

## Unlocking the Secrets Behind the Resin-Gel Synthesis for the Controlled Formation of Anatase and Rutile

P. J. Franklyn\*, A. Narrandes†

*Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, WITS, 2050, South Africa*

(Received 23 June 2012; published online 13 August 2012)

Resin-gel synthesis has the ability to become a powerful technique for the synthesis of multi-phase nanoparticles. This study aimed to take further steps into investigating the mechanism of the resin-gel synthesis based on phase differentiation of titania, in the hope to describe optimal synthetic conditions for desired polymorph production with tailored particle size. Solvent, polymer chain length, heating rate and the use of citric acid has been varied previously. The results obtained suggested that the working theory of the resin-gel synthesis may be incorrect as there was significant phase differentiation based on the solvent used. This work explored the effects of the stoichiometric ratio of PEG to  $\text{TiCl}_4$  and the effect of heating rates to clarify the reaction mechanism.

**Keywords:** Titania, Resin-Gel, PEG, XRD, TEM, Flame Synthesis.

PACS numbers: 61.46.Hk, 61.05.C –

### 1. INTRODUCTION

The resin-gel synthesis technique is a modification of the Pechini method for the fabrication of nanomaterials. It involves the addition of a long chain polymer to a stable solution of metal ions within a solvent matrix to form a polymeric resin [1]. It has been shown in previous research that the choice of solvent plays a role in determining the eventual products of the synthesis, even though the solvent is not present during the final burning stage when the particles are formed. The choice of ethanol leads almost exclusively to the formation of anatase, while using water with nitric acid leads to a mix of anatase and rutile dependent on the molecular weight of the polymer that is used. In addition it has been determined that the addition of citric acid to the solvent matrix leads to the almost exclusive formation of anatase.

The accepted working theory has been that the metal ions coordinate to the polymer initially and, following complete solvent evaporation, are then agglomerated into nanoparticles during flame synthesis of the reaction mixture [1]. Previous work we have performed has shown that this may not be the correct mechanism and that the formation of local clusters of metal ions that are coordinated by the solvent and any other species present in the liquid medium followed by coordination of these clusters to the polymer is a more likely mechanism.

Although relatively unexplored, resin-gel synthesis affords the opportunity to synthesize a multi-phase material using a single reaction step. This is in contrast to most other synthesis methods that invariably produce the phase corresponding to a global energy minimum. Hence, it has the potential to become a much sought after, powerful technique for the fabrication of a wide range of multi-phase nanomaterials.

Titanium dioxide is a well understood material. Phase transition temperatures, abundance, stability and many other properties have been extensively stud-

ied and reported [2]. In addition, its nanoparticulate form has found numerous applications in the field of photocatalysis, photovoltaics and sensors [3 -5]. The most common and stable phase of titania is rutile followed by anatase and then brookite [2]. Numerous literature reports state that under the correct conditions of temperature and/or pressure, anatase and brookite will irreversibly convert to rutile – the thermodynamically stable polymorph [6 – 9]. This conversion property of  $\text{TiO}_2$  makes it an ideal candidate on which to model the resin-gel synthesis technique to produce multi-phase titania in a single sample.

The primary aim of this study was to further advancements into understanding the mechanism of operation of the resin-gel synthesis. This task was undertaken by considering the effect of changing some of the parameters that influence the resin-gel synthesis method. Using a  $\text{TiCl}_4$  precursor, the heating rate and the stoichiometric amount of polymer relative to the amount of  $\text{TiCl}_4$  at several PEG chain lengths was explored. The data generated from these variations allowed for the refinement of the new, proposed mechanism of resin-gel synthesis.

### 2. EXPERIMENTAL PROCEDURE

#### 2.1 The effect of PEG stoichiometry

To accommodate for the large quantities of PEG to be included in the reaction mixture, two batch solutions of  $\text{TiCl}_4$  in water were prepared. The first involved the addition of 6.0 ml of  $\text{TiCl}_4$  (0.055 mol) to excess distilled water (144 ml). Concentrated nitric acid (12 ml) was then added to aid solubility of  $\text{TiCl}_4$  in water. The resulting solution was split into six equal parts and half the stoichiometric quantity of PEG of different chain lengths was added to each such that the mole ratio of  $\text{TiCl}_4$ :PEG equalled 1:0.5. The actual quantities of PEG added to each solution are given in Table 1.

\* [Paul.Franklyn@wits.ac.za](mailto:Paul.Franklyn@wits.ac.za)

† [Ashvir.Narrandes@students.wits.ac.za](mailto:Ashvir.Narrandes@students.wits.ac.za)

For the second batch solution\*, 1.5 ml of  $\text{TiCl}_4$  (0.014 mol) was added to 36 ml excess distilled water followed by 3 ml of concentrated nitric acid. After the solution had been split into 3 equal parts, half the stoichiometric amount of PEG was added to each solution as given in table 1.

**Table 1** – Amounts of PEG of varying molecular weight used for synthesis in a 1:0.5 stoichiometric ratio with  $\text{TiCl}_4$ . PEG marked with a \* came from a second batch.

Average polymer molecular weight /g.mol <sup>-1</sup>	Theoretical amount required for stoichiometry /g	Actual amount used /g
200	0.92	0.918
400	1.84	1.91
1500	6.885	6.92
3000	13.77	13.50
4000	18.20	18.20
6000	22.22	22.28
8000	36.72	36.72
10000*	22.75	22.86
12000*	27.30	27.30
20000*	45.50	45.77

For the synthesis of the stoichiometric equivalent ratio ( $\text{TiCl}_4$ :PEG in a 1:1 ratio), two batch solutions were prepared for the same reason described above. For the first batch,  $\text{TiCl}_4$  (2.5 ml, 0.023 mol) was added to 60 ml distilled water and 5 ml of concentrated nitric acid was then introduced. The actual amount of polymer added to each solution is given in Table 2.

The second batch<sup>‡</sup> involved the addition of 0.75ml of  $\text{TiCl}_4$  (6.8 mmol) to 18 ml of distilled water followed by 1.5 ml of concentrated nitric acid. Appropriate amounts of different molecular weight PEG were then added to the three equally divided solutions (table 2).

Each mixture mentioned above was stirred and heated sufficiently to ensure complete homogeneity; and prepared in duplicate to allow for two different heating rates prior to fame synthesis.

**Table 2** – Amounts of PEG of varying molecular weight used for synthesis in a 1:1 stoichiometric ratio with  $\text{TiCl}_4$ . PEG marked with ‡ came from a second batch

Average polymer molecular weight /g.mol <sup>-1</sup>	Theoretical amount required for stoichiometry /g	Actual amount used /g
200	0.92	0.92
400	1.84	1.89
1500	6.885	6.87
3000	13.77	13.50
4000	18.20	18.20
6000	22.22	22.29
8000	36.72	36.72
10000‡	22.75	22.76
12000‡	27.29	27.490
20000‡	45.48	45.21

## 2.2 Variation in the heating rate

Following the complete evaporation of excess solvent from each polymer mixture, two different heating methods were used to engage flame synthesis of the polymer.

The first method involved the conventional heating of the polymer mixture. Each mixture was added into a crucible. The crucible was placed in a sand bath (so as to ensure uniform heating) and heated until each mixture had reached its auto-ignition point. A flame source was then used to ignite each sample. The black appearance of the samples suggested that a carbon coating had been deposited onto the nanoparticles, hence each sample was allowed to cool before being calcined in a muffle furnace at 773 K for one hour.

The second heating method involved heating a cast iron vessel to 1173 K in a muffle furnace. Following complete evaporation of excess solvent from each mixture, the molten polymer gel was added to the vessel. As was expected, due to the high temperatures, the polymer samples spontaneously ignited on account of them passing their flash points. The excessive temperatures also promoted the calcination of each sample immediately following polymer pyrolysis.

## 2.3 Characterization and Analysis

PXRD and TEM were used as the main forms of characterization techniques to deduce the presence of the different phases and particle sizes of titania.

A Bruker D2 Phaser diffractometer using Co K $\alpha$  radiation in conjunction with a 0.6 mm slit and primary and secondary soller slits at 2.5°. A LYNXEYE® detector was used with this diffractometer. Each sample was placed on a zero background sample holder and analysed between 20° and 60° 2 $\theta$  angles in increments of 0.026°. TEM analysis was used to confirm the data obtained using XRD. A Tecnai F20 at 200 kV was employed for this task.

The Spurr and Myers equation was used to determine the mass per cent of anatase and rutile produced in each sample synthesised. The equation considers the intensities of the anatase (101) and rutile (110) peaks and has an inherent 5 % error by mass. Particle size analysis was performed using the instrumentally corrected Scherrer equation with K = 0.91.

## 3. RESULTS AND DISCUSSION

It should be noted here that crystallite size data was only obtained from samples that showed significant amounts of either polymorph. Using the current data extraction method for crystallite size analysis, a significantly non-intense peak was difficult to analyse for crystallite size and phase composition data.

### 3.1 Conventional heating

Figures 1 and 2 compare the mass per cent of anatase and rutile formed across a range of PEG molecular weights at different mole ratios using the conventional heating rate. Comparing these figures, it is apparent that the ratio of metal ions to PEG had a significant bearing on the phase that was produced. When half as much PEG was employed, the amount of rutile appeared to increase across the range of PEG chain lengths. However, when the mole ratio of PEG to Ti ions was the same, the amount of rutile decreased as a function of increasing polymer chain length. This effect may be explained in terms of a protecting effect inferred by the polymer on the forming nanoparticle. If this is thought

to be true then the greater the amount of polymer within any sample, the greater the protecting effect will be and the less likely anatase will convert to rutile.

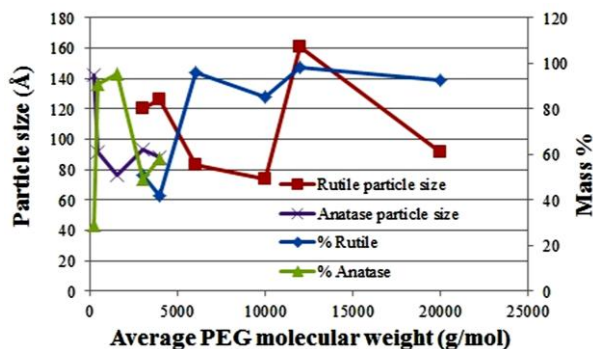


Fig. 1 – Variation of anatase and rutile mass per cent and particle size formed as function of increasing PEG molecular weight in a Ti:PEG 1:0.5 conventional heat synthesis

The amount of anatase formed does not exhibit a similar trend. In figure 2, it is clear that the amount of anatase formed across the range of PEG molecular weights first increases then decreases. Longer chain lengths promote the formation of anatase.

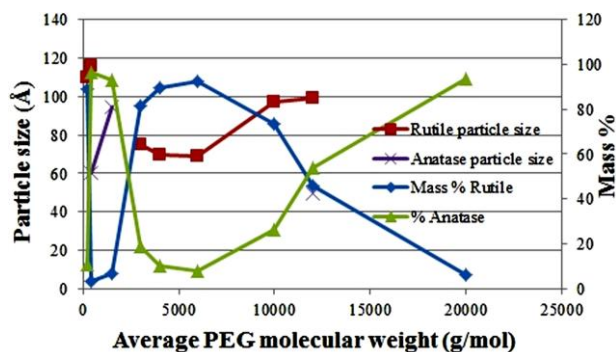


Fig. 2 – Variation of anatase and rutile mass per cent and particle size formed as function of increasing PEG molecular weight in a Ti:PEG 1:1 conventional heat synthesis

The relationship between particle size and the amount of each phase formed was interesting. For both anatase and rutile, larger particles were formed when the amount of that particular phase was lower for a given sample. This inverse relationship may serve as a means to refine a component of the mechanism of the resin-gel synthesis in the following manner: it is assumed that during the burn process, reaction chambers are formed that contain the developing nanoparticle. These chambers are governed by the size of the polymer chain post flame induced scission. The size of the chamber will govern the size of the nanoparticles. If there is very little space, only anatase will form. Given the small, cubic nature of the particles (as witnessed in HRTEM – figure 3) it is possible that these anatase particles will form in great numbers.

This will result in large amounts of small anatase particles being formed. If however, the reaction chamber is larger, anatase will convert to rutile nanorods (figure 4A). If the chamber is bigger still, the formed nanorods will cluster together around a single crystal axis into a ball (figure 4B). Therefore, large rutile particles are formed in small numbers.

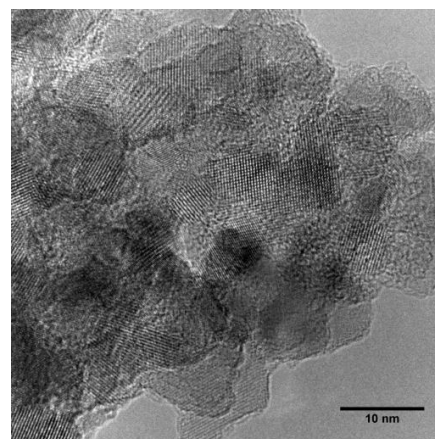


Fig. 3 – Anatase nanoparticles with approximate cubic morphology from short-chain PEG synthesis

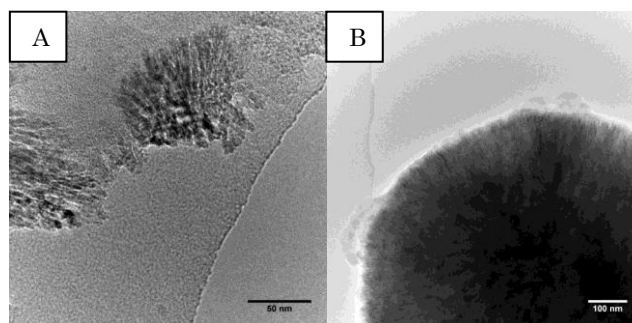


Fig. 4 – A) Rutile particles forming nanorods. B) Rutile nanorods clustering into a nanoball

As was expected, particle size increased dramatically post-calcination (figures 5 and 6). This is due to particles sintering together into larger clusters. Calcination also had the effect of converting some of the formed anatase particles into rutile. This result was also expected.

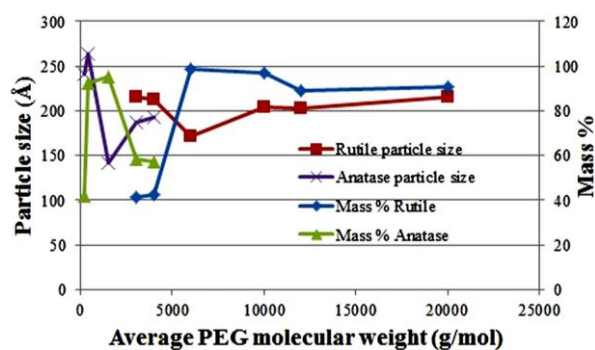


Fig. 5 – Variation of anatase and rutile mass per cent and particle size formed as a function of increasing PEG molecular weight in a Ti:PEG 1:0.5 conventional synthesis (post-calcination)

### 3.2 Rapid heating

Figures 7 and 8 depict the changes in mass percentage and particle sizes formed during the rapid heat synthesis at two different metal ion:PEG ratios.

Figure 7 shows an interesting trend with regard to the amount of rutile formed as a function of increasing molecular weight. There appears to be an oscillating trend whereby some chain lengths produce more rutile

and others less. It is thought that scission of the chain occurs at specific points for different polymers depending on the length of the chain used in the synthesis.

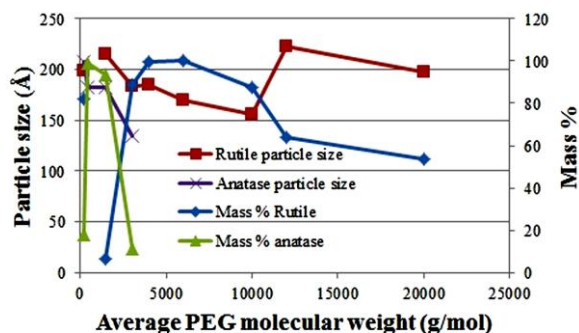


Fig. 6 – Variation of anatase and rutile mass per cent and particle size formed as function of increasing PEG molecular weight in a Ti:PEG 1:1 synthesis (post-calcination)

The inverse trend of particle size and the mass percentage of each phase formed was again observed and pronounced for rutile. Figure 7 also shows a clear trend of the size of each polymorph as a function of polymer chain length. Figures 7 and 8 show that rutile particles were larger than anatase particles. This, together with the oscillating trend observed for rutile may be rationalised in terms of the reaction chambers mentioned above. The clear trends observed from figure 7 are not witnessed in figure 8. While the inverse relationship between the amount of rutile and particle size formed was maintained, the oscillating nature described above was non-existent. From figure 8, the 8000 g/mol PEG produced a small amount of rutile in comparison to the other chain lengths.

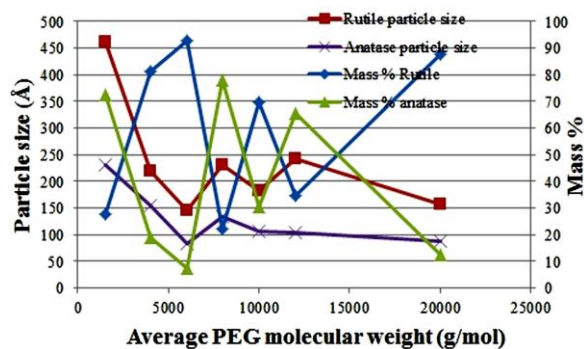


Fig. 7 – Variation of anatase and rutile mass per cent and particle size formed as a function of increasing PEG molecular weight in a Ti:PEG 1:0.5 rapid heat synthesis

## REFERENCES

1. J. Lin, M. Yu, C. Lin, X. Liu, *J. Phys. Chem. C* **111**, 5835- (2007).
2. X. Chen, S.S Mao, *Chem. Rev.* **107**, 2891 (2007).
3. M.R Hoffman, S.T. Martin, W. Choi, D.W. Wahneman. *Chem. Rev.* **95**, 69 (1995).
4. *Optoelectronics Properties of Inorganic Compounds* (Ed. D.M. Roundhill, J.P. Facker) (New York: Plenum: 1999).
5. G. Sheveglieri, *Gas Sensors* (Dordrecht: Kluwer: 1992).
6. Y. Hwu, Y.D. Yao, N.F. Cheng, C.Y. Tung, M.H. Lin, *Nanostruct. Mater.* **9**, 355 (1997).
7. X.Y. Ding, X.H Liu, *J. Mater. Res.* **13**, 2556 (1998).
8. H. Zhang, J.F Banfield, *J. Mater. Chem.* **8**, 2073 (1998).
9. X. Ye, J. Sha, Z. Jiao, L. Zhang, *Nanostruct. Mater.* **8**, 919 (1998).

The differences observed across the stoichiometric ratios may be attributed to the polymer affording protection to the forming nanoparticle, as mentioned.

Comparing figures 1 and 7, across the series of different polymer chain lengths, for the Ti:PEG in a 1:0.5 ratio, rutile formation is enhanced when the samples are burned according to the conventional method. A plausible explanation for this observation is that if the samples were heated rapidly, the formed anatase particles would not have sufficient time to cluster together and form rutile. If, however, they were heated slowly, the forming anatase would have sufficient time to react with other anatase particles, thereby forming larger amounts of rutile. A similar trend could not be obtained at the higher stoichiometric ratio (comparing figures 2 and 8).

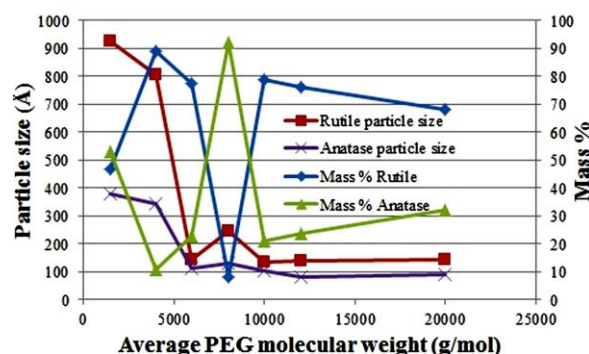


Fig. 8 – Variation of anatase and rutile mass per cent and particle size formed as a function of increasing PEG molecular weight in a Ti:PEG 1:1 rapid heat synthesis

## 4. CONCLUSION

The molecular weight and relative molar amount of PEG in the reaction mixture affect phase and particle size formation. The results indicate that the presence of large amounts of polymer protect the forming anatase particle, inhibiting its conversion to rutile. The reproducible trend of the inverse relationship between particle size and the mass percent of a respective phase lends support to the formation of reaction chambers, within which anatase forms and is allowed to convert to rutile in different ways, depending on the size of the chamber. A rapid ignition of the mixtures does not provide sufficient time for the conversion of anatase to rutile and so lends itself to the formation of anatase. No explanation is yet available for the large amount of rutile formed when a high mole ratio of PEG was employed and the ignition performed at a rapid rate. The sometimes random variation in rutile ratios is a factor that is still under investigation. Further work is also continuing to determine the crystallite size:rutile ratio relationship with respect to synthesis conditions.