Synthesis of high temperature stable anatase TiO₂ photocatalyst

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ABSTRACT: In the absence of a dopant or precursor modification, anatase to rutile transformation in synthetic TiO_2 usually occurs at a temperature of 600 °C to 700 °C. Conventionally, metal oxide dopants (*e.g.* Al_2O_3 and SiO_2) are used to tune the anatase to rutile transformation. A simple methodology is reported here to extend the anatase 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 using a 1:1 (Ti (OPr)₄: urea) composition and 11% anatase composition is retained even after calcining the powder at 900 °C. On comparison a sample which 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)₄:urea) has also been studied and compared. The investigation concluded that the stoichiometric modification by urea 1:1 (Ti (OPr)₄:urea) composition is most effective in extending the anatase to rutile phase transformation by 200 °C compared to the unmodified samples. In addition, BET analysis carried out on samples calcined at 500 °C showed that the addition of urea up to 1:1 (Ti (OPr)₄:urea) increased the total pore volume (from 0.108 cm³/g to 0.224 cm³/g) and average pore diameter (11 nm to 30 nm) compared to the standard sample. Samples prepared using 1:1 (Ti (OPr)₄: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 (0.016 min⁻¹, decoloration in 120 mins) to the urea-modified sample (0.06 min⁻¹, decoloration in 50 mins).

KEYWORDS; Titania, high temperature stable anatase, photocatalysis.

1. Introduction

Nanocrystalline titania (TiO_2) has received significant attention in the last few decades due to the photo-induced electron transfer properties associated with the anatase metastable phase.¹⁻³ Titania usually exists in three different forms; anatase (tetragonal, $a=b=3.78\text{\AA}$; $c=9.50\text{\AA}$), rutile (tetragonal, $a=b=4.58\text{\AA}$; $c=2.95\text{\AA}$) and brookite (rhombohedral, $a=5.43\text{\AA}$; $b=9.16\text{\AA}$; $c=5.13\text{\AA}$). These crystalline structures consist of $[\text{TiO}_6]^{2-}$ octahedra, which share edges and corners in different manners while keeping the overall stoichiometry as TiO_2 .⁴⁻⁷ Even though anatase has more edge sharing octahedra, the interstitial spaces between octahedra are larger which makes rutile denser than anatase (density of anatase is 3.84 g/cm^3 and of rutile is 4.26 g/cm^3).⁴⁻⁷ Among the various phases of titania reported, anatase shows a better photocatalytic activity and anti-bacterial performance.⁸⁻¹² A stable anatase phase up to the sintering temperature of the ceramic substrates is most desirable for applications on anti-bacterial self cleaning building materials (*e.g.* bathroom tile, sanitary wares *etc.*).¹³⁻¹⁵ These applications require high purity titania with a definite phase composition.¹³⁻¹⁵ 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 $600\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$.¹⁶⁻¹⁸ Phase transition to rutile is non-reversible due to the greater thermodynamic stability of rutile phase.¹⁹⁻²⁰ Researchers at Toto Ltd. recently reported²¹ a method to produce photoactive titania-Ag coatings on ceramic materials. The composition contains up to 7% anatase present at $900\text{ }^\circ\text{C}$.²¹ Any improvement in the anatase phase composition at these high temperatures is expected to show a higher photocatalytic activity.²¹ Conventionally metal oxide doping is used to extend the anatase to rutile transformation temperature above $700\text{ }^\circ\text{C}$.²²⁻²⁶ Various metal oxide dopants such as Al_2O_3 , NiO , SiO_2 , ZrO_2 , ZnO and Sb_2O_5 have already been studied to assess the effect on both anatase to rutile transformation and alteration of modification on textural properties of titania.²²⁻²⁶ Formation of secondary impurity phases (*e.g.* Al_2TiO_5 , NiTiO_3) 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.²⁷⁻²⁸ Recent research showed that urea has little effect on the phase

formation in titania.²⁹ Previously, urea has been employed to improve the pore parameters and morphology by utilising it as a pore forming agent.²⁹⁻³¹ Zheng *et al.* reported preparation of mesoporous titania *via* sol-gel reactions by using urea as a template.³² Bakardjieva *et al.* showed the formation of TiO₂ nanocrystals from titanyloxychloride by using urea as a precipitating agent.³³ 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.³⁴⁻³⁷ 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)₄) using 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 using 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)₄:Urea) molar ratio calcined at 900 °C show 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 Method

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

The same procedure is adopted to synthesise 1:0.25 and 1:0.5 (Ti (OPr)₄: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 $\text{CuK}\alpha$ radiation. The amount of anatase in the sample was estimated using the Spurr equation (equation 1).³⁸

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

where, F_A is the mass fraction of anatase in the sample, $I_A(101)$ and $I_R(110)$ is 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 using a Micromeritics Gemini 2375 surface area analyser. The measurements were carried out at liquid nitrogen temperature after degassing the powder samples for 1 hour 30 minutes 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 $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere.

The FTIR spectra of the gel dried at 80°C was measured by using a spectrum GX-FTIR spectrophotometer in the wave number range $4000\text{--}400\text{ cm}^{-1}$ 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 $\text{K}\alpha$ X-ray source ($h\nu = 1486.6\text{ eV}$) which was used at 140 W. The area of analysis was approximately $500\text{ }\mu\text{m}$ diameter for the samples analysed. For survey spectra a pass energy of 100 eV and a 0.4 eV step size were employed. For C_{1s} and Ti_{2p} high resolution spectra a pass energy of 20 eV and a 0.1 eV step size

were used. For O1s high resolution spectra a pass energy of 20 eV and a 0.2 eV step size were used. For N1s high resolution spectra a pass energy of 50 eV and a step size of 0.2 eV were used. Charge compensation was achieved 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 non-linear Shirley background. The manufacturer's Advantage software was used which incorporates the appropriate sensitivity factors and corrects for the electron energy analyser transmission function.

Photocatalysis studies

In a typical experiment, 0.06 g standard sample calcined at 900 °C was dispersed in 50 mL of Rhodamine 6G solutions having a concentration 5×10^{-6} M. The above suspension was irradiated in a Q-Sun Xenon solar simulator chamber (0.68 W/m^2 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 Equation (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 and Discussions

3.1 FTIR Spectroscopy. FTIR spectra of the precursor samples dried at 80 °C have been recorded. The absorption band at $3500\text{-}3000 \text{ cm}^{-1}$ and 1600 cm^{-1} in all spectra indicate hydroxyl group stretching vibrations.²⁹ The broad peak at 500 cm^{-1} found in the standard and urea modified samples indicate the Ti-O-Ti stretching vibrations.²⁹ The peak observed at 1035 cm^{-1} 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.²⁹ The peaks corresponding to Ti-O-C bond increases 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 organic and inorganic components by the condensation reaction. The peak obtained at 1154 cm^{-1} is assigned to the stretching vibration of C-N.²⁹ The peak obtained at 1453 cm^{-1} is due to the deformation mode of ammonium ions formed by the decomposition of excess urea.⁴⁰ FTIR results thus show a strong chelation of urea molecules to the titania precursor. It has been observed that the peaks at 1035 cm^{-1} (which is assigned for Ti-O-C bond) and 1154 cm^{-1} (C-N) were absent above a calcinations temperature of $200\text{ }^{\circ}\text{C}$ and all additional peaks except Ti-O stretching is absent above $300\text{ }^{\circ}\text{C}$.

Figure 1. FTIR spectra of the $80\text{ }^{\circ}\text{C}$ dried titania precursor a) standard sample b) sample of 1:1 (Ti(OPr)₄:Urea) composition

3.2. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) studies have been carried out (Figure 2.) to investigate the amorphous to crystalline transition of the titania precursor. An endothermic peak at $170\text{ }^{\circ}\text{C}$ has been observed for the 1:1 (Ti(OPr)₄:Urea) sample and this peak has been assigned as the thermal decomposition of the titania-urea precursor. The exothermic peaks (Figure 2 a and b) at $250\text{ }^{\circ}\text{C}$ and 356

°C respectively for the standard and 1:1 (Ti(OPr)₄:Urea) samples indicate the amorphous to crystalline formation.²⁷ It is therefore evident from the Figure 2 that the amorphous to crystalline formation is delayed in the case of the urea modified sample. XRD analysis have been further carried out to confirm the crystallization characteristics at 250 °C and an amorphous phase was obtained for the 1:1 (Ti(OPr)₄:Urea) samples while a crystalline anatase phase was observed for the standard sample (Supplementary information).

Figure 2. Differential scanning calorimetry of a) standard b) sample of 1:1 (Ti(OPr)₄:Urea) composition.

3.3. Surface area measurements. BET surface area and total pore volume are calculated at $p/p_0=0.99$ by BET method for the samples calcined at 500 °C. The results are shown in Table 1. Both isotherms for the standard and urea added samples show type IV behaviour indicating mesoporosity of the prepared sample (Supporting Information Figure 2.). An earlier report³² shows that the urea is a good pore forming agent so that it will help in the generation of mesoporosity in the titania framework. The current study also confirms that the addition of urea (1:1) increases the pore diameter to 30 nm compared to the 11 nm pore diameter of the standard sample (Table 1). BET analysis of the samples calcined at higher temperatures showed that the 1:1 (Ti(OPr)₄:Urea) sample processes a higher surface area (15 m²/g) at

800 °C compared the standard sample calcined ($5 \text{ m}^2/\text{g}$) at the same temperature. The surface area of both the 1:1 ($\text{Ti}(\text{OPr})_4$:Urea) sample as well as the standard sample showed surface areas of $5 \text{ m}^2/\text{g}$ and $4 \text{ m}^2/\text{g}$ respectively.

TABLE 1: BET surface area analysis at 500 °C

Material	Surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm) $\pm 10\%$
standard TiO_2 sample	38	0.108	11
1:1 $\text{Ti}(\text{OPr})_4$:Urea composition	30	0.224	30

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

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

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

Figure 4. XRD of the samples calcined at 800 °C A= Anatase; R=Rutile a) standard sample b) sample prepared by 1:1 (Ti(OPr)₄:Urea) composition.

At 700 °C the standard sample showed rutile as the major phase with 12% anatase (Figure 3; Supporting Information Figure 4) while the samples with 1:0.25 and 1:0.5 (Ti(OPr)₄:Urea) composition showed the presence of 40% and 86% anatase respectively (Supporting Information Figure 4.). At 800 °C standard (Figure 2., 4. and Supporting Information Figure 5.), 1:0.25 and 1:0.5 (Ti(OPr)₄:Urea) composition showed a lower anatase content (0, 23 and 27% respectively). A significantly high anatase content (97%) was obtained for sample with the highest urea content *i.e.* 1:1 (Ti(OPr)₄:Urea) up to a temperature of 800 °C (Figure 3 and 4). All the samples except a sample with composition of 1:1 (Ti(OPr)₄:Urea)

turned to fully rutile at 900 °C. The sample with a composition of 1:1 (Ti(OPr)₄:Urea) showed 11% anatase at 900 °C (Supporting Information).

XRD studies concluded that the modification by urea 1:1 (Ti (OPr)₄: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 Figure 5 and 6) and 1:1 (Ti(OPr)₄:Urea) titania samples. Figure 5 and 6 shows Raman spectra obtained with samples of composition 1:1 (Ti(OPr)₄:Urea) calcined at 800 °C and 900 °C. According to factor group analysis anatase phase consists of six and rutile phase consists of five Raman active modes. (*i.e.* anatase- 144 cm⁻¹, 197 cm⁻¹, 399 cm⁻¹, 513 cm⁻¹ and 639 cm⁻¹; rutile - 144 cm⁻¹, 446 cm⁻¹, 612 cm⁻¹ and 827 cm⁻¹.) Figure 5 shows a strong peak at 197 cm⁻¹ which is the characteristic peak of anatase phase. The peak at 197 cm⁻¹ appears along with other characteristic rutile phases in Figure 6 indicates the presence of anatase phase in the 900 °C calcined sample. These two Raman spectra are consistent with the XRD results.

Figure 5. Raman spectra of titania sample with 1:1 (Ti(OPr)₄:Urea) calcined at 800 °C.

Figure 6. Raman spectra of titania sample with 1:1 (Ti(Opr)₄:Urea) calcined at 900 °C.

3.6. X-ray Photoelectron Spectroscopy (XPS)

XPS measurements have been carried out to find out N or C incorporation above 500 °C. The presence of C (Ca.11%) and N (Ca. 0.5%) was confirmed in the XPS analysis (Table 2). It was previously reported that N_{1s} peak will show a binding energy value of 400-402 eV and C_{1s} will show a binding energy 281 to 287eV. *Ref 1* The weak signal at 400 eV was explained previously as a result of the molecular chemisorbed nitrogen. *Ref 2,3* However, there was no indication of Ti-N bond formation observed (396 eV). *Ref 2*

TABLE 2: XPS analysis of the 1:1 (Ti(OPr)₄:Urea) sample calcined in the range of 500 to 800 °C

O ₂ SampleTi	C1s / 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

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) *Ref 1*. It can be seen from the XPS spectra of C_{1s} that majority of the C present in the TiO₂ matrix as a solid solution (285 eV). A small surface adsorbed C 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 Ti-C phase formation. The solid solubility of C is occurred with in the tetrahedral and octahedral interstices existing in anatase crystal *Ref 1*

Figure 7 XPS plots of 1:1 Ti (OPr)₄:Urea sample calcined at 800 °C a) C_{1s} b) N_{1s}

3.7 Photocatalytic studies. Photocatalytic studies have been carried out by the decomposition reaction of rhodamine dye in the presence of standard and the urea modified samples. The urea modified sample 1:1 (Ti(OPr)₄:Urea) shows more than three times the activity of the unmodified titania. The fully decolourisation of the rhodamine dye occurred within 50 minutes in the case of 1:1 Ti (OPr)₄:Urea sample calcined at 900 °C whereas the standard sample takes more than 120 minutes 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 $0.016 \pm 0.002 \text{ min}^{-1}$ ($R^2 = 0.98$) for the standard sample and $0.06 \pm 0.006 \text{ min}^{-1}$ ($R^2 = 0.94$) for the urea modified sample. The value of the latter is probably underestimated, as there is an initial lag time, after which degradation occurs at a rate of 0.08 min^{-1} ($R^2 = 0.99$), over four times the rate of the standard sample. A similar trend is observed with the urea modified sample calcined at 800 °C, which has more than twice the degradation rate (Supporting Information Figure.8). An initial lag is also observed with this sample. This lag time was about 10 minutes for both sample 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 hours showed little change in absorbance. The kinetic plots and the progress of the reactions are shown in Figure 7.

Figure 8. Kinetic study of standard sample and 1:1 (Ti(OPr)₄:Urea) calcined sample at 900 °C. A₀ is the initial absorbance and A is the absorbance after a time of the rhodamine dye degradation. (Error bars $\pm 10\%$) 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)₄:Urea) (right inset).

4. Discussion

Titanium tetraisopropoxide hydrolyses vigorously with water and polycondensates of $[\text{Ti}(\text{OH})_n\text{X}_m]^{z-}$ ions are initially formed. (When the alkoxide reacts with water the metal ion increases its coordination by employing its vacant *d*- orbitals to accept oxygen lone pairs from ligands such as OH groups). The linkage between TiO_6^{2-} octahedron is formed by the dehydration reaction of $[\text{Ti}(\text{OH})_n\text{X}_m]^{z-}$. It is previously reported that the anatase phase has edge shared TiO_6^{2-} octahedra structure while rutile has

corner shared octahedra.⁴ The condensation reaction can also be catalysed in acidic or basic conditions to make TiO_6^{2-} octahedral from $[\text{Ti}(\text{OH})_n \text{X}_m]^{z-}$. Urea is used here to modify the condensation reaction since gel modifiers are known to control the pore characteristics.²⁷ The current investigation also showed that a modifier, urea, can extend the anatase formation to higher temperatures without using any metal or metal oxide dopants. It was previously proved that the precursor processing conditions could influence significantly the high temperature properties of various nanocrystalline metal oxides such as ZnO .⁴¹⁻⁴³ It should also be noted that high temperature anatase phase stability has been achieved previously by using copper sulphate as a dopant precursor.⁵² However, when a precursor without any metal ions (1:1 ($\text{Ti}(\text{OPr})_4:\text{H}_2\text{SO}_4$)) was used a major rutile phase was (63.13%) formed at 800 C. (Supplementary information).

One of the major problems in the preparation of nanocrystalline TiO_2 is the fast reactivity of inorganic precursor towards hydrolysis and condensation.⁴⁴⁻⁴⁶ Urea molecules chelated to the Ti ions have amino groups with a high electronegativity which retard the condensation reactions of titanium isopropoxide by altering the reaction pathway.²⁹ The chelation is evidenced from FTIR data which shows a strong peak at 1035 cm^{-1} corresponding to the Ti-O-C bond formed by the interaction between Ti-O inorganic network and C=O of urea (Figure 1.). As the urea content is increased the chelation becomes stronger and this facilitates a stronger titania gel network. This is clearly seen from the FTIR results where the band at 1035 cm^{-1} is weaker at lower urea concentration and increases in intensity with an increase in urea concentration. It has been previously reported that a gel network with little branching and cross linking with a smaller void region is morphologically weak and collapses easily on calcinations.³⁹ Therefore strengthening the gel network using urea assists the retention of the anatase phase to higher temperatures. Furthermore, the uniform distribution of titania precursor molecules in a urea stabilised gel network is considered to have caused the reduction in the anatase/anatase contact points which possibly reduces the growth process of anatase particles and this subsequently promotes pore growth.¹⁸ Therefore the onset of nucleation process associated with rutile formation is delayed.

The efficiency of electron-hole formation in a photocatalytic reaction is dependent on the band gap and the frequency of incident light, and how competitive electron-hole recombination is with the parallel electron-oxygen and hole-water reactions.⁴⁷⁻⁴⁹ The anatase phase is found to be a better photocatalyst than rutile in spite of the fact that the band gap of rutile (3.0 eV) is smaller than that of anatase (3.2 eV). A faster electron-hole recombination is feasible in rutile as the recombination probability is inversely proportional to the magnitude of the band gap.⁴⁸ It has also been reported that a mixture of anatase and rutile is more photoactive than 100% anatase.^{47,48} The commercial photocatalyst Degussa P-25 consisting of an anatase/rutile proportion 70/30 is more active than pure anatase or pure rutile.⁴⁷ Various preparation methods of the sample which results in different crystal structures or surface morphologies was also found to produce different recombination lifetimes and interfacial electron transfer rate constants.⁴⁹⁻⁵¹ It has been observed in the current study that a anatase/rutile proportion 11/89 only required less than half of the time to degrade rhodamine dye compared to 100% rutile sample. The larger amount of anatase phase is the most likely cause for higher activity of the urea modified sample towards the degradation of the rhodamine dye.

5. Conclusions

A method for making high temperature stable anatase phase without using any complex dopants has been reported. 97% anatase phase has been obtained at 800 °C using a 1:1 (Ti(OPr)₄:Urea) composition and 11% of anatase is obtained even after calcining at 900 °C. The current technique is, therefore, found to be effective in extending the anatase to rutile phase transformation by at least 200 °C compared to the standard samples. A significantly higher photoactivity has been achieved for sample modified using urea, calcined at 900 °C compared to the sample prepared without using urea calcined under similar conditions. Kinetic analysis shows that for the urea modified sample at 900 °C, the decomposition rate of rhodamine 6G is more than four times faster due to the presence of anatase. This methodology is therefore suitable for the high temperature photocatalytic application in building materials (*e.g.* ceramics, glass and bricks).²¹ A high temperature stable anatase phase, good photocatalytic activity and

simplicity of processing are the main advantages of this method. The characterisation of the materials has been supported by XRD, Raman, FTIR and surface area analysis. The investigation confirmed the use of urea as a potential candidate both, as a pore forming agent to create mesoporosity in titania and also to obtain high temperature stabilised anatase phase. This approach is very effective and significant to a considerable extent in dispensing with the conventional use of metal oxide dopants to retain anatase phase at high temperatures. The transformation temperature is expected to increase at a much higher temperature with the simultaneous use of precursor modification and metal oxide dopant addition. More studies are underway in this direction.

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SUPPORTING INFORMATION

Supporting Information Figure 1. FTIR plots of standard and urea modified samples

Supporting Information Figure 2. BET surface area plots of standard and 1:1 (Ti(OPr)₄:Urea)

Supporting Information Figure 3.

XRD of the standard and urea modified samples at 600 °C.

Supporting Information Figure 4. XRD of urea modified samples at 700 °C.

Figure 3. XRD of the samples calcined at 700 °C A= Anatase; R=Rutile a) standard sample b) sample prepared by 1:1 (Ti(OPr)₄:Urea) composition.

Figure 5. XRD of the samples calcined at 900 °C A= Anatase; R=Rutile a) standard sample b) sample prepared by 1:1 (Ti(OPr)₄:Urea) composition.

Supporting Information Figure 5. XRD of urea modified samples at 800 °C.

Supporting Information Figure 6. Raman spectrum of standard sample at 800 °C

Sample 1 ... TiO₂ @ 500°C.

Sample 2 ... TiO₂ @ 600°C.

Sample 3 ... TiO₂ @ 700°C.

Supporting Information Figure 7. Raman spectrum of standard sample at 900 °C

Supporting Information Figure 8. Kinetic study of standard sample and 1:1 (Ti(OPr)₄:Urea) calcined sample at 800 °C. A_0 is the initial absorbance and A is the absorbance after a time of the rhodamine dye degradation. (Error bars $\pm 10\%$) 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)₄:Urea) (right inset).

Supporting Information Figure 10 XRD of the sample prepared using sulphate ions and calcined at 800 °C

FIGURE CAPTIONS

Figure 1. FTIR spectra of the 80 °C dried titania precursor a) standard sample b) sample of 1:1 (Ti(OPr)₄:Urea) composition.

Figure 2. Anatase content in the samples calcined at various temperatures a. standard b, c and d are 1:0.25, 1:0.5 and 1:1 Ti(OPr)₄:Urea samples respectively.

Figure 3. XRD of the samples calcined at 700 °C A= Anatase; R=Rutile a) standard sample b) sample prepared by 1:1 (Ti(OPr)₄:Urea) composition.

Figure 4. XRD of the samples calcined at 800 °C A= Anatase; R=Rutile a) standard sample b) sample prepared by 1:1 (Ti(OPr)₄:Urea) composition.

Figure 5. XRD of the samples calcined at 900 °C A= Anatase; R=Rutile a) standard sample b) sample prepared by 1:1 (Ti(OPr)₄:Urea) composition.

Figure 6. Raman spectra of titania sample with 1:1 (Ti (Opr)₄ : Urea) calcined at 800 °C.

Figure 7 Raman spectra of titania sample with 1:1 (Ti (Opr)₄ : Urea) calcined at 900 °C.

Figure 8. Kinetic study of standard sample and 1:1 (Ti(OPr)₄ : Urea) calcined sample at 900 °C. A₀ is the initial absorbance and A is the absorbance after a time of the rhodamine dye degradation. (Error bars ± 10%) Inset: Absorption spectra of rhodamine dye degradation using standard sample (left inset) and sample with 1:1 (Ti (OPr)₄ : urea) (right inset).

Table Title **Table 1** BET surface area analysis at 500 °C.