Electron Microscopy and Analysis Group Conference 2013 (EMAG2013) IOP Publishing
Journal of Physics: Conference Series **522** (2014) 012074 doi:10.1088/1742-6596/522/1/012074

Synthesis and characterization of a mixed phase of anatase TiO_2 and TiO_2(B) by low pressure chemical vapour deposition (LPCVD) for high photocatalytic activity

Y. Chimupala[1], **G. Hyett**[2], **R. Simpson**[1] **and R. Brydson**[1]

[1] Institute of Materials Research, SPEME, University of Leeds, Leeds, LS2 9JT,UK.
[2] Department of Chemistry, University of Southampton, Southampton, SO17 1BJ Highfield, UK

Email: pmyc@leeds.ac.uk

Abstract. This project is concerned with enhancing photocatalytic activity by preparing a mixed phase of nano-sized TiO_2. TiO_2 thin films were synthesized by using Low Pressure Chemical Vapour Deposition (LPCVD). Titanium isopropoxide and N_2 gas were used as the precursor and carrier gas respectively. The effects of reaction temperature, carrier gas flow rate and deposited area were studied. TiO_2 thin films with nano-sized TiO_2 particles were obtained under suitable conditions and SEM, TEM, powder XRD and Raman spectroscopy were employed to characterize the phase and physical appearance of synthesized materials. Preliminary results show that a dual phase (TiO_2(B) and anatase) thin film nanopowder was successfully prepared by LPCVD with needle- and polygonal plate-shape crystallites respectively. This thin film deposit produced a preferred orientation of TiO_2(B) needles in the [001] direction of average crystallite size 50-80 nm in length and 5-10 nm in width, whilst the crystallite size of anatase polygonal-plates was around 200 nm. The optimal LPCVD condition for preparing this mixed phase of TiO_2 was 600°C with a 1 mL/s N_2 flow rate.

1. Introduction

Two of the most important world issues are currently energy consumption and environmental pollution. TiO_2 semiconductor photocatalysts are one of the potential solutions to these problems owing to their potential ability for substantial energy production which is cost effective, highly stable and environment friendly [1]. Photocatalytic water-splitting to produce hydrogen using TiO_2 has been investigated however generally the efficiency is low. Currently improvement strategies focus on the use of ultrafine particle sizes and modification of the semiconductor band gap.

Engineering of the TiO_2 band gap by mixing two different phases of TiO_2 (such as anatase/rutile and antase/TiO_2(B) [2]), directly affects the charge transfer process between the different phases reducing recombination of photo-generated electrons and so enhancing the photocatalytic activity [2,3]. TiO_2 (B) has been of significant interest over the last decade because of the distinctive crystal structure which exhibits bigger channels and voids along the c axis in its monoclinic crystal structure as compared with anatase and rutile tetragonal structures [4]. Commonly, alkaline metal titanates have been used as precursors for TiO_2(B) preparation in many synthetic methods such as sol-gel, hydrothermal and wet chemical process [5]. In this research, the LPCVD method was employed to synthesis (for the first time) dual phase anatase and TiO_2(B) thin films for use as a photocatalyst for the water splitting reaction.

2. Experimental Procedure

2.1. Preparation procedure for dual phase TiO_2

Dual phase TiO_2 thin films were prepared by chemical vapour deposition under low pressure at 25 mbar. Titanium tetra-isoproproxide (TTIP, 97%) was used as the chemical vapour precursor and a bubbling chamber settled in an oil bath at 90°C was filled with 5-10 mL TTIP. The TTIP vapour generated was carried into aquartz tube reaction by N_2 at a flow rate of 1mL/s. Titanium oxides were deposited onto a silica glass slide of dimensions 12.5 mm × 150 mm × 1 mm (width × length × thickness) via thermal decomposition of TTIP. The reaction temperature in the tube furnace was varied between 450 and 600°C with a reaction time of 15 min.

2.2. *Materials Characterization*

The deposited microscope glass slide was divided into 12 square samples each of dimensions 12.5 mm × 12.5 mm × 1 mm before being characterized. The samples represented different reactor positions relative to the gas entry point (square 1). The samples were characterised by both in-plane and out-of-plane X-ray diffraction (XRD) and also Raman spectroscopy. The thin film surface morphology and film thickness were studied by scanning electron microscopy (SEM) both in plan view and in cross-section. For transmission electron microscopy (TEM) the deposited materials were scraped off the glass substrate with a scalpel onto a holey carbon film supported on a Cu TEM grid.

3. Results and Discussion

The most interesting synthesis condition was found to be 600°C for 15 min of 5 mL TTIP. All of 12 square deposited glass slides were studied by out of plane XRD as partially shown in figure 1.

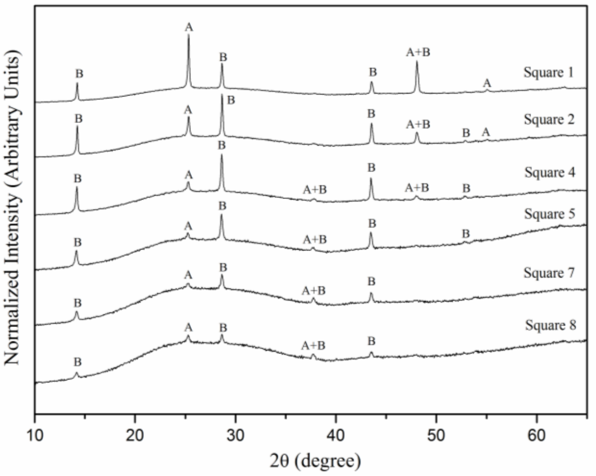


Figure 1. Out of plane XRD patterns of TiO_2 thin film prepared by LPCVD at 600°C: A and B refer to the assignment of the anatase and TiO_2(B) phases respectively.

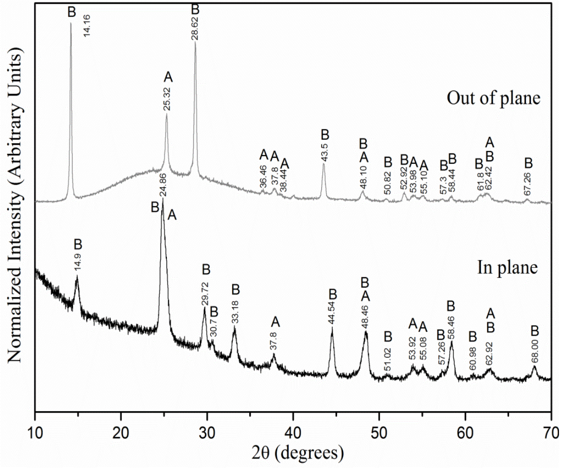


Figure 2. In plane and out of plane XRD patterns of Square 4: A and B refer to anatase and TiO_2(B) phases respectively.

XRD patterns illustrate that all of prepared materials are a mixed phase combination of both TiO_2 anatase and TiO_2(B). In Square 1 the majority phase is anatase, however in all other reactor positions, the main component is the TiO_2(B) phase. It can be seen that two XRD peak positions of anatase at around $2\theta = 38°$ and 48° which corresponds to (112) and (200) peaks respectively, are nearly at the same peak positions as the (401) and (020) peaks of TiO_2(B). Both in-plane and out-of-plane XRD were used to confirm the existence of the mixed phase by focusing on the Square 4 sample, as shown in figure 2.

The in-plane XRD pattern shows different peaks of TiO_2(B) to the out-of-plane pattern which can also be indexed as TiO_2(B) phase. Not only does this confirm the existence of the TiO_2(B) phase it reveals a preferred [001] crystallographic orientation of TiO_2(B) as illustrated at 2θ = 14.16, 28.62 and 43.5 degrees.

Raman spectroscopy was employed to confirm the dual phase (figure 3). The intense peak at 144.96 cm^{-1} and four other peaks at 197.86, 394.4, 515.6 and 638.6 cm^{-1} are the Raman active modes for anatase. The remaining peaks, especially two strong peaks at 121.95 cm^{-1} and 144.96 cm^{-1} indicate the Raman active modes of the TiO_2(B) phase [6].

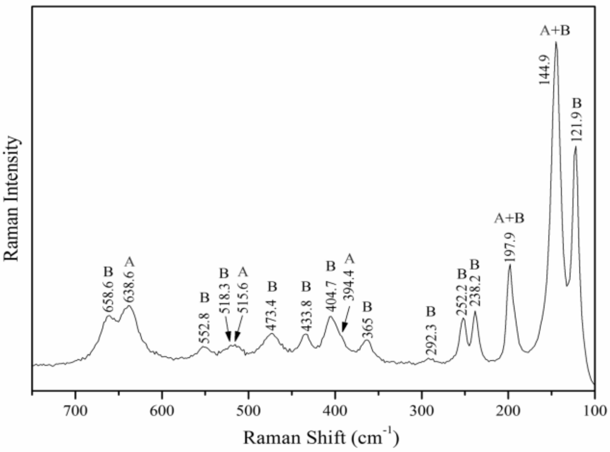
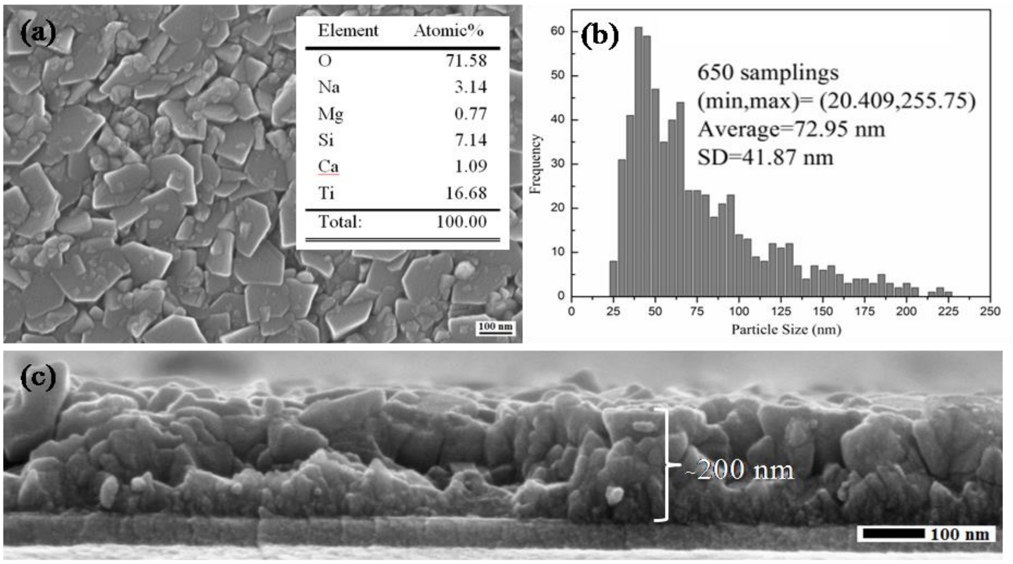


Figure 3. Raman spectrum of Square 4: A and B indicates the anatase and TiO_2(B) phases respectively.

A SEM plan view image of Square 4 is shown in figure 4a and illustrates that there are two kind of particle morphology, one is a large plate with particle size about 100-200 nm, whilst the other one is a nearly round small particle with a diameter of around 20 nm. The average primary particle size of this bimodal distribution at the film surface is 72.95 (S.D =41.87) nm as elucidated from the Particle Size Distribution in figure 4b. SEM/EDX results, shown inset in figure 4a, confirm the presence of Ti and O in the thin film. However, Na, Mg, Si, Ca and excess atomic percentage of O are also present which may come from the glass-slide substrate owing to the large electron beam interaction volume which is bigger that the TiO_2 film thickness of 200 nm as shown in the SEM cross-section in figure 4c. It is also worth nothing that it appears that the thin film again contains two kinds of particles; again a smaller, more equiaxed particles predominantly occurring at the glass substrate/film boundary and the other plate-like particles predominantly deposited on the film surface. This may suggest that the small particles are acting as a seeding layer on the substrate.



Element	Atomic%
O	71.58
Na	3.14
Mg	0.77
Si	7.14
Ca	1.09
Ti	16.68
Total:	100.00

Figure 4. (a) SEM secondary electron image of TiO_2 thin film from Square 4; (b) Primary Particle Size Distribution measured from measurement of 650 particles; (c) SEM cross-sectional image of thin film thickness after fracturing the glass slide.

Both XRD and Raman results indicate the coexistence of anatase and TiO_2(B) therefore the prepared thin film should provide two type of particle morphology as suggested by the SEM images. A typical TEM image, figure 5a, also shows two distinct types of particle morphology which are large polygonal plate-like and smaller needle-shaped. The crystallite size of the needles is in the range 50-80 nm in length and 5-10 nm in width, very much smaller than the polygonal plate of size around 200 nm.

Both of the morphologies were investigated by HRTEM and the relationship between nanostructure and physical appearance determined as shown in figures 5b and 5c. In Figure 5b, a needle shape clearly shows a lattice spacing of 3.18Å and 2.91Å which can be tentatively assigned to the lattice spacings of $(\bar{1}11)$ and (400) of TiO_2(B). The measured angle between two lattice planes is 88° which is close to the theoretical angle of 83°. Moreover, the TEM selected area diffraction pattern of a group of needles confirms the existence of TiO_2(B). When combined with the XRD results, this suggest the needles must be growing preferentially along their long axis ([001] direction), i.e oriented vertically. Figure 5c shows that the polygonal plate is anatase as it reveals lattice spacings of 3.47Å, 2.38Å and 2.28Å which correspond to (101), $(\bar{1}03)$ and (112) spacings respectively.

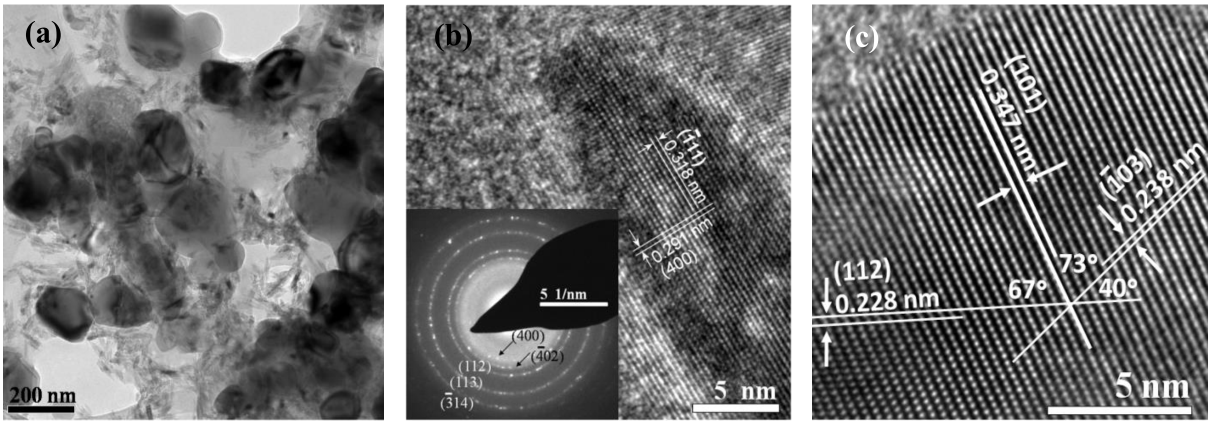


Figure 5. (a) A TEM image taken from Square 4, showing both anatase polygonal plates and TiO_2(B) needle-shaped particles; (b) HRTEM of a TiO_2(B) needle and SADP of a group of the needles; (c) HRTEM image of an anatase polygonal plate.

4. Conclusions

200 nm thick TiO_2 thin films consisting of dual phase monoclinic TiO_2(B) needles and larger anatase polygonal plates have been prepared by an LPCVD method at 600°C for 15 min of 5 mL TTIP precursor. To our knowledge, this is the first time the monoclinic TiO_2(B) phase has been prepared by CVD. The small nano-needles of the TiO_2(B) phase exhibit a preferred orientation along [001].

Acknowledgements

Acknowledgements to the Royal Thai Government for a scholarship to YC.

References

[1] Hoffmann M R , Martin S T, Choi W and Bahnemann D W 1995 *Chem. Rev.* **95** 69
[2] Jiefang Z, Jinlong Z, Feng C and Masakazu A 2005 *Mater. Lett.* **59** 3378
[3] Meng N, Michael K H L, Dennis Y C L and Sumathy K 2007 *Renew. Sust. Energ. Rev.* **11** 401
[4] Marc E, Concepcion D and Jose A A 2010 *Mater. Lett.* **64** 2357
[5] Xiang G L, Li T Y, Zhuang J and Wang X 2010 *Chem. Commun.* **46** 6801
[6] Mouna B Y, Frederic L, Thomas B, Jean S F, Mireille R P, Luc B and Marie L D 2009 *J.Chem. Phys.* **130** 204501