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# Synthesis and tuning of ordering and crystallinity of mesoporous titanium dioxide film

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## ABSTRACT

Synthesis of well-organized and highly crystalline mesoporous titania ( $\text{TiO}_2$ ) film is demonstrated using triblock copolymer (Pluronic P123) as a structure directing template, through the evaporation induced self-assembly (EISA) process. The issue of thermal and structural stability of a mesoporous  $\text{TiO}_2$  film was addressed via optimization of annealing temperature and time. An anatase phase, high crystallinity  $\text{TiO}_2$  film with ordered pores was obtained at 430 °C after annealing for 15 min. The synthesized film was crack free with  $\text{TiO}_2$  nanoparticle size of 10–15 nm, quasi-hexagonal pore diameter in the range of 8–10 nm and film thickness of ~150 nm.

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## 1. Introduction

$\text{TiO}_2$  has attracted worldwide attention of researchers due to its extraordinary optical properties, electrical properties, easy methods of synthesis and good chemical stability. However, after the demonstration of the hierarchically ordered uniform mesoporous  $\text{TiO}_2$  thin films by Grosso et al. [1], a new avenue of  $\text{TiO}_2$  applications was opened. Since then, ordered porous films of  $\text{TiO}_2$  have been used in photocatalyst [2], water purification [3], gas sensing [4], and photovoltaic devices [5].

It has been shown that ordered mesoporous  $\text{TiO}_2$  film can increase the efficiency of the photovoltaic devices. This comes from the benefits of increased surface roughness, surface area and uniform porosity [6–8]. Moreover, well-ordered mesopores with their crystalline nature provide good absorption of sunlight and direct path with low recombination rate for transport of charge carriers [9]. The challenge is, however, to achieve high degree of crystallinity and at the same time preserve the ordering of the mesoporous structure. Although much work has been done, there is still scope to understand the mechanisms and parameters involved. In the present work, mesoporous titania films were synthesized and changes in morphology of the film were studied by varying annealing temperatures and time. Sol-gel process through evaporation induced self-assembly (EISA) [10] was used since it provides a direct route for large area synthesis at low cost.

## 2. Experimental details

For synthesis, 1.2 g triblock copolymer  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{OH}$  designated  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  or Pluronic P123

was added slowly into 20 g ethanol. Another solution was prepared by slowly adding 3.4 g of titanium ethoxide into 0.3 ml concentrated HCl. The precursor solution was prepared by mixing the two solutions under vigorous stirring for 2–3 h. The sol solution was then aged in a sealed container at 13 °C for 2 days. Dip coating, based on solvent evaporation, was used to prepare mesoporous films on Si substrates. The deposited film was calcinated at 350–500 °C with a heating rate of 1 °C/min and dwell for 15–30 min in nitrogen ambient before cooling down naturally to room temperature.

Structural characterization of the synthesized films was done using X-ray diffraction (XRD) on Philips X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.540589 \text{ \AA}$ ). The morphology of synthesized  $\text{TiO}_2$  film was obtained using JEOL-2100 high resolution transmission electron microscope (HRTEM) with accelerating voltage of 300 kV, along with selected area electron diffraction (SAED) pattern and JEOL FEG JSM 6700 F scanning electron microscope (SEM) operating at 5 kV. X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB MKII spectrometer equipped with a non-monochromatized Mg-K $\alpha$  X-ray source (1253.6 eV photons). Removal of polymer template (P123) was verified using Fourier transform infrared spectroscopy (FTIR) on Perkins Elmer spectrum 2000.

## 3. Results and discussion

Apart from alignment of pores, high degree of crystallization is necessary for efficient photovoltaic operation, which requires calcination of the metal oxide films at high temperatures. These temperatures are much higher than the degradation temperature of polymer P123. During the calcination process, the oxidation of polymer P123 takes place, which results in degradation of the hydrophilic chains, eventually forming pores. It has been shown that at lower temperature, cleavage of

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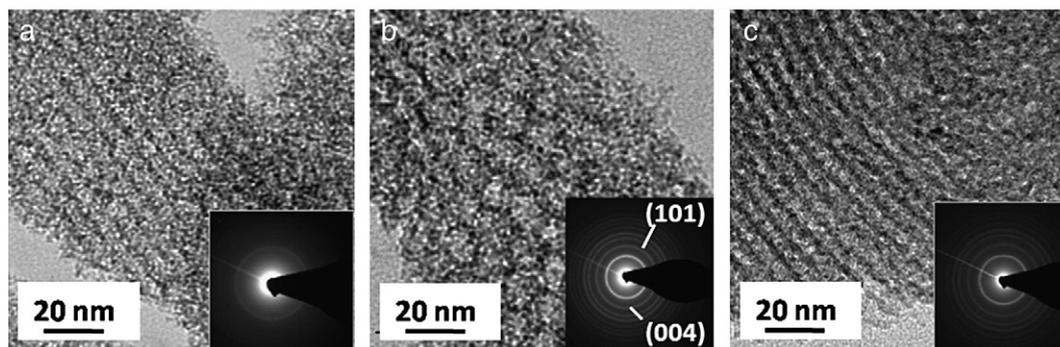


Fig. 1. HRTEM images after annealing at (a) 350, (b) 550 and (c) 430 °C for 15 min. Inset shows the corresponding SAED pattern.

C–O bond takes place, while at higher temperature C–C cleavage and dehydration becomes favorable leading to pore formation [11]. However, it is known that upon calcination at higher temperatures, the mesoporous matrix collapses, due to thermal diffusion of TiO<sub>2</sub> species. Therefore, a delicate balance is required to synthesize ordered mesoporous film with high crystallinity. In the present work, calcination temperature and time were optimized to achieve high crystallinity without compromising the alignment of pore.

In order to observe changes in pore alignment and crystallinity, films were synthesized at various temperatures and analyzed using TEM. Fig. 1 shows TEM images of the mesoporous TiO<sub>2</sub> films synthesized at three different temperatures. The film grown at 350 °C for 15 min showed ordered pores (Fig. 1a) with diffused rings in SAED indicating that the film is amorphous (inset 1a). However, upon calcination at 550 °C for 15 min, the ordered matrix of the pores collapsed (Fig. 1b). Distinct diffraction rings were observed (inset 1b) and the first few rings are indexed as (101) and (004). Hence, as the temperature increases from 350 to 550 °C, crystallinity improves while ordering of the mesoporous structure collapses. Fig. 1c shows TiO<sub>2</sub> film synthesized at 430 °C for 15 min. The film shows ordered porous structure with good crystallinity. The mesoporous film prepared at optimal conditions (430 °C for 15 min) was thermally stable and had a well-organized structure. The average pore size estimated from the TEM analysis is ~9 nm.

In addition, the film morphologies were corroborated through SEM imaging. Fig. 2a shows SEM image of TiO<sub>2</sub> film synthesized at 430 °C for 15 min. The ordered quasi-hexagonal pores on a crack free film are clearly revealed in the image. This film has pore size in the range of 8–10 nm with film thickness of approximately 150 nm. The pore size and pore volume are adjustable to a certain extent, simply by varying the concentration of the triblock copolymer organic compound. However, TiO<sub>2</sub> film annealed at 550 °C resulted in the aggregation of TiO<sub>2</sub> nanoparticles and the collapse of the quasi-hexagonal pores (Fig. 2b).

After achieving the right conditions, the titania films grown at optimized conditions were further characterized. All the characterization techniques discussed henceforth, were on mesoporous TiO<sub>2</sub> films obtained by calcination at 430 °C for 15 min.

Fig. 3a shows the XRD pattern of mesoporous titania film after calcination at 430 °C, which confirms the formation of crystalline oxide and well-organized structured film. The XRD pattern obtained clearly shows well-resolved, sharp peaks of anatase phase with peaks at  $2\theta = 25.6^\circ$ ,  $38.1^\circ$ ,  $48.03^\circ$  and  $54.05^\circ$  (JCPDS no. 21-1272). The crystallinity and planes of the titania film revealed by the XRD pattern are consistent with the SAED results.

Effective removal of the organic template was verified by FTIR, obtained for both the as-prepared and annealed films [Fig. 3a (i) and (ii)]. The C–O stretching band,  $1025\text{--}1250\text{ cm}^{-1}$  was used to determine the presence of surfactant (P123) before and after ethanol extraction and calcination at 430 °C. For the as-prepared film, the symmetrical and asymmetrical –CH<sub>2</sub> stretchings occurred at  $2877$  and  $2969\text{ cm}^{-1}$  along with a sharp peak at around  $1081\text{ cm}^{-1}$ , due to incomplete condensation. These peaks were reduced after heat treatment. Strong transmittance observed at  $1714$  and  $3300\text{ cm}^{-1}$  arising from vibrations of –CH<sub>3</sub> and C–H bonds was also reduced after calcination.

The XPS spectra for Ti of the as-prepared sample show two peaks for Ti2p<sub>3/2</sub> at 457 and 458.7 eV (Fig. 4a), implying two different chemical environments for Ti ions. The binding energy of 457 eV corresponds to formation of Ti<sub>2</sub>O<sub>3</sub> [12], while 458.8 eV signifies TiO<sub>2</sub>. Fig. 4b shows the Ti2p spectra for the annealed film with binding energy for Ti2p<sub>3/2</sub> at 458.2 eV, while for Ti2p<sub>1/2</sub> at 463.6 eV, indicating the formation of anatase TiO<sub>2</sub> [13]. The Ti<sub>2</sub>O<sub>3</sub> at 457 eV is not observed in the annealed film (Fig. 4b), since it is fully converted to TiO<sub>2</sub> upon thermal annealing. Fig. 4c shows O1s for the as-prepared sample, fitted with three peaks. Binding energy of 529.5 eV signifies Ti–O in TiO<sub>2</sub> and 531 eV corresponds to hydroxyl groups (–OH) and physisorbed water. The peak at 532.7 eV corresponds to C–O bonds

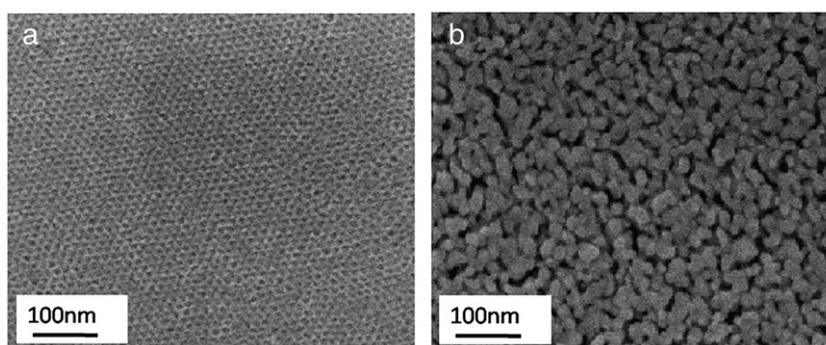


Fig. 2. SEM images of mesoporous titania film obtained after calcination at (a) 430 and (b) 550 °C for 15 min.

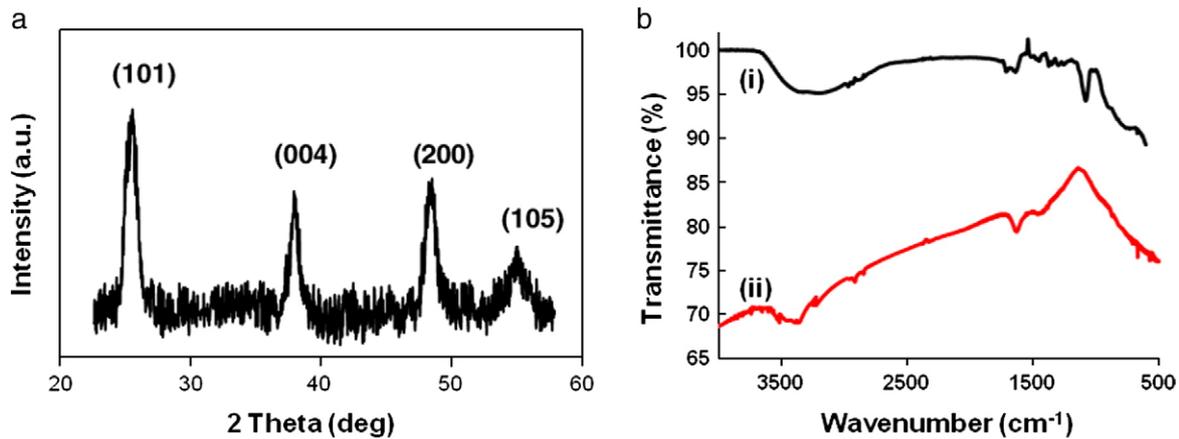


Fig. 3. (a) XRD pattern obtained from mesoporous TiO<sub>2</sub> film after calcination at 430 °C for 15 min and (b) FTIR spectra of mesoporous TiO<sub>2</sub> film (i) before and (ii) after calcination.

[14]. The large hydroxyl content is attributed to the nature of the mesoporous surface which reacts rapidly with moisture to form hydroxylated surface as a means of producing better neutralization of charge, following Pauling's rule of electro-neutrality [15]. Also, the defective sites on the TiO<sub>2</sub> film surfaces are known for good water molecules adsorbents [16]. The binding energy due to C–O bonds disappears upon thermal treatment of the film (Fig. 4d), due to removal of organic content.

The mesoporous TiO<sub>2</sub> is obtained through micellization using amphiphilic triblock copolymer P123 as a structure directing agent. The structural packing (cubic or hexagonal) are determined by various micelle crystal phase (spherical or cylindrical micelles). The type of micelle crystal phase formed is determined by a balance of interactive forces due to change in pH, polymer concentration etc. At a low

polymer concentration, less than the critical micellar concentration (CMC), copolymer molecules self-assemble into spherical micelles. However, beyond the CMC, copolymer micelles aggregate and align to form cylindrical micelles which allow the transformation from a random alignment of pores into a well-ordered one. As the well-aligned micelle crystal is formed, the condensed inorganic species are constrained to the remaining interstitial spaces, thereby forming an aligned mesoporous structure.

#### 4. Conclusion

TiO<sub>2</sub> ordered mesoporous film was synthesized using Pluronic P123. The microstructure of the titania film was studied at different calcination temperatures. As these parameters influence the film

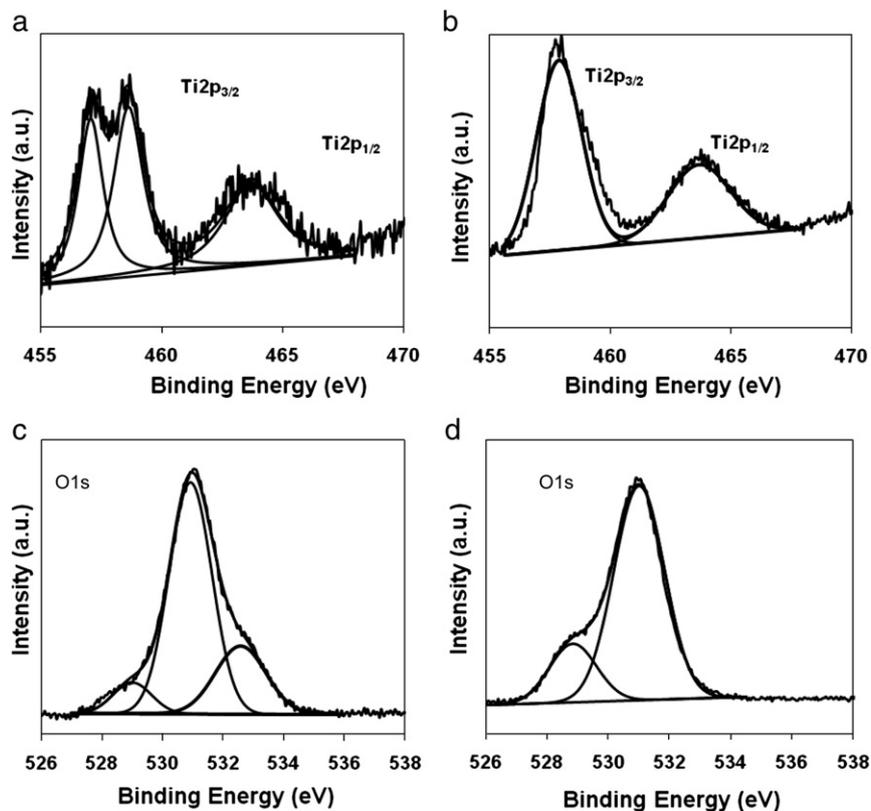


Fig. 4. XPS spectrum of Ti2p for (a) the as-prepared film and (b) optimized film and of O1s for (c) the as-prepared film and (d) optimized film.

ordering and crystallinity, they were optimized to obtain an ordered, crack free and thermally stable film. A highly porous film with anatase phase was achieved by heating at 430 °C for 15 min. Film thickness was ~150 nm with pore diameter in the range of 8–10 nm.

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### References

- [1] Grosso D, Soler-Illia GJ de AA, Babonneau F, Sanchez C, Albouy PA, Brunet-Bruneau A, Balkenende AR. *Adv Mater* 2001;13:1085–90.
- [2] Hoffman MR, Martin ST, Choi W, Bahneman DW. *Chem Rev* 1995;95:69–96.
- [3] Miller LW, Tejedor-Tejedor MI, Anderson MA. *Environ Sci Technol* 1999;33:2070–5.
- [4] Guidi V, Carrota MC, Ferroni M, Martinelli G, Paglialonga L, Comini E, et al. *Sens Actuators B* 1999;57:197–200.
- [5] Kamat PV, Dimitrijević NM. *Sol Energy* 1990;44:83–98.
- [6] Yu JC, Zhang L, Yu J. *Chem Mater* 2002;14:4647–53.
- [7] Takeshi M, Nishizawa K, Suzuki K, Kato K. *Mater Lett* 2004;58:2751–3.
- [8] Coakley KM, McGehee MD. *Appl Phys Lett* 2003;83:3380–2.
- [9] Soler-Illia GJ de AA, Louis A, Sanchez C. *Chem Mater* 2002;14:750–9.
- [10] Zhang Q, Gao L, Guo J. *Appl Catal B Environ* 2000;26:207–15.
- [11] Lattimer RP. *J Anal Appl Pyrolysis* 2000;56:61–78.
- [12] McKay JM, Henrich VE. *Surf Sci* 1984;137:463–72.
- [13] Browne M, Gregson PJ, West RH. *J Mater Sci Mater Med* 1996;7:323–9.
- [14] Kilpadi DV, Raikar GN, Liu J, Lemons JE, Vohra Y, Gregory JC. *J Biomed Mater Res* 1998;40:646–59.
- [15] Sham TK, Lazarus MS. *Chem Phys Lett* 1979;68:426–32.
- [16] Fujishima A, Rao TN, Tryk DA. *J Photochem Photobiol C* 2000;1:1–21.