

HYDROTHERMAL SYNTHESIS OF TiO₂ NANOTUBES: MICROWAVE HEATING VERSUS CONVENTIONAL HEATING

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ABSTRACT

The influence of the method of synthesis in the properties of the tubular structures derived from TiO₂ was investigated using XRD, SEM and BET analysis. The use of microwave irradiation resulted in the formation of TiO₂ tubes comprising anatase and rutile phases. Conventional heating resulted in the formation of tubes with a titanate structure. The two methods yielded tubular structures with similar size dimensions, surface areas and morphologies. The two methods gave 100 % yields of tubes with different degrees of crystallinity.

INTRODUCTION

Synthesis and engineering of nanostructured semiconductors based on metal oxides have received considerable attention due to their unique physical and chemical properties, and their potential applications in industry and technology [1-2]. Whilst various methods have been used to synthesize TiO₂ nanoparticles, the hydrothermal synthesis in the presence of a base solution, has proved to be an effective approach to prepare 1D nanostructures of TiO₂. This is because the method utilizes minimum reagents and produces relatively purer materials. However, the main attention is directed towards controlling the structure and morphology of the particles by varying the synthesis conditions such as temperature, pressure and time of processing during hydrothermal processing [3-4].

The use of microwave irradiation in the synthesis of nanomaterials is becoming an important tool to fabricate materials with specific properties [5]. The fact that energy is delivered to the reactants through molecular interactions with electromagnetic field holds promise of improved synthesis [6-7]. It can provide accelerated reaction rates, high energy density and short reaction times leading to nanoparticles with improved crystallinity. It is envisaged that this would allow for the control of particle size, degree of crystallinity and morphology [8-11].

In our study, TiO₂ nanostructures are synthesized using conventional heating and microwave-assisted hydrothermal procedures. The effects of heating on the size, shape and crystallinity of materials are studied. Microwave heating is particularly interesting because of the utilization of higher energy density and shorter reaction times leading to nanoparticles that are weakly agglomerated, with high crystallinity and narrow particle size distribution.

EXPERIMENTAL

Synthesis

The synthesis of TiO₂ derived nanotubes (TNT) was carried out using a procedure described elsewhere [12-13]. In a typical procedure about 23 g of TiO₂ powder, P25 Degussa, was mixed with 200 ml of 18 M of aqueous solution of KOH. The mixture was either heated at 150 °C in an autoclave with constant stirring for 24 hours or irradiated in a microwave reactor for 15 minutes with the power of 600 W and maximum temperature set at 150 °C. The products were then washed with deionised water and then dried in an oven at 120 °C for 14 hours. The sample generated by using conventional heating in the autoclave was designated TNT-A, whereas the sample obtained by microwave irradiation was designated TNT-B.

Characterization

The surface area measurements were taken using a BET Tristar III instrument. XRD patterns on powdered samples were measured on a Phillips X'Pert materials research diffractometer using secondary graphite monochromated Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$) at 40 kV/50 mA. Measurements were taken using a glancing angle of incidence detector at an angle of 2°, for 2 θ values over 10° – 90° in steps of 0.05° with a scan speed of 0.01° 2 θ .s⁻¹. The SEM measurements were carried out in a Leo, Zeiss FE-SEM microscopy operated at 2 kV electron potential difference and equipped with a semiconductor detector that allows for detection of energy dispersive X-rays (EDX).

RESULTS AND DISCUSSION

It is noteworthy to realise that the two samples TNT-A and TNT-B were obtained under optimum conditions for each method. TNT-A showed a specific surface area of 246 m²/g whereas TNT-B showed the specific surface area of 240 m²/g. The specific surface areas obtained for both materials are comparable showing that the surface area is not largely influenced by the method of synthesis and can attest to the similar morphologies of the products.

Table 1: Physical properties of TNT-A and TNT-B

Sample	Heating Method	Oven Temperature (°C)	S _{BET} (m ² /g)
TNT-A	Conventional	150	245.9
TNT-B	Microwave	150	239.9

The crystal phases of both TNT-A and TNT-B were characterised by XRD as shown in **Fig. 1**. The XRD pattern of TNT-A shows the presence of fewer and broader peaks than TNT-B. The peaks could not be indexed to either the anatase or rutile phase. However, from our previous results and exhaustive literature search the peaks were found to correspond to a titanate structure, KTiO₂(OH) [13-17]. The XRD pattern of TNT-B shows the presence of sharper peaks which could be indexed to both anatase and rutile phases. Though the material is mainly comprised of anatase and rutile a reasonable amount of titanate structure, Ti₃O₇, was also found to be present. The phase identification for anatase with XRD was based on (1001) (004) (200) (105) (211) (204) and (116) peaks at 25.34, 37.81, 48.10, 53.92, 55.14, 62.75 and 68.81 2-theta degrees respectively [18] whereas the rutile phase identification

was based on (110) (101) (111) (211) (220) and (301) peaks at 27.45, 36.09, 41.23, 54.32, 56.64, and 69.01 2-theta degrees respectively [19]. The titanate peak is more prominent at 2-theta value of about 10 degrees. Through semi-quantitative XRD analysis, the volumetric fractions of the anatase, rutile and titanate phases in TNT-B were estimated to be about 35, 41 and 24%, respectively. This clearly shows that the tubes in this sample are of TiO_2 (76%) and Ti_3O_7 (24%) forms and that anatase, rutile and titanate phases co-exist in TNT-B. The crystallinity of the sample synthesized using microwave irradiation (TNT-B) was found to be better than that of the sample prepared by conventional heating (TNT-A) evident from the peak sharpness. This is attributed to the difference in structural composition and possibly the short reaction time for microwave processing.

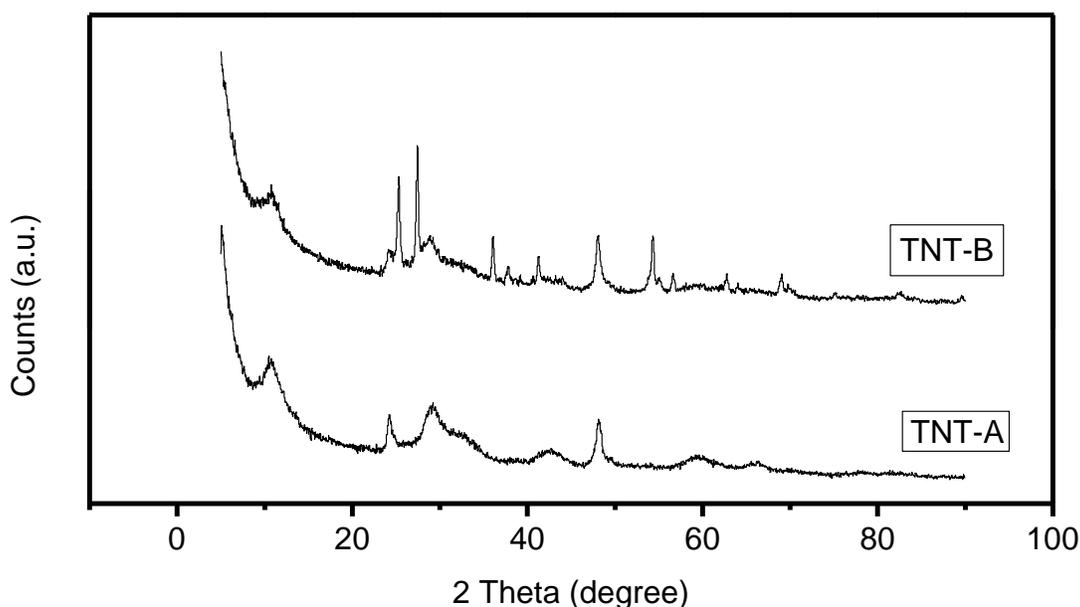


Figure 1: XRD patterns of TNT-A and TNT-B

The SEM results of the samples prepared using conventional heating (TNT-A) and microwave heating (TNT-B) are shown in **Fig. 2**. Both samples are composed of tubular structures with diameter range of 8-11 nm. Though the methods of synthesis and conditions for both TNT-A and TNT-B are different, the size dimensions are comparable. TNT-A formed relatively more and bigger bundled tubular structures than TNT-B. This implies that TNT-A is more agglomerated than TNT-B. This is ascribed to the difference in reaction times and surface charges. The presence of K^+ ions in the TNT-A sample could lead to increased surface charge and electrostatic attraction of individual tubes subsequently leading to agglomeration. The EDX results (not shown) of TNT-B did not reveal the presence of potassium indicating that the tubes obtained by microwave processing are TiO_2 and Ti_3O_7 .

Even though the dimensions and morphologies of the tubes are similar, the structural compositions are different. This suggests a possibility of different growth mechanisms. The difference in the required times of processing is evident of the mechanisms path being either kinetically or thermodynamically controlled. It is therefore envisaged that the conventional heating method follows the thermodynamic pathway that result in the formation of $\text{KTiO}_2(\text{OH})$ and that TiO_2 and Ti_3O_7 nanotubes form under kinetic conditions. From this observation the relative stability of the products can be deduced. The kinetically formed products are usually less stable compared to the

thermodynamically formed products and this would explain the co-existence of anatase, rutile and titanate phases in the microwave synthesized TiO_2 derived nanostructures. However TiO_2 (probably without Ti_3O_7 phase) nanotubes are more desirable than $\text{KTiO}_2(\text{OH})$ nanotubes due to their potential applications. The microwave process with further manipulation; as a result of its rapid growth rate, can therefore result in the attainment of relatively purer (structures made up of only Ti and O atoms) tubular structures.

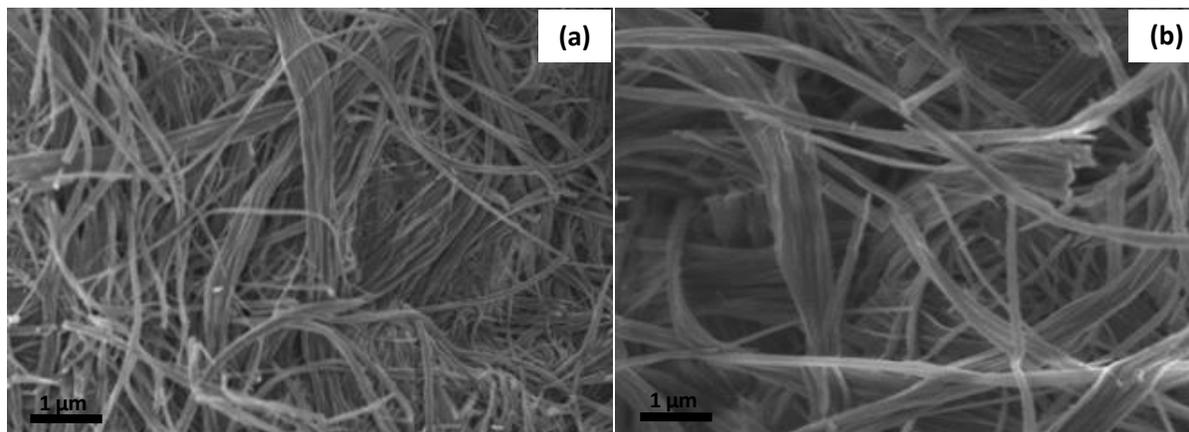


Figure 2: SEM images of (a) TNT-A and (b) TNT-B samples.

CONCLUSION

The results showed that the TiO_2 derived tubes obtained by conventional heating and microwave irradiation differ in their structural and phase composition. TNT-A (obtained by conventional heating) showed a titanate structure whilst TNT-B (obtained by microwave irradiation) gave a TiO_2 structure with anatase, rutile and titanate phases in different proportions.

The results also showed that microwave irradiation leads to rapid heat generation in the sample that the morphological transformation occurs without the reduced structural transformation. Subsequently, this leads to the formation of material with the co-existence of anatase, rutile and titanate phases. Although the two methods employed for the synthesis of TiO_2 derived nanotubes yielded tubes with similar morphology, size dimensions, and surface area the molecular structure, crystal structure and crystallinity were influenced by experimental conditions and method of synthesis. Tubes synthesized by long processing procedure using conventional heating (TNT-A) tended to agglomerate easily due to surface charge accumulation.

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