</sup> The crystallite size of TiO<sub>2</sub>-30h, TiO<sub>2</sub>-42h and TiO<sub>2</sub>-70h calculated from the (101) reflections using

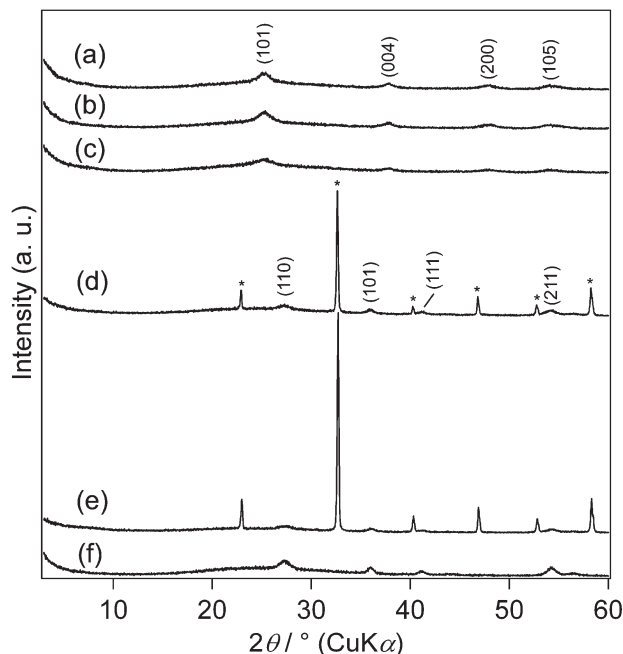


Fig. 2 XRD patterns of (a) TiO<sub>2</sub>-30h, (b) TiO<sub>2</sub>-42h, (c) TiO<sub>2</sub>-70h, (d) TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>-urea, (e) TiO<sub>2</sub>-water-urea and (f) TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> (\*: NH<sub>4</sub>Cl).

Scherrer's formula<sup>33</sup> were 8.7, 8.9 and 8.3 nm, respectively. These results demonstrate that the crystalline phase and particle size of these products remained unchanged, regardless of the reaction time.

The products were further characterized by Raman spectroscopy (Fig. 3). The Raman spectrum of TiO<sub>2</sub>-30h shows bands at 154.4, 398.9, 514.6 and 639.7 cm<sup>-1</sup>. Bands at 153.1, 399.2, 513.4 and 640.0 cm<sup>-1</sup> are present in the Raman

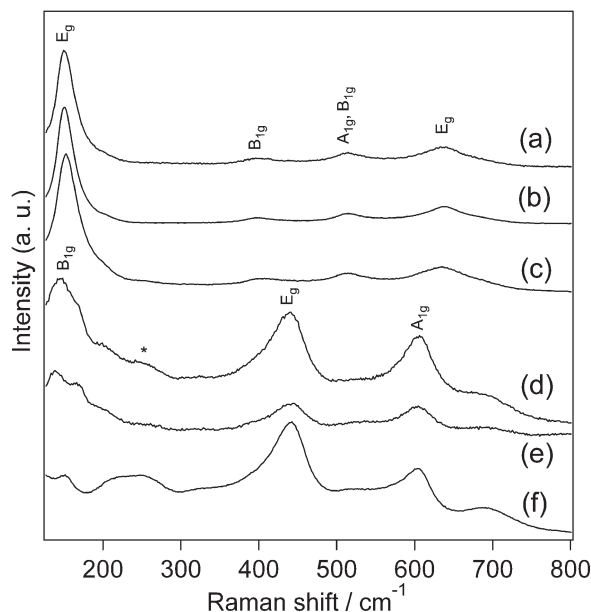


Fig. 3 Raman spectra of (a) TiO<sub>2</sub>-30h, (b) TiO<sub>2</sub>-42h, (c) TiO<sub>2</sub>-70h, (d) TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>-urea, (e) TiO<sub>2</sub>-water-urea and (f) TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> (\*: two phonon scattering).



spectrum of TiO<sub>2</sub>\_42h. The Raman spectrum of TiO<sub>2</sub>\_70h exhibits bands at 153.1, 399.2, 513.4 and 640.0 cm<sup>-1</sup>. These bands are assignable to anatase TiO<sub>2</sub>,<sup>34</sup> as shown in Fig. 3. Thus, the Raman results are in accordance with the XRD observations. It was reported that the Raman shifts of the strongest *E<sub>g</sub>* band near 154 cm<sup>-1</sup> was sensitive to the particle size of TiO<sub>2</sub> NPs, and the variations in the *E<sub>g</sub>* band positions have been discussed in terms of phonon confinement,<sup>34,35</sup> oxygen deficiency,<sup>36,37</sup> and internal stress/surface tension effects.<sup>38,39</sup> Thus, the Raman results are consistent with the formation of anatase TiO<sub>2</sub> NPs.

Fig. 4 shows the IR spectra of the products and UHP. The O–O stretching band at 871 cm<sup>-1</sup><sup>21</sup> of UHP disappears in all the spectra of the products, indicating that UHP did not remain as a solid. Broad bands between 950–700 and 600–400 cm<sup>-1</sup>, characteristic of the Ti–O stretching modes,<sup>40</sup> are present in the spectra of all the products, which is consistent with TiO<sub>2</sub> formation. In addition, bands assignable to urea are observed at ~3420 [br, *v<sub>as</sub>*(NH<sub>2</sub>)], ~3230 [br, *v<sub>s</sub>*(NH<sub>2</sub>)], 1640 [*v*(CO), *ρ*(NH<sub>2</sub>)], 1561–1562 (the assignment of this band will be discussed in the following paragraph), 1399–1401 [*v*(CN)], and 1154–1156 [*ρ*(NH<sub>2</sub>)] in the spectra of TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h.<sup>41</sup> In addition, the <sup>13</sup>C CP/MAS NMR spectrum of TiO<sub>2</sub>\_30h exhibits a signal that is assignable to urea at 163 ppm<sup>42</sup> (Fig. S2, ESI†).

The adsorption of urea on anatase TiO<sub>2</sub> surfaces has been investigated using IR. It was reported that urea molecules adsorbed on anatase TiO<sub>2</sub> surfaces exhibited characteristic bands at 1562–1552 cm<sup>-1</sup>, and based on the IR results, coordination of one of two nitrogen atoms in the urea molecule to the anatase TiO<sub>2</sub> surface was proposed.<sup>43</sup> IR spectra simulated for similar coordination arrangements as well as those

of urea adsorbed on anatase TiO<sub>2</sub> surfaces *via* the vapour phase were reported, and similar bands were present.<sup>44</sup> Thus, the presence of the bands at 1561–1562 cm<sup>-1</sup> strongly suggests a similar interaction between urea and the anatase TiO<sub>2</sub> surfaces in the present study, and the bands are accordingly assigned to the *v<sub>as</sub>*(Ti–OCN–Ti) mode.

Further structural characterization of the products was carried out using TEM and FE-TEM. Fig. 5 shows the TEM and FE-TEM images of TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h. The TEM images of TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h show aggregated spheroid TiO<sub>2</sub> NPs in aggregation sizes of about 10, 10–25 and 25–100 nm, respectively. In addition, the FE-TEM images of the products show the formation of spheroid NPs with a long axis of ~5 nm. This particle size is close to the crystallite size values estimated by Scherrer's formula. Thus, spheroid NPs with a long axis of ~5 nm tend to aggregate with an increase in reaction time. The lattice fringe, with a spacing of 0.35 nm, corresponds to the spacing of the (101) planes of anatase TiO<sub>2</sub>. It was reported that amines acted as shape controllers to yield spheroid NPs by their specific adsorption to the crystal planes parallel to the *c*-axis of TiO<sub>2</sub> NPs.<sup>45,46</sup> Since the IR results suggest that the NH<sub>2</sub> groups of urea interacted with anatase TiO<sub>2</sub>, spheroid NPs are also likely to be obtained in the present study because of urea adsorption on TiO<sub>2</sub> NPs.

The specific surface areas were estimated by the BET method (*S<sub>BET</sub>*). Fig. S3 in the ESI† shows nitrogen adsorption–desorption isotherms of TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h, and TiO<sub>2</sub>\_70h. The *S<sub>BET</sub>* values of TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h were 231, 281, 247 m<sup>2</sup> g<sup>-1</sup>, respectively.

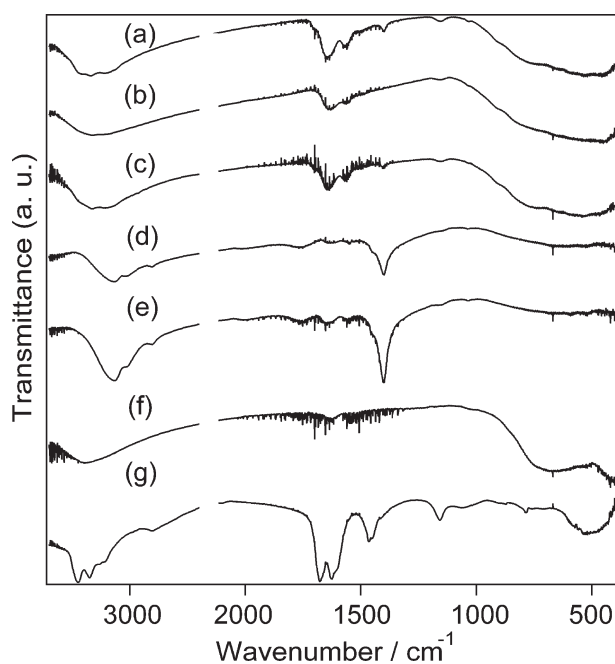


Fig. 4 IR spectra of (a) TiO<sub>2</sub>\_30h, (b) TiO<sub>2</sub>\_42h, (c) TiO<sub>2</sub>\_70h, (d) TiO<sub>2</sub>·H<sub>2</sub>O<sub>2</sub>·urea, (e) TiO<sub>2</sub>·water·urea, (f) TiO<sub>2</sub>·H<sub>2</sub>O<sub>2</sub> and (g) UHP.

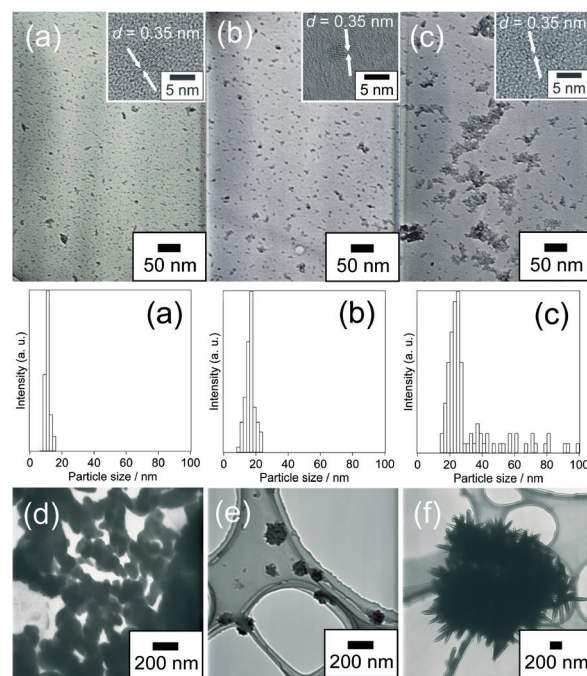


Fig. 5 TEM and FE-TEM images of (a) TiO<sub>2</sub>\_30h, (b) TiO<sub>2</sub>\_42h, (c) TiO<sub>2</sub>\_70h, (d) TiO<sub>2</sub>·H<sub>2</sub>O<sub>2</sub>·urea, (e) TiO<sub>2</sub>·water·urea, (f) TiO<sub>2</sub>·H<sub>2</sub>O<sub>2</sub> and size distributions are shown for (a)–(c).





Fig. S4 in the ESI† shows the TG curves of the products. The total mass losses up to 1000 °C of TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h are 23.7, 17.0 and 18.9 mass%, respectively. The molar ratios of Ti and urea in the products were measured by ICP and CHN analyses. The amounts of urea per Ti in TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h were 0.28, 0.12 and 0.17 (in mol), respectively (Table 1). The urea and adsorbed water ratios of the products were calculated based on the total mass loss of the TG curves and the molar ratios of Ti and urea. By assuming that all the organics are present as urea, the mass losses due to the thermal decomposition of urea in TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h are estimated to be 15.5, 6.6 and 9.8 mass%, respectively. The mass losses due to the evaporation of adsorbed water in TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h are calculated to be 8.0, 10.4 and 9.1 mass%, respectively (Table 1). Thus, the content of urea on the surface of the TiO<sub>2</sub> NPs is increasing in the following order: TiO<sub>2</sub>\_40h < TiO<sub>2</sub>\_70h < TiO<sub>2</sub>\_30h.

The amounts of urea can be discussed using the surface excess value reported for the urea adsorbed at the electrode/electrolyte interface,  $4.96 \times 10^{-6}$  mol m<sup>-2</sup>.<sup>47</sup> Since the surface areas of TiO<sub>2</sub> NPs without urea are not available, we utilize the surface areas of the TiO<sub>2</sub> NPs with urea, 231–281 m<sup>2</sup> g<sup>-1</sup>. The maximal values of urea for 1 g of the TiO<sub>2</sub> NPs can thus be estimated to be 0.0688–0.0837 g. The values listed in Table 1, on the contrary, correspond to 0.080–0.202 g of urea for 1 g of unmodified TiO<sub>2</sub> NPs. Thus, it is likely that large portions of the TiO<sub>2</sub> NP surfaces are covered with urea, and excess urea may be present in TiO<sub>2</sub>\_30h, in particular.

The amounts of Cl<sup>-</sup> were measured by IC analysis. The amounts of Cl<sup>-</sup> in TiO<sub>2</sub>\_30h, TiO<sub>2</sub>\_42h and TiO<sub>2</sub>\_70h were all below the limit of detection, indicating that no Ti–Cl bonds remained after the reaction for 30 h. On the other hand, the presence of Cl<sub>2</sub> gas was investigated with a gas detection tube. The amount of Cl<sub>2</sub> evolved upon opening the autoclave in a glovebag was 2.50 ppm for TiO<sub>2</sub>\_30h.

### Photocatalytic activity of the TiO<sub>2</sub> nanoparticles dispersed in water

TiO<sub>2</sub>\_30h and TiO<sub>2</sub>\_42h were readily dispersed in water without ultrasonic treatment (Fig. S5, ESI†). The aqueous TiO<sub>2</sub> NP dispersions were clear and colourless. This excellent dispersibility of the TiO<sub>2</sub> NPs is likely to originate from the presence of hydrophilic urea on the surface. On the contrary, TiO<sub>2</sub>\_70h was not dispersed in water, probably because of its larger aggregation size.

The UV-Vis spectra of the dispersions were measured to estimate the energy band gap ( $E_g$ ) (Fig. S6, ESI†). Absorptions

below ~400 nm are present, and the  $E_g$  values can be estimated by the Kubelka–Munk function.<sup>48</sup> The estimated  $E_g$  values of TiO<sub>2</sub>\_30h and TiO<sub>2</sub>\_42h are 3.33 and 3.31 eV, respectively. These  $E_g$  values are almost equal to or slightly larger than that of pure anatase ( $E_g = 3.30$  eV).<sup>2</sup>

Fig. 6 shows the photocatalytic degradation behaviour of methylene blue over TiO<sub>2</sub>\_30h and TiO<sub>2</sub>\_42h. The absorbance at 664.5 nm, assignable to methylene blue, decreases gradually under UV light irradiation. It is clearly shown that TiO<sub>2</sub>\_42h exhibits better photocatalytic activity. A possible reason for the higher photocatalytic activity of TiO<sub>2</sub>\_42h is its lower urea content.

### Control experiments: preparation of the TiO<sub>2</sub> nanoparticles without using UHP

TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub>\_urea was a mixture of a yellow liquid and white solid. TiO<sub>2</sub>\_water\_urea was a mixture of a pale yellow liquid and white solid. TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub> was a mixture of a transparent liquid and white solid. White powders were obtained after these products were washed and dried. The Ti-based yields of TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub>\_urea, TiO<sub>2</sub>\_water\_urea and TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub> were 34, 23, and 63%, respectively.

Fig. 2 shows the XRD patterns of the control experiment products. TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub>\_urea and TiO<sub>2</sub>\_water\_urea consist of rutile TiO<sub>2</sub> (JCPDS no. 21-1276) and NH<sub>4</sub>Cl (JCPDS no. 7-8). The XRD pattern of TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub> corresponds to rutile TiO<sub>2</sub>. The crystallite sizes of TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub>\_urea, TiO<sub>2</sub>\_water\_urea and TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub> are calculated from the (110) reflections using Scherrer's formula<sup>33</sup> as 11, 11, 12 nm, respectively.

The control experiment products were further characterized by Raman spectroscopy (Fig. 3). The Raman spectrum of TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub>\_urea shows bands at 148.3, 241.4, 437.6, and 604.7 cm<sup>-1</sup>. Bands are present at 141.7, 243.0, 437.6, and 604.3 cm<sup>-1</sup> in the Raman spectrum of TiO<sub>2</sub>\_water\_urea. The Raman spectrum of TiO<sub>2</sub>\_H<sub>2</sub>O<sub>2</sub> shows bands at 151.5, 236.6, 439.1, and 612.1 cm<sup>-1</sup>. These bands are consistent with the

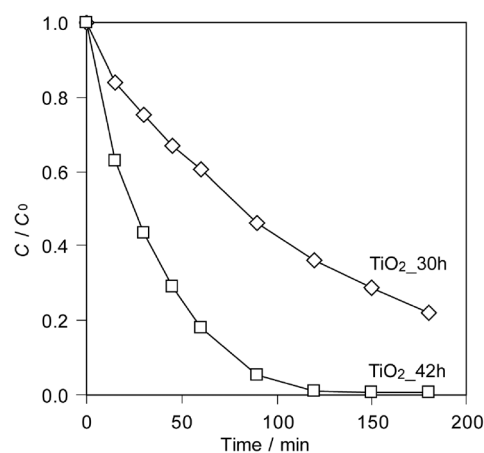


Fig. 6 Photocatalytic degradation of methylene blue by TiO<sub>2</sub>\_30h and TiO<sub>2</sub>\_42h under UV irradiation.

Table 1 The amounts of urea and water estimated by TG, ICP and IC results

Product name	Amount of urea/mass%	Amount of water/mass%
TiO <sub>2</sub> _30h	15.5	8.0
TiO <sub>2</sub> _42h	6.6	10.4
TiO <sub>2</sub> _70h	9.8	9.1



bands observed for rutile  $\text{TiO}_2$ ,<sup>48,49</sup> consistent with the XRD observation.

Fig. 4 shows the IR spectra of the control experiment products. A triply degenerate bending band of  $\text{NH}_4^+$  is present at around  $1400\text{ cm}^{-1}$ <sup>50</sup> in the spectra of  $\text{TiO}_2\text{-H}_2\text{O}_2\text{-urea}$  and  $\text{TiO}_2\text{-water-urea}$ . This result suggests that  $\text{NH}_4^+$  ions of  $\text{NH}_4\text{Cl}$  were present in  $\text{TiO}_2\text{-H}_2\text{O}_2\text{-urea}$  and  $\text{TiO}_2\text{-water-urea}$ . Thus, the IR spectral results are in accordance with the XRD observation.

Fig. 5 shows the TEM images of  $\text{TiO}_2\text{-H}_2\text{O}_2\text{-urea}$ ,  $\text{TiO}_2\text{-water-urea}$  and  $\text{TiO}_2\text{-H}_2\text{O}_2$ . The control experiment products were not dispersed in water, partly because larger aggregates were present.  $\text{TiO}_2\text{-H}_2\text{O}_2\text{-urea}$  shows the presence of connected spherical  $\text{TiO}_2$  with sizes between 200–300 nm.  $\text{TiO}_2\text{-water-urea}$  consists of undulating spherical aggregates with sizes between 100–200 nm.  $\text{TiO}_2\text{-H}_2\text{O}_2$  is composed of the rod-like  $\text{TiO}_2$  form echinoid-like aggregates with sizes of about 400 nm.

The presence of  $\text{Cl}_2$  gas in the autoclaves was studied with a gas detection tube. The amount of  $\text{Cl}_2$  in the products of  $\text{TiO}_2\text{-H}_2\text{O}_2\text{-urea}$  was below the limit of detection, 0.1 ppm.

These results clearly demonstrate that the control experiments gave rutile  $\text{TiO}_2$ , different from the synthesis using UHP, which gave anatase  $\text{TiO}_2$ . Thus, it is likely that the reaction paths for the control experiments are different from those for the synthesis using UHP. The formation conditions for rutile and anatase  $\text{TiO}_2$  in aqueous media can be discussed based on their structural characteristics. It is widely accepted that rutile  $\text{TiO}_2$  forms preferentially under acidic conditions in which the number of  $\text{OH}^-$  is low. Such acidic conditions are advantageous for the corner-sharing bonding of  $\text{TiO}_6$  octahedra, leading to the formation of rutile  $\text{TiO}_2$ .<sup>48,51</sup> Anatase  $\text{TiO}_2$  is preferentially formed under basic conditions, on the other hand, since the presence of a large number of  $\text{OH}^-$  increases the probability of edge-shared bonding and promotes the formation of anatase  $\text{TiO}_2$ .<sup>48,51</sup> In the control experiments conducted without the use of UHP, the system should consist of two immiscible phases, an aqueous phase and a  $\text{CH}_2\text{Cl}_2$  phase. Thus,  $\text{TiCl}_4$  is likely to be hydrolyzed at their interface, leading to the formation of a highly acidic aqueous phase *via* the formation of  $\text{HCl}$ . (Note that urea and ammonia, which is a hydrolysis product of urea, are weak bases, and the  $\text{Cl}:\text{N}$  molar ratio was 1:1.) Thus,  $\text{TiO}_2$  should be formed under acidic conditions to generate rutile  $\text{TiO}_2$ . (The addition of urea in the preparation of  $\text{TiO}_2$  from a  $\text{TiCl}_4$  aqueous solution promoted the crystallization of anatase  $\text{TiO}_2$ , but strongly acidic aqueous phases in the control experiments seem to cause rutile  $\text{TiO}_2$  formation.)<sup>52</sup> In the synthesis conducted using UHP, on the contrary, the reaction starts in a homogeneous system. It is likely that UHP directly oxidizes  $\text{TiCl}_4$  in the early stage of the process, leading to the formation of anatase  $\text{TiO}_2$ . The direct reaction between  $\text{TiCl}_4$  and UHP is consistent with the evolution of  $\text{Cl}_2$  only in the synthesis with UHP, since the  $\text{Cl}_2$  evolution indicates the presence of a redox reaction. This also indicates that, even in the

presence of  $\text{H}_2\text{O}_2$ , the reactions proceed mostly *via* hydrolysis in the control experiments.

Another characteristic of the  $\text{TiO}_2$  NPs obtained by the synthesis conducted using UHP is high dispersibility in water, a result contrary to the control experiments results. This may be ascribable to the effective adsorption of urea on the surface. Urea could be released in  $\text{CH}_2\text{Cl}_2$ , and stabilized by coordinating to the Lewis acid site on the  $\text{TiO}_2$  NPs.

Based on the results, the reaction mechanisms of  $\text{TiO}_2$  formation are proposed, as shown in Fig. 7. In the UHP system,  $\text{TiCl}_4$  is likely to be oxidized directly by UHP to form anatase  $\text{TiO}_2$  in the early stage of the process. Released urea molecules appear to be adsorbed on the surface of the generated  $\text{TiO}_2$ , leading to the formation of spheroid anatase  $\text{TiO}_2$  NPs. Since  $\text{HCl}$  is likely to form during this procedure (as suggested by the formation of  $\text{NH}_4\text{Cl}$ ), hydrolysis seems to be involved in the latter stage. In the control reaction experiments, on the contrary,  $\text{TiO}_2$  seems to be formed mostly *via* hydrolysis and rutile  $\text{TiO}_2$  is formed in highly acidic aqueous media. (Note that hydrogen peroxide is available only in aqueous solutions.)

Since variations in crystallite size are not evident after 30 h, the formation of anatase  $\text{TiO}_2$  NPs is essentially completed by 30 h. The main difference between  $\text{TiO}_2\text{-30h}$  and  $\text{TiO}_2\text{-42h}$  is the amount of adsorbed urea, possibly due to hydrolysis *via* contact with water, released from UHP. A comparison of  $\text{TiO}_2\text{-30h}$  and  $\text{TiO}_2\text{-42h}$  shows a tendency towards aggregation, and  $\text{TiO}_2\text{-70h}$  exhibits clear aggregation of the  $\text{TiO}_2$  NPs. Since the addition of  $\text{NH}_4\text{Cl}$  promoted the aggregation of  $\text{TiO}_2$  NPs,<sup>53</sup> we assume that the formation of a large amount of  $\text{NH}_4\text{Cl}$  (as shown in Fig. S1, ESI†) causes the aggregation of  $\text{TiO}_2$  NPs in  $\text{TiO}_2\text{-70h}$ .

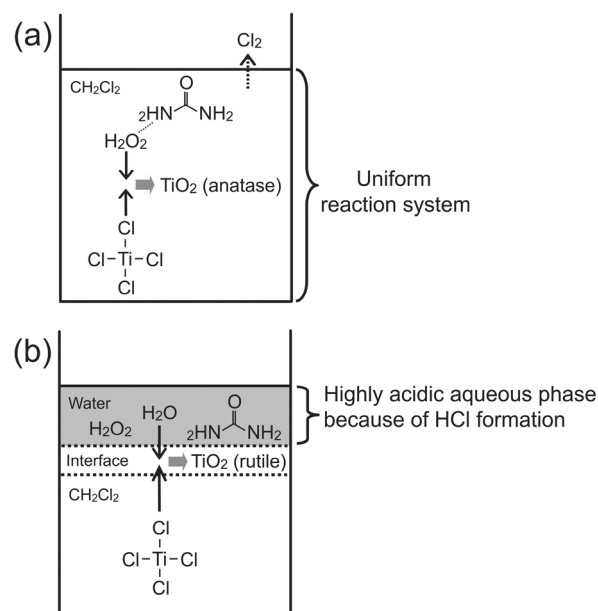


Fig. 7 Proposed mechanism of the preparation of  $\text{TiO}_2$ , (a) the  $\text{TiCl}_4\text{-UHP-CH}_2\text{Cl}_2$  system (in the early stage) and (b) the control experiments.



## Conclusions

Spheroid anatase TiO<sub>2</sub> NPs have been successfully prepared from TiCl<sub>4</sub> using urea hydrogen peroxide (UHP) as an oxygen donor through a reaction at 80 °C for 30–70 h. The anatase TiO<sub>2</sub> NPs exhibited high dispersibility in water, probably due to the presence of urea. The formation of Cl<sub>2</sub> as well as a comparison with the results of control experiments performed without UHP suggests that anatase TiO<sub>2</sub> NPs were formed *via* direct oxidation by UHP. The photocatalytic activity of the water-dispersible products (the reaction periods were 30 and 42 h) was estimated, and the product with a lower urea content exhibited better photocatalytic activity. The present results indicate that UHP can be utilized as an oxygen donor in preparations of TiO<sub>2</sub> NPs, and its use could be extended to preparations of various metal oxides.

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## Notes and references

- G. A. Ozin and A. C. Arsenault, *Nanochemistry – A Chemical Approach to Nanomaterials*, RSC Publishing, London, 2006.
- D. P. Macwan, P. N. Dave and S. Chaturvedi, *J. Mater. Sci.*, 2011, **46**, 3669–3686.
- B. L. Cushing, V. L. Kolesnichenko and C. J. O'Connor, *Chem. Rev.*, 2004, **104**, 3893–3946.
- J. A. Chang, M. Vithal, I. C. Baek and S. I. Seok, *J. Solid State Chem.*, 2009, **182**, 749–756.
- D. A. H. Hanaor and C. C. Sorrell, *J. Mater. Sci.*, 2011, **46**, 855–874.
- X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891–2959.
- S. M. Gupta and M. Tripathi, *Cent. Eur. J. Chem.*, 2012, **10**, 279–294.
- Z. R. Ismagilov, L. T. Tsikoza, N. V. Shikina, V. F. Zarytova, V. V. Zinoviev and S. N. Zagrebelnyi, *Russ. Chem. Rev.*, 2009, **78**, 873–885.
- M. Niederberger and G. Garnweitner, *Chem.-Eur. J.*, 2006, **12**, 7282–7302.
- J. N. Hay and H. M. Raval, *Chem. Mater.*, 2001, **13**, 3396–3403.
- P. H. Mutin and A. Vioux, *Chem. Mater.*, 2009, **21**, 582–596.
- A. Vioux, *Chem. Mater.*, 1997, **9**, 2292–2299.
- P. Arnal, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *Chem. Mater.*, 1997, **9**, 694–698.
- A. Aboulaich, B. Boury and P. H. Mutin, *Chem. Mater.*, 2010, **22**, 4519–4521.
- L. Y. Yang, G. P. Feng and T. X. Wang, *Mater. Lett.*, 2010, **64**, 1647–1649.
- R. S. Sapieszko and E. Matijević, *J. Colloid Interface Sci.*, 1980, **74**, 405–422.
- Z. Ji, S. Zhao, C. Wang and K. Liu, *Mater. Sci. Eng., B*, 2005, **117**, 63–66.
- D. Wang, Z. Ma, S. Dai, J. Liu, Z. Nie, M. H. Engelhard, Q. Huo, C. Wang and R. Kou, *J. Phys. Chem. C*, 2008, **112**, 13499–13509.
- M. Kakihana, M. Kobayashi, K. Tomita and V. Petrykin, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 1285–1308.
- Y. Qian, Q. Chen, Z. Chen, C. Fan and G. Zhou, *J. Mater. Chem.*, 1993, **3**, 203–205.
- H. Ichinose, M. Terasaki and H. Katsuki, *J. Ceram. Soc. Jpn.*, 1996, **104**, 715–718.
- H. Ichinose, M. Terasaki and H. Katsuki, *J. Sol-Gel Sci. Technol.*, 2001, **22**, 33–40.
- N. Sasirekha, B. Rajesh and Y. W. Chen, *Thin Solid Films*, 2009, **518**, 43–48.
- M. S. Cooper, H. Heaney, A. J. Newbold and W. R. Sanderson, *Synlett*, 1990, 533–535.
- C. L. Fan, W.-D. Lee, N.-W. Teng, Y.-C. Sun and K. Chen, *J. Org. Chem.*, 2003, **68**, 9816–9818.
- M. Marigo, J. Franzén, T. B. Poulsen, W. Zhuang and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2005, **127**, 6964–6965.
- M. C. Ball and S. Massey, *Thermochim. Acta*, 1995, **261**, 95–106.
- C.-S. Lu, E. W. Hughes and P. A. Giguère, *J. Am. Chem. Soc.*, 1941, **63**, 1507–1513.
- S. Taliansky, *Synlett*, 2005, 1962–1963.
- A. Hasaninejad, G. Chehardoli, M. A. Zolfigol and A. Abdoli, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2011, **186**, 271–280.
- A. M. Bernhard, D. Peitz, M. Elsener, A. Wokaun and O. Kröcher, *Appl. Catal., B*, 2012, **115**, 129–137.
- C. Wang, C. Shao, Y. Liu and X. Li, *Inorg. Chem.*, 2009, **48**, 1105–1113.
- K. Del Ángel-Sánchez, O. Vázquez-Cuchillo, M. Salazar-Villanueva, J. F. Sánchez-Ramírez, A. Cruz-López and A. Aguilar-Elgueababal, *J. Sol-Gel Sci. Technol.*, 2011, **58**, 360–365.
- V. Swamy, A. Kuznetsov, L. S. Dubrovinsky, R. A. Caruso, D. G. Shchukin and B. C. Muddle, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 184302.
- S. Kelly, F. H. Pollak and M. Tomkiewicz, *J. Phys. Chem. B*, 1997, **101**, 2730–2734.
- J. C. Parker and R. W. Siegel, *J. Mater. Res.*, 1990, **5**, 1246–1252.
- J. C. Parker and R. W. Siegel, *Appl. Phys. Lett.*, 1990, **57**, 943–945.
- M.-H. Lee and B.-C. Choi, *J. Am. Ceram. Soc.*, 1991, **74**, 2309–2311.
- W. Ma, Z. Lu and M. Zhang, *Appl. Phys. A: Mater. Sci. Process.*, 1998, **66**, 621–627.
- T. Busani and R. A. B. Devine, *Semicond. Sci. Technol.*, 2005, **20**, 870–875.
- J.-G. Li, X. Yang and T. Ishigaki, *J. Phys. Chem. B*, 2006, **110**, 14611–14618.



- 42 X. Xiang, L. Guo, X. Wu, X. Ma and Y. Xia, *Environ. Chem. Lett.*, 2012, **10**, 295–300.
- 43 M. A. Larrubia, G. Ramis and G. Busca, *Appl. Catal., B*, 2000, **27**, L145–L151.
- 44 A. M. Bernhard, I. Czekaj, M. Elsener and O. Kröcher, *Appl. Catal., B*, 2013, **134–135**, 316–323.
- 45 T. Sugimoto, X. Zhou and A. Muramatsu, *J. Colloid Interface Sci.*, 2003, **259**, 53–61.
- 46 K. Kanie and T. Sugimoto, *Chem. Commun.*, 2004, 1584–1585.
- 47 F. M. Kimmerle and H. Ménard, *Can. J. Chem.*, 1977, **55**, 3312–3320.
- 48 X. Shen, J. Zhang and B. Tian, *J. Hazard. Mater.*, 2011, **192**, 651–657.
- 49 G. A. Samara and P. S. Peercy, *Phys. Rev. B: Solid State*, 1973, **7**, 1131–1148.
- 50 N. E. Schumaker and C. W. Garland, *J. Chem. Phys.*, 1970, **53**, 392–407.
- 51 L. Kong, I. Karatchevtseva, M. Blackford, I. Chironi and G. Triani, *J. Am. Ceram. Soc.*, 2012, **95**, 816–822.
- 52 K. Ooi, Y. Miyai, S. Katoh and K. Sugasaka, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2721–2726.
- 53 W.-Y. Cheng, J. R. Deka, Y.-C. Chiang, A. Rogeau and S.-Y. Lu, *Chem. Mater.*, 2012, **24**, 3255–3262.

