

A simple method to synthesize visible light active N-doped anatase (TiO₂) photocatalyst

Aditi R. Gandhe* and Julio B. Fernandes

Department of Chemistry, Goa University, Talegao Plateau, Goa 403206

Abstract : This paper discusses a simple route to synthesize an N-doped anatase titania. While titanium tetra-isopropoxide was used as the source of Ti, urea was used as the nitrogen source. The catalyst showed visible light absorption as evident from the DRUV-VIS spectrum and was found to be an active photocatalyst in sunlight.

Keywords: TiO₂, N-doping, anatase, rutile, photocatalyst

Email. aditigandhe@rediffmail.com

There is an increasing interest in the synthesis of N-doped TiO₂ photocatalysts and related areas as these narrow band gap semiconducting materials can be used for visible light photocatalysts. While Asahi et al. [1] reported the synthesis of N doped titania in 2001, by the sputtering of TiO₂ targets with nitrogen and argon gas mixtures, there have been several reports thereafter which have discussed several ways to synthesize the same. N-doped titania has been synthesized via sputtering techniques [2], CVD [3] as well as mechanochemical mixing of titania with ammonium carbonate [4], via a solvothermal process using TiCl₃-hexamethylamine-alcohol solution [5]. It has also been synthesized via a hydrazine precursor route [6]. However all these processes either require a special apparatus for synthesis or require tight control of experimental conditions. While all these methods brought about the incorporation of N in the lattice, there is no clear indication about the mechanism of the same. Sathish et al [7] have recently reported the synthesis of N-doped titania using TiCl₃ and ammonia, along with Na₂S, wherein Na₂S functioned as a reducing agent and was found crucial for N-doping.

We have recently reported the synthesis of an N-doped titania (R2) of rutile phase by a simple process using TiCl₃ and urea as the source of Ti and N

respectively [8]. The presence of the Ti-N bond was confirmed by XPS analysis (peak at ~397 eV). The sample thus synthesized was yellow in colour, showed excellent absorption in the visible region and was an active photocatalyst in sunlight.

Here, we describe a simple method to synthesize an N-doped anatase TiO₂ (A2) catalyst by use of titanium tetraisopropoxide (TIP) as the source of Ti instead of TiCl₃ as reported for the rutile sample (R2). Synthesis involved mixing calculated quantities of TIP and urea such that the Ti: Urea ratio in the final solution was 1:2. This solution was then evaporated to dryness on a steam bath. The dry residue was transferred to a horizontal muffle furnace and heated at 400 °C for 4h to obtain the final sample. The crystal phase was determined from the XRD pattern recorded on a Shimadzu Lab-X 700 diffractometer. Fig. 1 shows the XRD pattern of A2 in comparison to R2, the N-doped rutile sample. A2 was confirmed to be of the anatase phase and was yellow in colour.

The diffuse reflectance spectra, of the samples was measured using UV-VIS spectrophotometer (Shimadzu UV-2450). Fig. 2 gives DRUV-VIS spectra of the R1, R2 and A2 catalysts. Where R1, is a blank sample prepared using just acidified TiCl₃ without urea. Thus, A2 in addition to being yellow in colour also

exhibited good visible light absorption as was seen from Fig 2. The N₂ adsorption and desorption isotherms

were collected at -196 °C on a Quantachrome Autosorb 1 sorption analyzer.

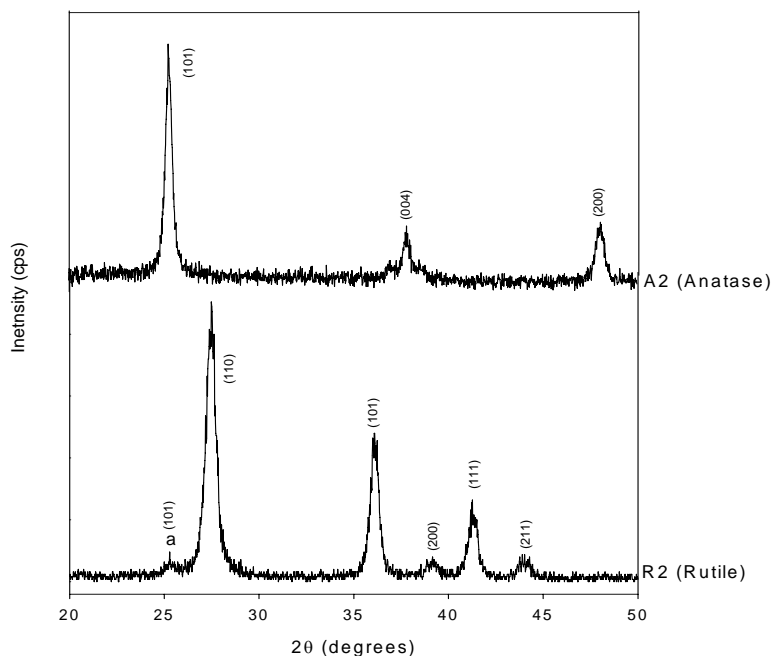


Fig. 1 XRD patterns of A2 (anatase) and R2 (rutile), where ‘a’ symbolizes the presence of anatase in the rutile sample R2.

The specific surface area was calculated using the BET model and was found to be 58 m²/g and 36 m²/g for A2 and R2 respectively.

The photocatalytic activity of the catalysts was evaluated using methylene blue (MB) degradation as a test reaction. The experiment was carried out simultaneously in bright sunlight for 120 min, between 10.00 am to 12.00 noon. 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 clear supernatants was determined at 660 nm wavelength against appropriate blanks. Fig. 3 shows the methylene blue degradation profiles of A2, R2, and R1. As seen from Fig. 3, the N-doped anatase as well as rutile sample showed complete dye degradation in 120 min. The rate of degradation was found to be higher in the anatase sample A2. The catalyst R1 prepared without urea, was found to be photocatalytically inactive. The band gaps of R2 and A2 were calculated by the equation

$$E_g = 1239.8/\lambda \quad [9]$$

where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edges in the spectrum. The band gap for

A2 and R2, as calculated for the absorption edge in the visible region was found to be 2.25 eV and 2.35 eV respectively. Thus, the lowered band gap of rutile could lead to a certain extent of

a higher electron-hole recombination in R2 in comparison to A2. This in addition to the comparatively larger surface area of the anatase A2, could be responsible for its slightly higher rate of degradation

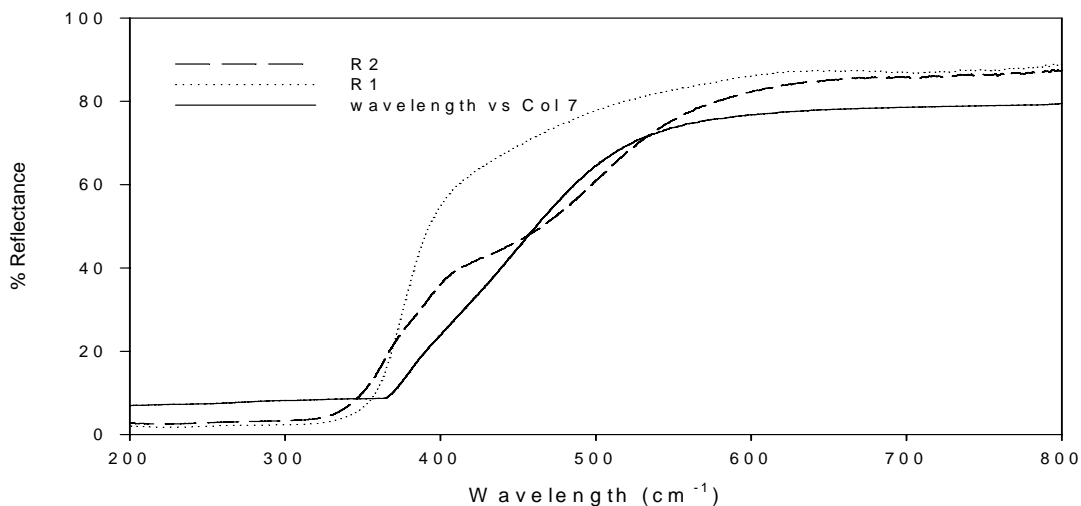


Fig. 2 Diffuse Reflectance Ultraviolet-Visible Spectra of A2 (anatase) and R2 (rutile)

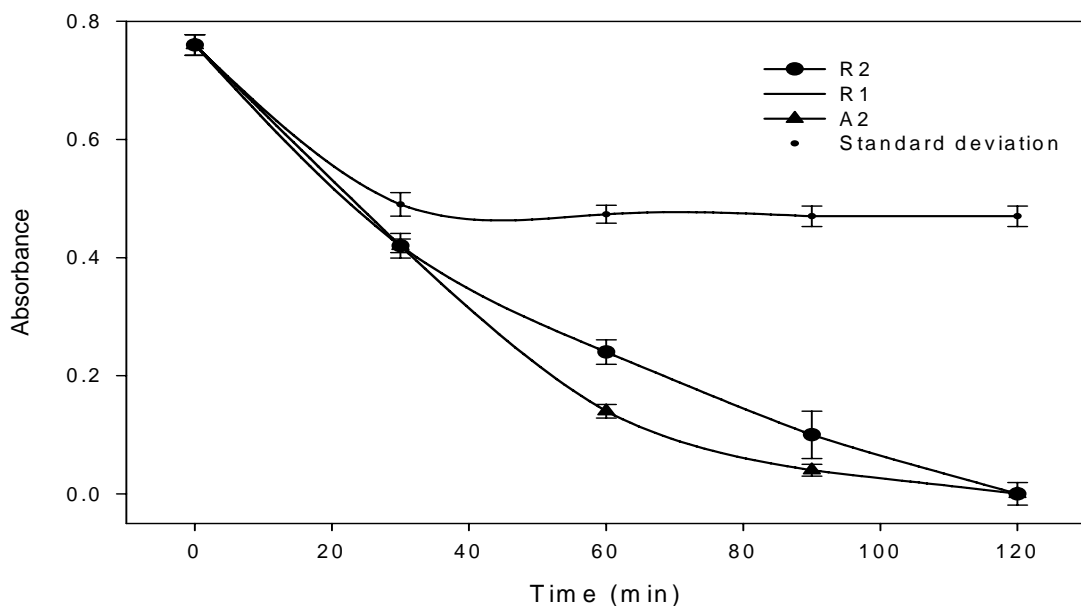


Fig. 3 Methylene blue degradation in sunlight over the catalysts A2 and R2, with 0.4 g of catalyst/100 ml of 10^{-4} M dye solution, duration 120 min (10 am to 12 noon), pH 7.5 (each point is an average value from three or more experiments, the vertical lines represent the error associated with each reading expressed as standard deviation)

In conclusion we found that N-doped anatase titania could be prepared by a simple method using titanium tetraisopropoxide and urea.

Acknowledgement

The research work was sponsored by UGC New Delhi, vide F-540/04/DRS/2002 (SAP-III) and the DST-FIST research fund 2004 (New Delhi).

References

1. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 293 (2001) 269.
2. T. Lindgren, J. Lua, A. Hoel, C-G. Granqvist, G. Romualdo Torres, S-E. Lindqvist, *Solar Energy Materials and Solar Cells* 84 (2004) 145
3. Y. Suda, H. Kawasaki, T. Ueda, T. Ohshima, *Thin Solid Films* 453 (2004) 162
4. S. Yin, H. Yamaki, Q. Zhang, M. Komatsu, J. Wang, Q. Tang, F. Saito, T. Sato, *Solid State Ionics* 172 (2004) 205
5. Y. Aita, M. Komatsu, S. Yin and T. Sato, *J. Solid State Chem.* 177 (2004) 3235
6. K.S. Rane, R. Mhalsikar, T. Sato, S. Yin, K. Cho, E. Dunbar and P. Biswas, *Proceedings, ISCAS-2005*, Pg. 28
7. M.Sathish, B.Viswanathan, R.P.Viswanath and C. S.Gopinath, *Chem. Mater.* 17 (2005) 6349
8. A.R. Gandhe and J.B. Fernandes, *J. Solid State Chem.* 178 (2005) 2953
9. B.O. Regan, M. Gratzel, *Nature*, 353 (1991) 737.