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A simple method to synthesize N-doped rutile titania with enhanced photocatalytic activity in sunlight

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Abstract

This study demonstrates a simple route for the synthesis of nanocrystalline N doped rutile titania by calcination of acidified $TiCl_3$ in presence of urea. Urea was used as a source of nitrogen. The N doped rutile titania was yellow in colour and showed excellent photocatalytic activity in sunlight.

Keywords: TiO_2; Anatase; Rutile; N-doped; Photocatalyst

1. Introduction

Titanium dioxide is a semiconductor material having a large number of applications and is also one of the most widely investigated photocatalyst. This is mainly due to its favourable properties like non-toxicity, chemical inertness, stability over a wide pH range under irradiation conditions [1–3] and its relatively favourable disposition of band edges [4]. However the photocatalytic activity of TiO_2 is found to be phase dependent. Of the three crystalline forms of TiO_2 viz. anatase, rutile and brookite, the metastable anatase phase is found to be photocatalytically active [1,5,6]. Inspite of the fact that the band gap of rutile is some 0.4 eV smaller than that of anatase [5], the reports of this stable rutile phase being photocatalytically active are few [7,8]. The explanation for this observed low activity is still debatable. The possible reasons cited include, faster electron–hole (e^-–h^+) recombination [9,10], greater extent of O_2 adsorption on the surface of anatase TiO_2 [1], as well as the number and type of surface hydroxyls [11–13].

Thus TiO_2 inspite of its several favourable properties shows significant photoactivity generally in UV light and this limits its commercial viability in photocatalysis. Several efforts have been made to dope titania with various metals as well as non-metals so as to make it photocatalytically active in visible light [14]. Asahi et al. [15] reported the synthesis of N doped titania by sputtering TiO_2 targets with N_2 and Ar gas mixtures. These showed excellent visible light photocatalysis.

TiO_2 in general can be synthesized by several methods. Some of the methods for obtaining titania are thermal oxidation of Ti, plasma spraying, anodization and chemical vapour deposition [13]. However, most of these techniques require special apparatus, which is a major disadvantage. Highly active nanosize TiO_2 is also prepared by sol-gel route, either using Ti alkoxide or chlorides as the source of Ti [16]. It can also be obtained by the hydrothermal treatment of the alkoxide gel [17]. However, use of alkoxide in synthesis warrants tight control of experimental conditions such as pH, humidity etc because of the intense hydrolysis of

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alkoxide in air. Moreover high cost of alkoxide limit commercialization of this process.

We report herein a relatively simple method for the synthesis of nanocrystalline N doped rutile TiO_2 which showed excellent photocatalytic activity in sunlight.

2. Chemical synthesis

The N-doped rutile titania catalyst (R2) was synthesized by drop-wise addition of 0.5 M HNO_3 to a 15% $TiCl_3$ solution until its colour changed from violet to colourless. This was followed by the addition of urea such that the $TiCl_3$: Urea molar ratio in the final solution was 1:2. The resultant solution was evaporated to dryness on a steam bath. A small portion of the dry precursor was first analysed by TG/DSC studies in order to select the synthesis temperature [18]. A time period of 3 h was considered to be sufficient to burn off the organic matter. Subsequently the entire dry residue was then heated in a muffle furnace at 450 °C under continuous flow of dry air for 3 h to obtain the final sample. The reference samples used are R1, a commercial rutile (Loba Chemie, India) and DP25, the Degussa P25 TiO_2.

3. Catalyst characterization

The X-ray powder diffraction patterns (XRD) have been recorded on a Shimadzu LabX-700 diffractometer, using Ni filtered Cu K_α radiation ($\lambda = 1.5406\,\text{Å}$). The Scherrer crystallite sizes were determined using the formula $t = 0.9\lambda/\beta\cos\theta$ where λ is the wavelength characteristic of the Cu K_α radiation, β is the full width at half maximum (in radians) and is θ the angle at which the 100 intensity peak appears. The lattice parameters (a and c) were determined using the formula $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$, where h, k, l are the miller indices and d is the interplanar distance. The weight percent of anatase in the rutile phase was obtained from the equation

$$X_A = [1 + 1.26(I_R/I_A)]^-,$$

[19] where X_A is the weight fraction of anatase in the mixture, I_R and I_A were obtained from the peak areas of anatase (101) and rutile (110) diffractions, respectively.

Nitrogen adsorption and desorption isotherms were collected at −196 °C on a Quantachrome Autosorb 1 sorption analyzer. The specific surface area was calculated using the BET (Brauenner Emmet Teller) model. The zeta potentials as well as dynamic light scattering (DLS) particle sizes were determined on a Malverns Zetasizer instrument. The absorption edges and band gaps were determined from the onset of diffuse reflectance spectra of the samples measured using UV-VIS spectrophotometer (Shimadzu UV-2450). The presence of nitrogen was further confirmed by the N 1s binding energy peak in the XPS spectra recorded for a representative sample on a microtech multiple ESCA 3000 spectrometer.

4. Photocatalytic studies

Asahi et al. [15] have investigated photocatalytic activity of N doped TiO_2 using methylene blue (MB) degradation as a test reaction. In the present investigation similar experiments using MB were carried out in sunlight. Thus, experiments were carried out simultaneously for all the catalysts in bright sunlight for 120 min, between 10.00 a.m. and 12.00 a.m. (noon). Experiments were also repeated for all the catalysts simultaneously on three different days in order to confirm consistency of results. In a typical run, 100 mL of aqueous dye solution (0.012 g/L, pH 7.5) and 0.4 g of the catalyst was exposed to sunlight for the duration of the experiment. The pH was adjusted with 0.1 M NaOH solution. The solutions thus exposed to sunlight were stirred intermittently. After every 30 min, 2 mL aliquots were pipetted out, centrifuged and the absorbance of the

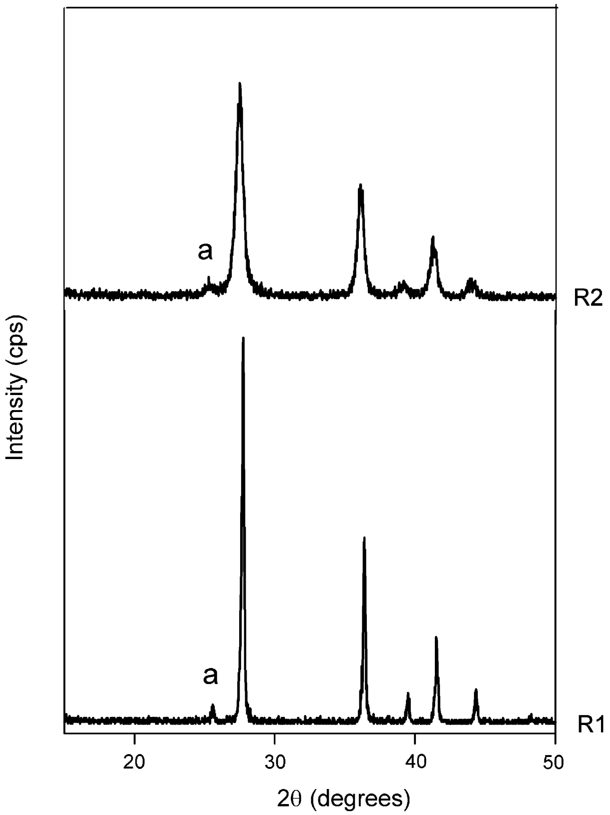

Fig. 1. XRD profiles of samples R1 and R2, where (a) shows the traces of anatase phase in the rutile samples.

Table 1
Structural properties of titania samples

Sample	Chemicals for synthesis	% Anatase	Particle size (nm)	Lattice parameters (Å) $a = b$	Lattice parameters (Å) c	BET surface area (m^2/g)	DLS particle size (nm)	pzc (mV)
R1	Commercial Loba Chemie	2.2	27.26	4.557	2.949	15	987	4.42
R2	$TiCl_3 + HNO_3 +$ Urea	3.5	9.09	4.583	2.953	36	589	5.17
DP25	Commercial Degussa P25	67	—	—	—	49	—	6.21[a]

[a] From literature [23].

clear supernatants was determined at 660 nm wavelength against appropriate blanks.

5. Results and discussion

Fig. 1 gives the XRD patterns of the samples R1 and R2. Both the samples showed a rutile crystal phase, with a trace amount of anatase phase as evident from the peak at $d = 3.49$ Å and $I/I_0 \sim 0.8\%$. The Scherrer crystallite sizes, lattice parameter, and other characteristics are as given in Table 1.

As seen from the Table 1 the lattice parameters of the synthesized sample R2 were in good agreement with those reported in literature [20]. Moreover, R2 showed Scherrer crystallite size of about 9 nm in comparison to the 27 nm of the commercial sample.

Fig. 2 shows the diffuse reflectance spectra of the titania samples. The band gap of the samples was determined by the equation

$$E_g = 1239.8/\lambda,$$

[21] where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edges in the spectrum. Thus, the synthesized sample R2 in addition to being yellow in colour showed excellent visible light absorption and two step absorption edges as evident from its spectrum in Fig. 2. On the other hand both the commercial rutile R1 and the Degussa P25 sample DP25 showed only a one step absorption edge. While the first edge ~400 nm, seen in all the three samples is thought to be related to the band structure of original titania, the second one around 550 nm as seen only in R2 is related to newly formed N 2p band which locates above O 2p valence band in $TiO_{2-x}N_y$ is in agreement with other recent reports [15,22,23]. Table 2 summarizes the absorption edges and the corresponding band gap values of the three samples.

The presence of N in R2 was further confirmed by the N 1s XPS spectrum. As seen from Fig. 3 the peak with binding energy around 396 eV which is characteristic of Ti–N bonding is observed [15,22,23].

Fig. 4 shows the MB degradation profiles of the various catalysts. The initial absorbance of the solution was found to be 0.76. The commercial rutile R1 showed a decrease in absorbance to the same extent as that of a blank experiment carried out in the dark. Thus the commercial rutile R1 used in this investigation was found to be photocatalytically inactive. The slight decrease in absorbance observed is therefore attributed to the adsorption of the dye on the titania particles. The catalysts R2 and DP25 showed high photocatalytic activity with 100% dye degradation.

The photocatalytic process mainly occurs on the surface of the photocatalyst and adsorption precedes photodegradation. Hence factors like point of zero charge (pzc) [22,23], colloidal particle size and surface area that influence the adsorption in turn could also influence the photocatalytic activity. As seen from

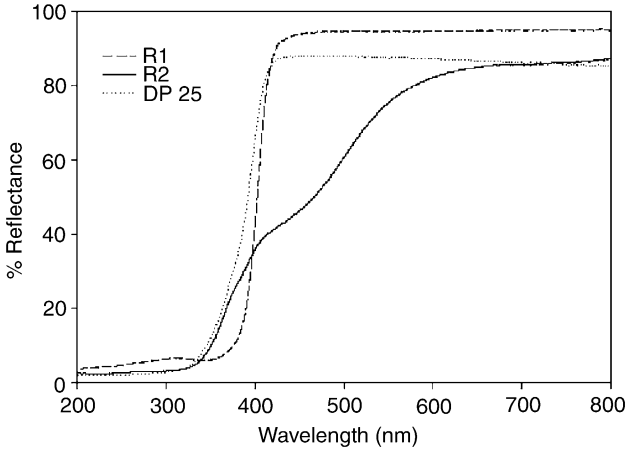

Fig. 2. Diffuse reflectance spectra of the samples R1, R2 and DP25.

Table 2
Absorption edges and band gaps of the titania samples

Catalyst	First absorption edge (nm)	Band gap (eV)	Second absorption edge (nm)	Band gap (eV)
R1	422	2.94	—	—
R2	404	3.06	550	2.25
DP25	418	2.97	—	—

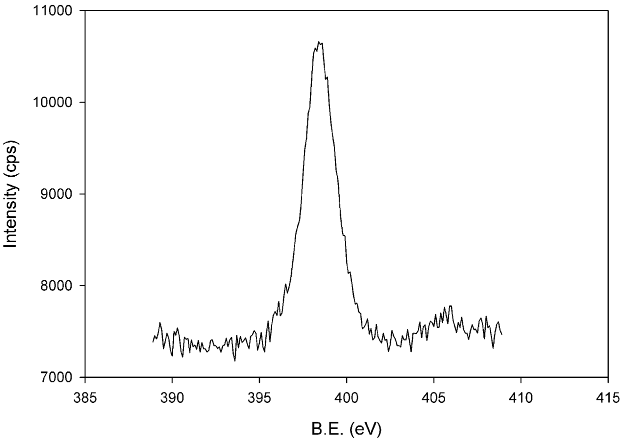

Fig. 3. XPS spectrum of rutile TiO_2 R2 in the N 1*s* BE region.

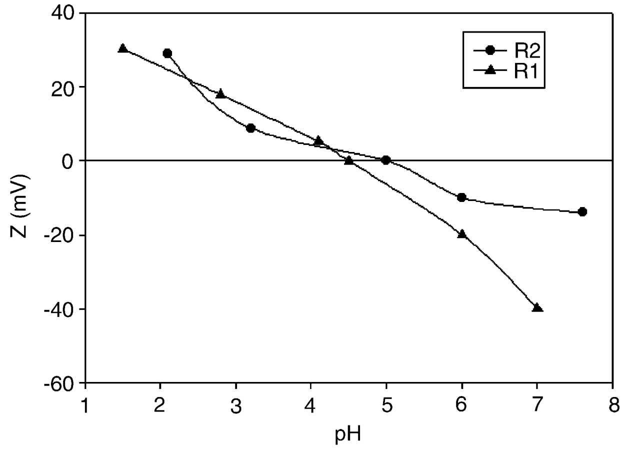

Fig. 4. Zeta potentials of R1 and R2.

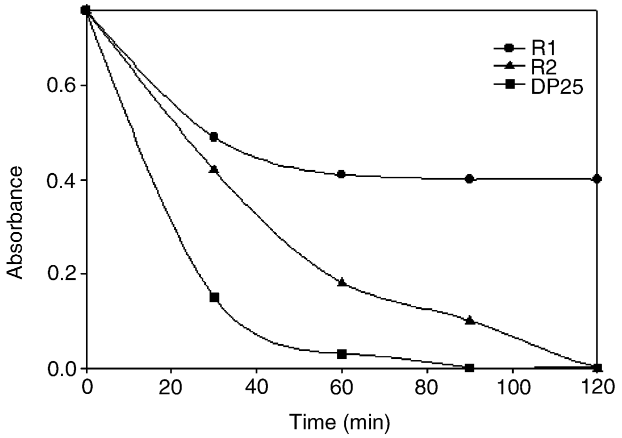

Fig. 5. Photocatalytic degradation profiles of the catalysts R1, R2 and DP25.

Table 1 the catalyst R2 had a comparatively smaller colloidal particle size (DLS) of about 589 nm and a lowered pzc value of 5.17 (shown in Fig. 5), as compared to the 6.21 of the Degussa P25 sample. This lowered pzc value might have in fact facilitated the adsorption of the cationic dye MB on the catalyst surface. And this may be one of the reasons why it showed photocatalytic activity quite comparable to that of Degussa P25.

The unusually high photocatalytic activity of the synthesized rutile sample R2 could be attributed to the unique synthesis strategy adopted employing urea which resulted in the incorporation of nitrogen into the system. Other factors like comparatively smaller particle size, higher surface area and lowered pzc value contributed to its enhanced activity.

6. Conclusions

(i) A nanocrystalline N-doped rutile TiO_2 has been synthesized by a simple method involving $TiCl_3$, HNO_3 and urea.
(ii) The synthesized N-doped rutile TiO_2 showed excellent visible light absorption.
(iii) The photocatalytic activity is evaluated using methylene blue degradation as a test reaction. The synthesized N-doped rutile titania showed very good photocatalytic activity in sunlight in comparison to the commercial rutile sample.

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References

[1] R.J. Gonzalez, R. Zallen, H. Berger, Phys. Rev. B 55 (1997) 7014.
[2] A. Pottier, C. Chaneac, E. Tronc, L. Mazerroles, J. Jolivet, J. Mater. Chem. 11 (2001) 1116.
[3] Y. Hsien, C. Chang, Y. Chen, S. Cheng, Appl. Catal. B 31 (2001) 241.
[4] K.T. Ranjit, B. Viswanathan, J. Photochem. Photobiol. A 108 (1997) 79.
[5] M. Schuisky, A. Harsta, A. Aidla, K. Kukli, A. Keisler, J. Electrochem. Soc. 147 (2000) 3319.
[6] H. Kominami, S.-Y. Murakami, J.-I. Kato, B. Ohtani, J. Phys. Chem. B 106 (2002) 10501.
[7] B. Ohtani, S.W. Zang, S. Nishimoto, T. Kaguja, J. Photochem. Photobiol. A 64 (1992) 223.
[8] R. Krol, A. Goossen, J. Scoonman, J. Electrochem. Soc. 144 (1997) 1723.
[9] T. Moritz, J. Reiss, K. Dresner, D. Su, A. Chemseddine, J. Phys. Chem. B 101 (1997) 8052.
[10] L. Kavan, M. Gratzel, S.E. Gilbert, H. Scheel, J. Am. Chem. Soc. 118 (1996) 6719.
[11] H. Gerischer, A. Heller, J. Phys. Chem. 95 (1991) 5261.
[12] S. Sato, J. Phys. Chem. 87 (1983) 3531.
[13] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[14] W. Choi, A. Termin, M.R. Hoffmann, J. Phys. Chem. 98 (1994) 13669.

[15] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.
[16] N. Negishi, K. Takeuchi, T. Ibusuki, J. Mater. Sci. 33 (1998) 5789.
[17] Y. Tanaka, J. Ceram Soc. Jpn. 107 (1999) 47.
[18] A.R. Gandhe, Thesis, Goa University, July 2004.
[19] R.A. Spurr, H. Myers, Anal. Chem. 29 (1957) 760.
[20] M. Schuisky, A. Harsta, S. Khartsev, A. Grishin, J. Electrochem. Soc. 147 (2000) 3319.
[21] B. Oregan, M. Gratzel, Nature 353 (1991) 737.
[22] T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki, Y. Taga, Jpn. J. Appl. Phys. 40 (2001) L561.
[23] Y. Aita, M. Komatsu, S. Yin, T. Sato, J. Solid State Chem. 177 (2004) 3235.