

Diethanoleamine Modification for High Temperature Stable Titanium Dioxide

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ABSTRACT

The nanocrystalline TiO₂ exhibits in different forms of anatase, rutile and brookite. Control of the structure of TiO₂, in particular the anatase to rutile phase transformation, is highly important because the performance of this material for a definite application depends on the phase structure (*e.g.* anatase is more preferred for photocatalytic application than rutile). In this study the effect of diethanoleamine (DEA) modification on anatase to rutile transformation is systematically studied by preparing different molar ratio samples of titanium isopropoxide and DEA. The material has been characterised with XRD, FTIR spectra, Raman and BET surface area measurements. As the molar concentration of diethanoleamine increased from 0 to 1 the transformation temperature is decreased from 700° C to lower temperature as low as 500° C.

KEY WORDS: Nanocrystalline TiO₂, anatase, diethanoleamine, rutile, brookite.

1. INTRODUCTION

Nanocrystalline TiO₂ has various applications in the fields such as catalysis, photocatalysis, photovoltaic, electrochromic display device, gas sensors *etc.* Titania exhibits in three different forms anatase, rutile and brookite. Most research work has been carried out with either the rutile or anatase phase, since these two phases are considered to be more useful for practical applications due to the easiness in synthesis. The rutile TiO₂ is more important for applications such as capacitors, in paint *etc* due to its high refractive index and high density in comparison to anatase TiO₂. anatase phase is more important than rutile for photocatalytic applications because anatase exhibits a higher photocatalytic performance compared to rutile. Therefore the control of the microstructure of titania, in particular the anatase to rutile phase transformation, is highly important because the performance of this material for a definite application depends on the phase structure.

Doping with metal cations in TiO₂ can be a useful way to control the phase transformation in TiO₂. The effect of metal ion doping on anatase to rutile transformation was studied extensively. Various main group metal ions (Al, Si) and transition metals ions (Ce, Cu, Ta, Nb, Sb, Zn, Pt, Ni, Fe, La) were studied as dopants to increase/decrease the anatase phase stability. In addition to metal doping, chemical modification method is also used to control the anatase to rutile transformation. In comparison with conventional method of metal ion doping, it avoids secondary impurity phase formation, uses low cost chemicals and facilitates an easy synthetic route. Chemical modification of titanium isopropoxide using non-metallic and low cost precursors such as urea, ammonium sulfate, sulfuric acid were already been studied on the anatase phase stability and photocatalytic activity.

Literature studies showed that diethanolamine was mainly used as a stabilising/chelating agent in sol-gel synthesis for the preparation of TiO₂ thin films on different substrate such as glass. This thin film fabrication was performed using dip/spin coating in the presence of various alcohol solvent such as polyethylene glycol, ethanol *etc* and studied the applications of such films in the fields of electrochromics, photovoltaics and photocatalysis. However, there is no systematic study reported on the dependence of diethanolamine on the phase transformation temperature of TiO₂ of such diethanolamine modified TiO₂. Here we are reporting a systematic study which describes the influence of diethanoleamine modification on the anatase to rutile transformation by taking different molar ratio of titanium isopropoxide and diethanoleamine precursors and its application in dye sensitized solar cells.

2. EXPERIMENTAL METHOD

The reagents used in this study were titanium isopropoxide (Aldrich) and diethanoleamine (Aldrich). In a typical experiment to synthesise 1:0.1 titanium isopropoxide: diethanoleamine solution, 1 mL of diethanoleamine was added to 29.7 mL titanium isopropoxide (Ti(OPr)₄) with constant stirring. To above solution 14.4 mL of water (8 mole times) was then added slowly as drop wise by continuing the stirring. 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 hrs. The dried powder was calcined at 400, 500, 600, 700 and 800 °C. An identical procedure was adopted to synthesise 1:0.5 and 1:1 (titanium isopropoxide:diethanolamine) samples. The samples were named as TD 0.1, TD 0.5 and TD 1. The TD

1 sample formed a highly viscous gel, hence the further modification is not carried out. A control sample (TD 0) without any diethanolamine was also prepared to compare the results.

The FTIR spectra of the gel dried at 80 °C was measured by using a spectrum GX-FTIR spectrophotometer in the wave number range 4000-400 cm⁻¹ using 70 scans per sample. The XRD patterns of the calcined gels were obtained with a Siemens D 500 X-ray diffractometer in the diffraction angle range 2 theta = 10–70° using CuK_α radiation. The amount of rutile in the sample was estimated using the Spurr equation (equation 1).

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

Where, F_R is the mass fraction of rutile 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 2 hrs at 200 °C.

3. RESULTS AND DISCUSSION

3.1. FTIR Analysis: The FTIR spectra of the samples dried at 80 °C was recorded to study the interaction between the titanium isopropoxide and diethanolamine. The Fig. 1 showed the FTIR of the control (TD 0) and diethanolamine modified (TD 0.1, TD 0.5 and TD 1) samples. All of them showed the bands around 1600 cm⁻¹ and 3500 cm⁻¹ are due to the presence of water. The 1600 cm⁻¹ indicates bending mode vibration and 3500 cm⁻¹ is the stretching mode vibration of hydroxyl group. The bands coming in the range 1300-1500 cm⁻¹ and 2800-3000 cm⁻¹ are usually due to organic moieties present in the compound. In this range there are three main peaks present at 1447, 1360 and 2800 cm⁻¹. These peaks are due to the ethyl and isopropyl groups. In control and lower amount of the diethanolamine modified sample (TD0 and TD 0.1) the peak at 2800 cm⁻¹ is not much visible, however it is more clear in the 1:0.5 and 1:1 samples indicating more diethanolamine is co-ordinated to the titania framework. The most important peak here is the peak at 1080 cm⁻¹. Usually the C-O stretching bond of pure diethanolamine appears at 1111 cm⁻¹. Here this band is shifted to 1080 cm⁻¹ due to the formation of Ti-O-C bond by the interaction between titanium isopropoxide and diethanolamine. As the molar concentration of diethanolamine increases from 0.1 to 1, this peak intensity also increases (Fig. 1) and there is no such peak is visible in the control sample. This is a strong evidence for the interaction of titanium isopropoxide and diethanolamine.

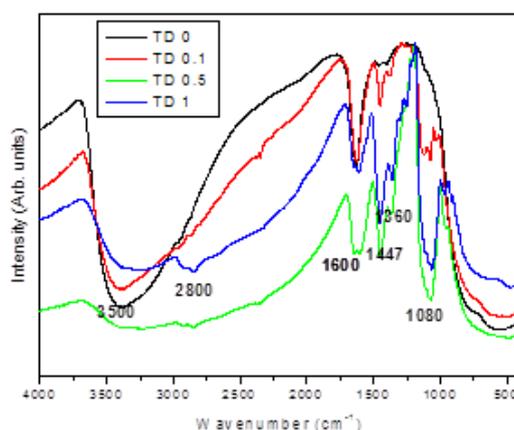


Figure.1. FTIR spectra of the titania gels dried at 80 °C a) control b) TD 0.1 c) TD 0.5 and d) TD 1

3.2. XRD analysis: The weight fraction of the rutile found in the sample was calculated by comparing the XRD integrated intensities of (101) reflection of anatase and (110) reflection of rutile as indicated by equation 1 in section 2. The Fig. 2 indicates the rutile percentage Vs calcination temperature for control and diethanolamine modified sample. All the samples heated up to 400 °C show only anatase phases (Fig. 2). The 500 °C heated samples show the presence of rutile phase in the case of TD 0.5 and TD 1, whereas the control and lower diethanolamine modified TD 0.1 sample showed complete anatase phase (Fig. 2 and 3). Rutile formation is drastic in the case higher concentration of diethanolamine modified samples above 400 °C. For example at 500 °C the TD 0.5 and TD 1 sample shows 24% and 41% rutile respectively (Fig. 2). The TD 1 sample showed the complete rutile at a temperature as low as 600 °C whereas the control one shows anatase content of 83% (Fig. 2).

The TD 0.1 shows 29% and TD 0.5 shows only 93% of rutile at 600 °C. At 700 °C calcined all the diethanoleamine modified samples are converted to rutile phase whereas the control one shows even 7% anatase (Fig. 2). At 800 °C the control sample also converted to rutile phase. As a summarization of XRD results the diethanoleamine modified samples showed a significant amount of decrease in transformation temperature of anatase to rutile. As the molar concentration of diethanoleamine increased from 0 to 1 the transformation temperature is decreased from 700 °C to a lower temperature as low as 500 °C.

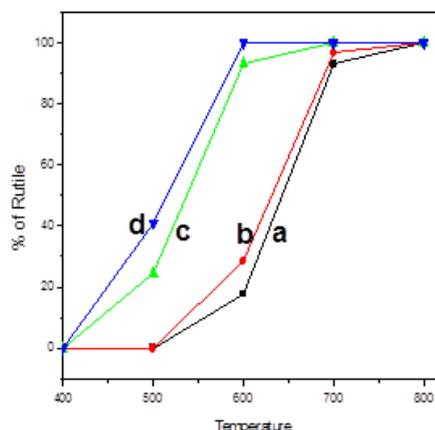


Figure.2. Rutile content in the samples calcined at various temperatures a) control b) TD 0.1 c) TD 0.5 and d) TD 1.

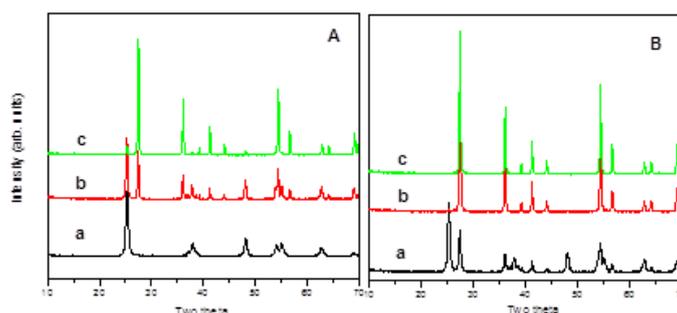


Figure.3. XRD spectra of A) control and B) diethanoleamine modified TiO_2 at a) 500 b) 600 and c) 700 °C.

3.3. Raman Spectroscopy: Raman spectroscopy was applied as an additional tool to study the phase formation of control and diethanoleamine modified sample. Fig. 4 indicates the Raman spectra of the control and diethanoleamine modified sample calcined at 600 °C. The control (Fig. 4a) shows anatase peaks at 197 cm^{-1} , 399 cm^{-1} , 513 cm^{-1} and 639 cm^{-1} and a strong rutile peak at 449 cm^{-1} . The diethanoleamine modified sample TD1 (Fig. 4b) shows a strong peaks at 231 , 449 , 612 cm^{-1} which are the characteristic peak of rutile phase indicates that all anatase is converted to rutile at 600 °C. These Raman results are in consistent with the XRD results.

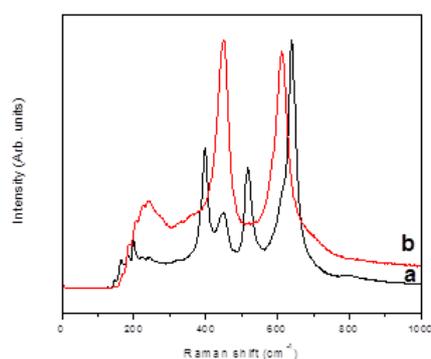


Figure.4. Raman spectra of the sample calcined at 600 °C a) control and b) TD 1.

3.4. BET analysis: 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 control and TD 1 samples are type IV-like in their behaviour. There is no previous reports available for the surface area measurement of the diethanoleamine modified samples. Since the rutile formation is taken place at 500 °C itself in the case of TD 1 modified sample, surface area should reduce for the diethanoleamine modified sample. Here the diethanoleamine modified sample shows only 32 m²/g and control shows 35 m²/g. Anatase crystallites are completely grown at 500 °C in the case of diethanoleamine modified sample and crystals are already converted to rutile phase having higher crystal size and density. These two factors will decrease the surface area.

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

Material	Surface area (m ² /g)	Average pore diameter (nm)
control	35	2.1
TD 1	32	2.1

4. CONCLUSIONS

Effect of diethanoleamine modification on anatase to rutile phase transformation has studied systematically. The materials has been characterised by XRD, BET, FTIR and Raman spectroscopy. The study showed that diethanoleamine modification lowered the anatase to rutile transformation temperature. The 1:1 molar ratio sample showed presence of rutile phase as low as 500 °C and completely transferred to rutile phase at 600 °C whereas the control sample prepared without diethanoleamine showed complete rutile only at 800 °C.

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