

STUDY OF THE FORMATION OF MESOPOROUS TiO₂ USING ISOPROPOXIDE PRECURSORS UNDER LESS WATER CONDITIONS

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ABSTRACT

The role of the synthesis parameters (the molar ratio of template, isopropyl alcohol, acetylacetone, and water with respect to titanium(IV) tetraisopropoxide) has been thoroughly investigated to understand their effects on the mesostructures and the formation of crystalline phases of mesoporous titania xerogels in less water condition (no added water) at 60 °C. The resultant mesoporous titania are more likely to have worm-hole like structure as the dominant stable structure. The template appears to play no significant role in structure directing at mesophase level. However, increasing the amount of the template delays the formation of anatase crystalline phase

Keywords: mesoporous titania, templating synthesis, anatase, evaporation-induced self-assembly

INTRODUCTION

The successful preparation of mesoporous silica by combining sol-gel chemistry with self-assembly of the surfactant moiety continues to inspire work on transition-metal oxides. These materials have potential applications in photocatalysis, energy conversion, sensors, lasers, optoelectronics and photonics. In particular, mesostructured titania [1-14], zirconia [4,11,15-18], and niobia [4,19-21] are very interesting materials which have been extensively explored. In general, mesoporous metal oxides tend to have thermal stability problem. This issue arises from the relatively weak interaction of organic-inorganic moieties [2,3], the higher reactivity of Ti(IV) toward condensation compared to Si(IV) [12,13], incomplete condensation of the walls [5] and the excessive growth of metal polymorphs during heat treatment for surfactant removal [22]. Careful control of the parameters involved in the sol-gel chemistry and the self-assembly process is crucial to overcoming such problems, and hence to achieving high thermal stability of the mesostructure.

A number of researchers have taken advantage of liquid crystalline order in aqueous surfactant systems to synthesise titania with lamellar [5,10,12], cubic [10, 12], and hexagonal

[5,9,10,12] topology. Typically, monomeric species present in the aqueous phase polymerise to form an inorganic mesostructure with shape primarily determined by the organization of the surfactant/water self-assembly. Mostly, these workers used an evaporation-induced self-assembly (EISA) method [13,23], a versatile method to prepare mesostructured transition metal oxides films, combined with dip-coating [4,10,12] or spin-coating [9,24] as the deposition techniques onto the substrates.

In this work, we report the importance of controlling the synthesis parameters, in order to obtain stable mesostructures with complimentary discussion on the formation of anatase phase. The composite titania-based materials exhibit bicontinuous wormlike mesophases. The existence of Anatase after heat treatment at low temperature brings the interesting feature of titanium dioxide – block copolymer composite for the use as a wide-band gap semiconductor material.

EXPERIMENTAL SECTION

Sample Preparation

Titanium isopropoxide (TTIP, 97%, Aldrich) was used as the titanium source, and block copolymer Pluronic P123 was used as received from BASF as the template. A typical synthesis was slightly modified from Yun *et al.* [9] as follows: firstly 2.5 g of Pluronic P-123 were dissolved in 14 g isopropyl alcohol. This surfactant solution was

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then added into a clear solution of 3.24 mL of TTIP, 1.1 mL of acetylacetone and 16.7 mL of 2-propanol under vigorous stirring. Drops of HCl (32%, BDH) were subsequently added to adjust the pH of the solution after 2h stirring followed by further stirring for 3h before gelled at 60 °C for 72h. Some variations of the synthesis were designed to obtain the optimum parameters, such as the amount of the template, acetylacetone, isopropyl alcohol, in term of molar ratios with respect to TTIP. The template-to-TTIP molar ratio was varied from 0-0.2. The acetylacetone-to-TTIP molar ratio was varied from 0-5, and the 2-propanol-to-TTIP molar ratio was investigated from 30-300. In all cases one parameter was changed while the others were held constant. Template removal was carried out at 300 °C (heating rate of 1 °C/min) for 4h in a muffle furnace in air.

Characterisation

The crystal phase of the resultant materials as well as the long-range order of the mesostructure was analysed by wide-angle X-ray diffraction (WAXRD) and small-angle X-ray diffraction (SA-XRD), respectively on a parallel-beam optic XRD (Bruker). For the small-angle measurement, detector scans were performed with the angle between the source and the specimen stage set at 0.5°. Evaluation of surface area and pore size distribution was performed at 77K using a Quantachrome instrument, Autosorb-1. The samples were out-gassed overnight at 200 °C under vacuum, prior the measurement. The specific surface area and the pore size distribution were determined by using BET and BJH models for the desorption branch, respectively. TEM analysis was accomplished by using FEI Tecnai-20 200kV TEM. Gel flakes were grinded in acetone, and then a drop was dispersed on a holey Cu carbon grid. TGA analysis was performed to analyse the template removal behavior using a Shimadzu TGA-50 instrument. Samples were loaded on platinum pan, which was heated to 600 °C (heating rate 10 K/min) under airflow of 80 mL/min with nitrogen as the purging gas.

RESULTS AND DISCUSSION

Influence of reactants composition on the formation of Anatase-based meso-structured titania under anhydrous system at 60 °C

The effect of reactants composition on the formation of mesostructured titania as well as the formation of Anatase phase of titania was investigated in the system of 1TTIP:(0-0.2)P123:(0-28)acac:(28.37-300)propan-2-ol:0.015HCl. Fig. 1

depicts the small-angle diffraction patterns of the as-synthesized and calcined samples prepared at varied molar ratios of template to TTIP, acac to TTIP, and 2-propanol to TTIP. Typically, they had only single broad peak at low angles and slightly shifted to higher angles after calcination. This phenomenon reveals a pore system lacking long-range order and pore shrinkage after thermal treatment, respectively. In general, the peaks are more prominent after calcination, when the template has been burned out leaving opened pores behind. However, an optimum condition on each reactant composition, which is evidenced by the more distinct and intense the peak, was observed. We chosen a system with template-to-TTIP molar ratio of 0.025 – 0.05; acac-to-TTIP molar ratio of 0.025 – 1; and 2-propanol-to-TTIP molar ratio of 50. The right amount of the template used is important for the formation of mesopores. The higher or the lower the amount of template diminished directing effect to the formation of mesopores (Fig. 1A and B). While, under constant template concentration, acetylacetone appeared to have no significant effect in directing the formation of mesopores (Fig. 1C and D). However, increasing the amount of acetylacetone will over-hold titanium isopropoxide back to interact with the template, resulted in poorer mesopore order, as well as observed when raising the amount of 2-propanol in respect to TTIP (Fig. 1E and F). On the other hand, the formation of Anatase phase after calcination at low temperatures is interestingly influenced by the sol composition.

Figure 2 shows the wide-angle XRD patterns of mesostructured titania derived from retarded hydrolysis of titanium tetraisopropoxide (TTIP) under anhydrous acidic medium at 60 °C for 72h, followed by calcinations at 300 °C for 4h. It can be seen that the titania gels were successfully crystallized to the Anatase phase at relatively low temperature with only a minor brookite peak (noted by asterisk (*) in Fig.3). This results show that even in the anhydrous system, the presence of HCl induces the formation of Anatase phase, as has been observed on hydrous system without the presence of template [25,26]. In this case, the phase formation is greatly affected by the sol composition.

Template Effect

Primarily, the molar ratio of template to TTIP affects the rate of the formation of Anatase phase. The deferral of Anatase formation occurred at very low and very high amount of templates. It is reasonable that the presence of high amount of template tends to suppress the crystal growth.

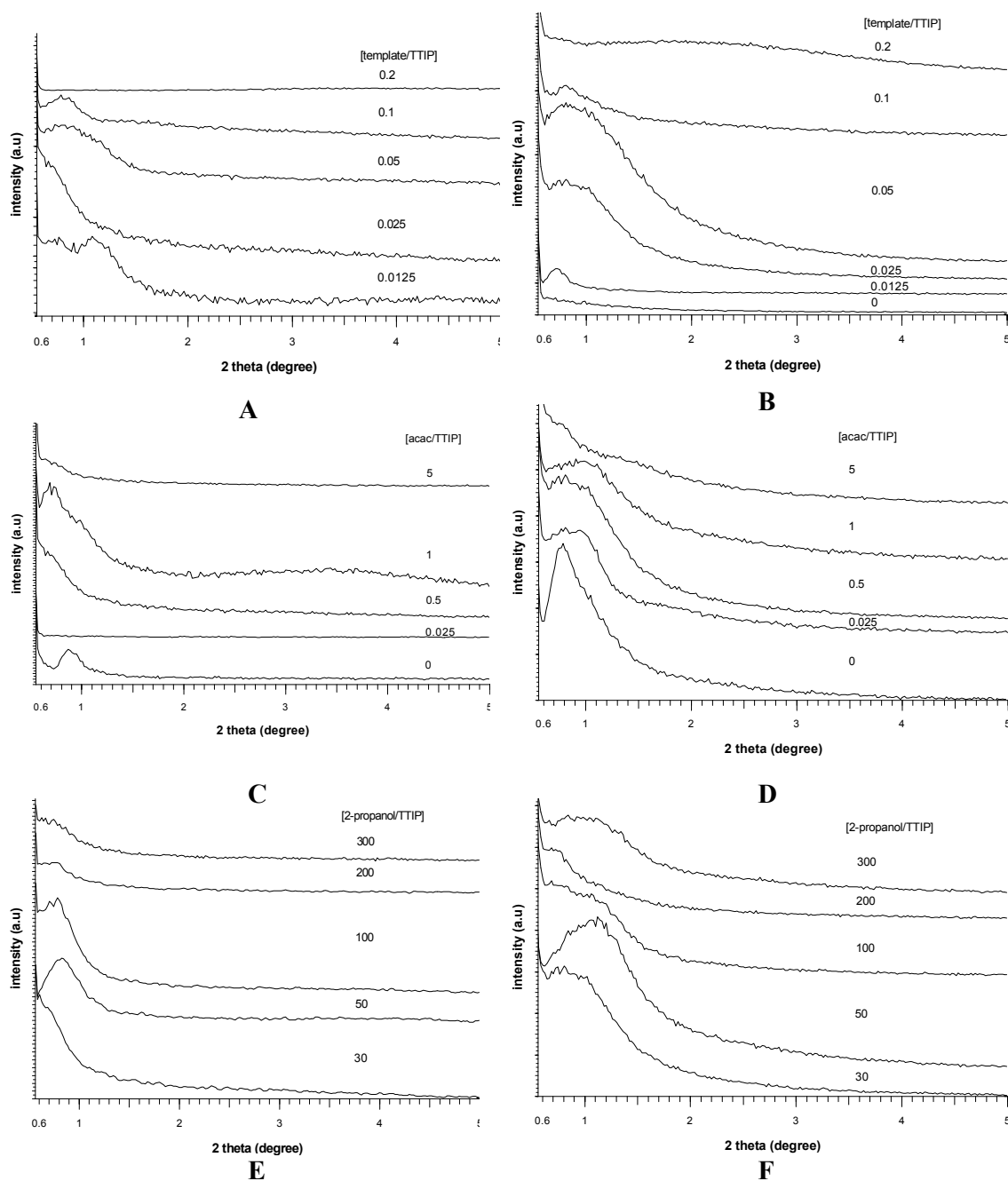


Fig. 1 Small-angle XRD patterns of mesoporous titania before (A,C,E) and after (B,D,F) calcination synthesized at different molar ratio of template to TTIP (A,B), acetylacetonate(acac) to TTIP (C,D), and 2-propanol to TTIP (E,F).

The primary titania particles were likely covered by the adsorbed block copolymer molecules and retarded from further crystal growth.

TEM image of calcined mesostructured titania prepared at molar ratio of template to TTIP 0.05, acac/TTIP 0.5, and 2-propanol to TTIP 30, is

presented in Fig. 3. It suggests the formation of worm-hole pore type of mesoporous titania and ordered structure with particle size of ~3.8-4 nm. The pore diameter is approximately between 3-3.8 nm. The particles are so overlapping, that causes difficulty to measure the right particle size or pore

diameter. However, the pore size range is in accordance with that measured by N_2 -adsorption/desorption analysis (Table 1). It can also be observed that the pores arise from interspaces between titania nanocrystallites.

Acetylacetonone Effect.

Meanwhile, there is also a limit in the molar ratio of acac to TTIP without significant effect to the

formation of Anatase. Increasing the concentration of acetylacetonone more than 1 tends to slow down the crystal phase formation. These limitations are in agreement with the limit observed for the formation of mesopore, as also have been observed by Ying and Antonelli [1]. The transparent solution of TTIP was turned yellow soon after the addition of acac. It suggests the formation of Ti-complex that makes the Ti-precursor to be bulkier.

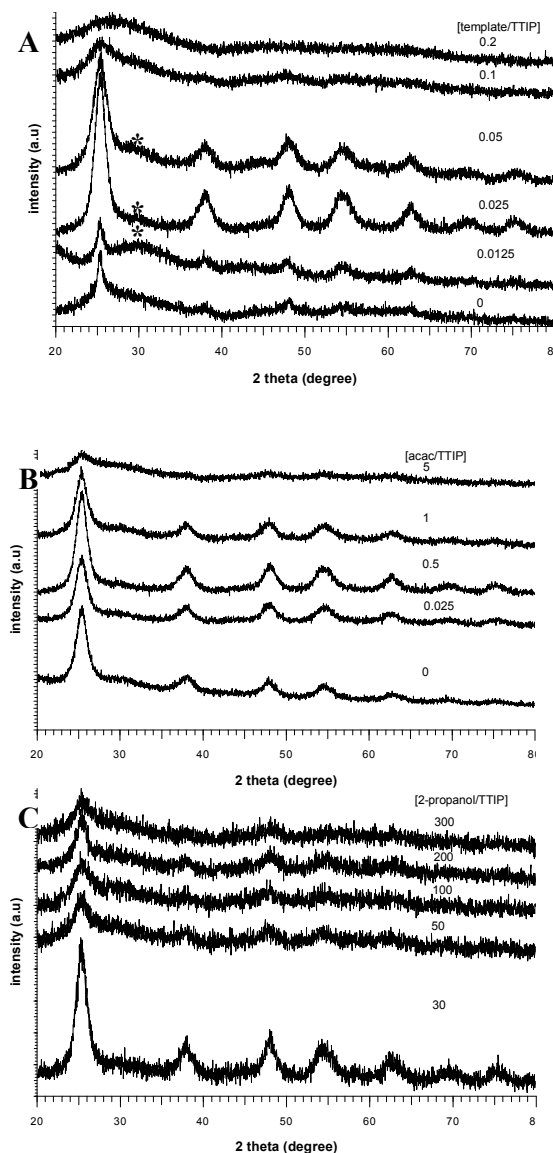


Fig. 2 Wide-angle XRD patterns of mesoporous titania after calcinations at 300 °C for 4h synthesized at different molar ratio of template to TTIP (A), acac to TTIP (B), and 2-propanol to TTIP (C).

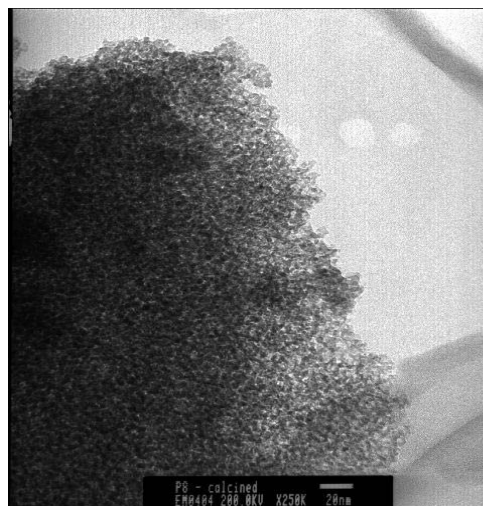


Fig. 3 TEM image of calcined mesostructured titania prepared at molar ratio of template to TTIP 0.05, 2-propanol to TTIP 300, and acac/TTIP 0.5. Condensation is performed for 72h at 60 °C.

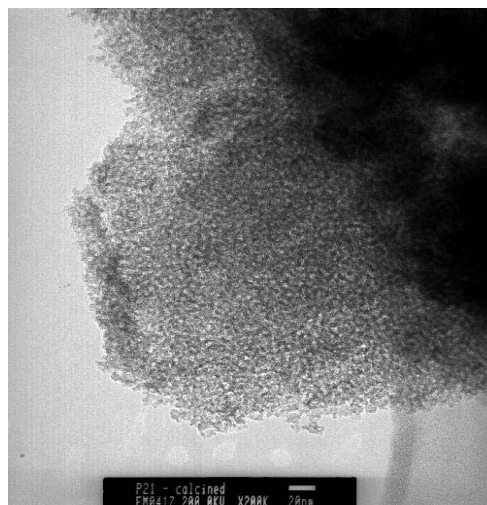


Fig. 4 TEM-image of calcined mesostructured titania prepared at molar ratio of 2-propanol to TTIP 300, template to TTIP 0.025, and acac/TTIP 0.5. Condensation is performed for 72h at 60 °C.

Isopropoxide groups are replaced by acac groups and Ti(IV) acetylacetonato tris-isopropoxide [25], which has mild reactivity upon hydrolysis, is formed. As a result, excess amount of acac will restrain the interaction between Ti-molecules causing suspension on crystal growth.

2-Propanol Effect

The presence of high amount of alcohol in the sol composition delays the Anatase formation as well. It is likely because of the lack of nuclei resulted from high polarity sols to grow into Anatase crystal phase. Considering polymerization of metal alkoxides [26], instead of formation of oxo-bridges Ti-O-Ti, the condensation stage results in water or alcohol as byproduct. The more alcohol in the system will shift the reaction equilibrium to the breakage of the oxo-bridges. As a consequence, the polymerization is inhibited and the formation of Anatase or other polymorph of titania will be delayed.

TEM-image of calcined mesostructured titania prepared at molar ratio of 2-propanol to TTIP of 300, template to TTIP of 0.025, and acac/TTIP of 0.5, is presented in Fig. 4. It shows the formation of worm-hole pore type of mesoporous titania. The pores are approximately between 4-5 nm diameters and arise from interspaces between titania particles, as observed for calcined sample has been discussed previously (Fig. 3).

Thermal Analysis

Figure 5 shows TGA curves for the thin film prepared at the molar ratio of template to TTIP of 0.05, acac/TTIP of 0.5, and 2-propanol to TTIP of 30 and block copolymer Pluronic P123. The curves

are similar to those previously reported by Yun *et al.* [9]. The path of weight loss from the as-synthesised film to the final oxide can be divided into 4 steps: below 150 °C, 150-300 °C, 300-450 °C, and above 450 °C. These can be described as follows: below 150 °C, the percent mass loss is due to the release of volatile matters, such as 2-propanol, water, and/or HCl. Then from 150-300 °C, the loss is associated with evolution process of the block copolymer template accompanied with further discharge of water, HCl, and possible organochlor compounds [2].

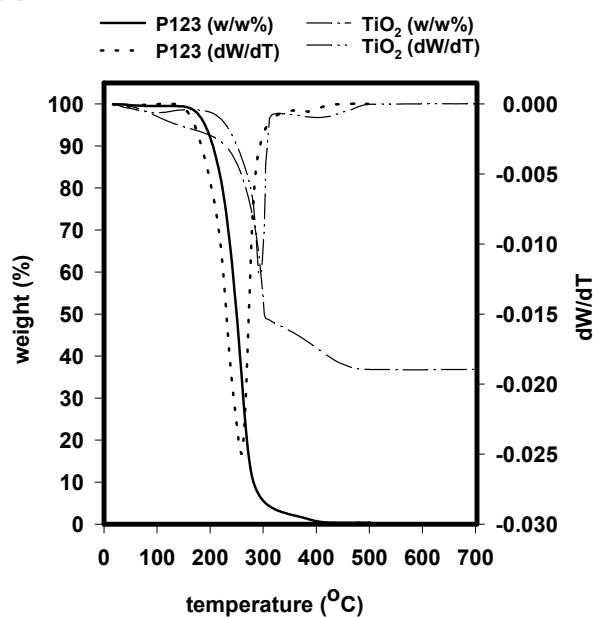


Fig. 5 TG-DTA curves of titania thin films (dashed lines) and pure Pluronic P123 (solid lines)

Table 1 Properties of calcined mesostructured titania obtained under anhydrous at 60 °C

Condition* (molar ratio)	Pore diameter (Å)	S _{BET} (m ² /g)	Total pore volume (cc/g)
T/TTIP 0	34.90	10.62	0.0179
T/TTIP 0.0125	23.70		
T/TTIP 0.025	29.91	250.60	0.1854
T/TTIP 0.05	45.50	352.60	0.4643
T/TTIP 0.1	30.37	500.60	0.4112
T/TTIP 0.1	21.13	556.00	0.3332
A/TTIP 0	35.42	548.40	0.4478
A/TTIP 0.025	36.00	315.00	0.3481
A/TTIP 0.5	45.46	352.60	0.4347
A/TTIP 1	36.03	378.00	0.3997
A/TTIP 5	35.57	275.50	0.2404
2P/TTIP 30	45.49	352.60	0.4347
2P/TTIP 50	35.60	580.70	0.5345
2P/TTIP 100	35.33	432.10	0.3743
2P/TTIP 200	34.75	296.00	0.2845
2P/TTIP 300	35.74	623.30	0.5835

*T= template (Pluronic P123), A= acetylacetonate, 2P= 2-propanol, TTIP= Titanium(IV) tetraisopropoxide

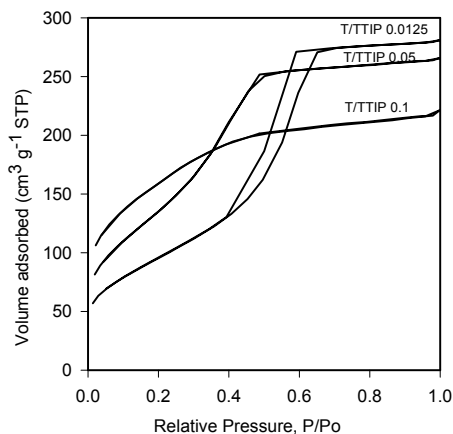


Fig. 6 N₂ adsorption-desorption isotherms of calcined samples prepared at various molar ratio of template to TTIP (T/TTIP)

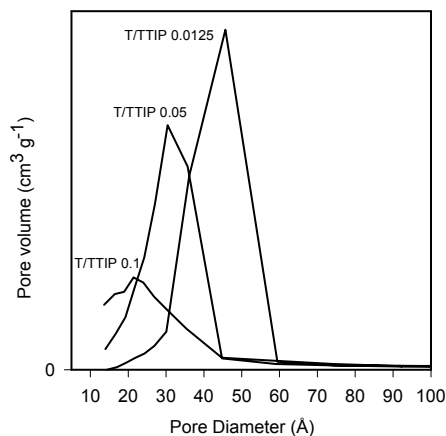


Fig. 7 Pore size distribution of calcined samples prepared at various molar ratio of template to TTIP (T/TTIP)

While from 300-450 °C, further oxidation of the organic backbone of the template and acetylacetonate occurred. Initial growth of Anatase phase is also possible in this region, as has been proven by wide-angle XRD pattern for calcined samples. Complete water loss followed by extended crystallization of Anatase will be responsible to the weight loss above 450 °C.

Textural properties of mesostructured titania synthesized in anhydrous system at 60 °C

Calcination of titania samples in air leads to high surface area titania, resulting in mean pore size in the range of mesoporosity [27]. Table 1 summarizes the effect of sol composition on the BET-surface area and porosity of the resultant gels.

Template Effect

Fig. 6 illustrates the N₂ adsorption-desorption isotherms for calcined mesostructured titania with varied template to TTIP molar ratios. The isotherms are of type IV, characteristics of mesoporous materials with different types of hysteresis loop, indicating different shape of pores. Samples prepared at T/TTIP 0.025 and 0.05 showed intermediate type of H2-H1 hysteresis loops [27] with inflection points at P/Po ~ 0.4. Desorption and adsorption branches are sloping nearly parallel over an appreciable gas uptake identifying narrow pore size distribution (Fig. 7), while H2 type is

typical for wormhole structured material [13]. At higher amount of template, the isotherm tends to resemble that of microporous materials, a combination of type I and IV. Similar results have also been observed by Soller-Illia *et al.* [13] for calcined titania at high temperatures. However, there is no observed macroporosity. Partial blocking of the channels due to residual carbonaceous material is likely to be the reason, therefore reduced pore size and hindered capillary condensation are both observed. In this case, high surface area was contributed by both mesopores and micropores. The presence of microporosity is more prominent with the sample obtained using T/TTIP 0.2, indicated by the presence of low-pressure hysteresis (isotherm not shown).

Acetylacetonate and 2-Propanol Effects

Figure 8 and 9 shows N₂ adsorption-desorption isotherms of mesostructured titania prepared at various molar ratios of acac to TTIP and 2-propanol to TTIP, respectively. It can be seen that these reactants have no drastic effect on the pore structure. They both generally have type IV isotherms with type H2-H1 hysteresis loops. Interestingly, higher amounts of alcohol resulted in higher surface area without significant presence of microporosity. However, as discussed previously, higher amount of alcohol delayed the Anatase formation. This is disadvantageous to the application as a wide band-gap semiconductor material.

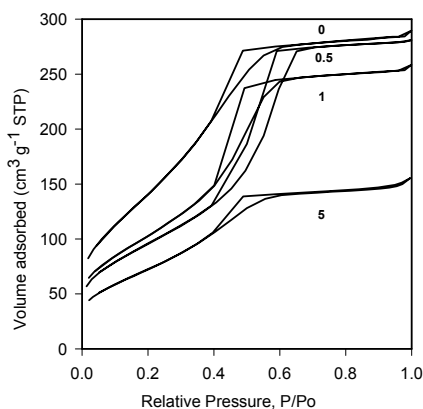


Fig. 8. N₂ adsorption-desorption isotherms of calcined samples prepared at various molar ratio of acetylacetone to TTIP

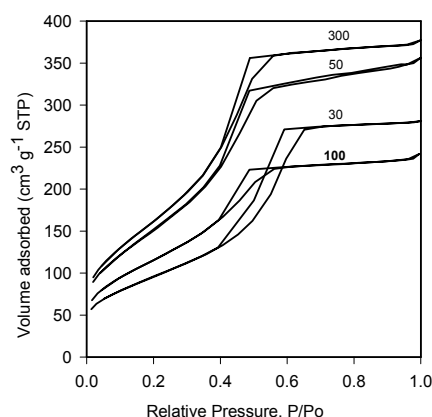


Fig. 9. N₂ adsorption-desorption isotherms of calcined samples prepared at various molar ratio of 2-propanol to TTIP

CONCLUSION

It has been shown that in the anhydrous system, rapid condensation (performed at 60 °C) leads to the formation of mesostructured titania with worm-hole like pore structure. On the other hand, high amount of template retards the formation of Anatase polymorph of titanium dioxide, so does alcohol. Therefore, careful choice of parameters involved during preparation of titanium-based thin films is important to obtain high degree mesophases organization with reasonable Anatase crystallinity. Current research focused on the effect of different titanium precursors as well as the pH of the system to the formation of well-defined mesostructured TiO₂-based thin films with Anatase domains. These mesostructured titania-based thin films of high surface area Anatase and better ordered mesophases present unique characteristics useful towards a wide-band gap semiconductor material application.

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