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Production of TiO_2 Nano-Rods Using Combination of Sol-Gel and Electrophoretic Methods

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Nano-rods of titanium dioxide have been developed by electrophoretic deposition in polycarbonate templates with 180 nm diameter. Characteristics of the produced nanostructures have been investigated in terms of microstructure, morphology, phase composition, thermal behaviour and chemical bindings using scanning electron microscope, X-ray diffraction and Fourier transform infra red. Scanning electron microscope micrographs demonstrated that the TiO_2 nano-rods have grown completely directional with thoroughly similar diameter. In addition, X-ray diffraction analysis revealed that the developed nano-rods have yielded a mixture of anatine and rutile structures after annealing at 530 ºC for 50 min.

Key Words: Nano-rod, Titanium dioxide, Electrophoresis, Sol-gel.

INTRODUCTION

Recently the researches have demonstrated that one-dimensional nanostructures of TiO_2 provide superior properties than other structures for application in photocatalysts, sensors, sun and photovolt cells and electrochemical equipments[1-6]. For many of these applications, sensitivity and performance is directly related to free surface of the material. One-dimensional nanostructures bear larger free surface in comparison with bulk materials and they are also more appropriate for investigation on their physical properties. Knowledge of making one-dimensional nanostructures has experienced great advancements during the recent years by techniques such as direct oxidation of metallic nano-rods[7], vapour-liquid-solid growth[8], chemical vapour deposition by heating[9], laser ablation method[10], hydrothermal synthesis[11] and deposition of colloidal oxide by template-assisted method[12]. Although some of these techniques are preferred to others in particular applications, choosing one proper technique based on limitations including dimensions of wire, degree of crystallization and production costs would be rather difficult. Among the previously mentioned methods, those in which templates are used to grow one-dimensional nanostructures have been known as efficient and appropriate techniques due to their controlled shape, size and distribution of nanostructures as well as their relatively low cost[13]. Applying deposition of colloidal particles by template-assisted methods can develop one-dimensional nanostructures of metallic oxides with sound control on their stoichiometric chemical composition. Nevertheless, more than 90 % of sol compounds or compounds are soluble, so nanostructures created by this method are usually voided[14]. A novel technique has been suggested to grow one-dimensional nanostructures of Ti while three methods of sol-gel, electrophoresis and template-assisted deposition have been utilized simultaneously. Sol-gel is a wet chemical method to synthesize and develop mineral and organic-mineral hybrids. It benefits from low temperature of process (lower than 100 ºC), homogeneity at molecular level and possibility of producing one-dimensional nanostructures of metallic complex[15]. This method includes a hydrolysis step in addition to compression of the molecules of the raw material. This raw material can be organic components such as metallic alkoxides or mineral salts. Organic or aqueous solvents are used to solve the raw material while a catalyst is employed to control and accelerate reactions. As a result, compression reactions of metallic oxide/hydroxide nano-clusters will be produced to which most of organic groups are connected. Size of the existing nano-clusters within sols, morphology and microstructure of the final product can be modified by controlling the parameters effective on hydrolysis and compression reactions namely type of solvent, catalyst, temperature, pressure and pH of the solution[16]. There are some important drawbacks in sol-gel technique. It has small driving force to grow nano-rods from the sol which is just provided by capillary action. It's solid content is also very small (5 vol. % approximately) such that compression of the solid particles will be inadequate though voids are loaded with sol[17]. Once the concentration of solid particles is increased in sol, solid particles will offer better compression but excessive concentration can lead to a highly viscous sol which makes it difficult to load voids and it is even possible for the sol to be instable. Therefore, density of the nano-rods produced by this method would be less than theoretical density which causes crack and deficiency within the nano-rods because of great change in their volume during drying as well as losing solvents from the nanostructure. Moreover, this contraction is large enough to deform initial shape and size of the nanocrystals they may be rendered as voided nanopipes. Some disadvantages of this technique can be solved by combining it with electrophoresis. Applying external electrical field to one stable electrostatic sol, the nano-clusters inside will show well-arranged diffusion along with field lines, they move towards the electrode with opposite charge and start deposition and precipitation the end of the void. Afterwards, particles of sol will occupy the whole template channels. Nano-rods made by electrophoresis-sol have exhibited higher density and quality as compared with those produced by the mere sol technique[18].

EXPERIMENTAL

Sol-gel has been used in combination with electrophoresis deposition to develop titanium dioxide nano-rods. For making the solution (sol), titanium tetra isopropoxide with minimum purity of 98 % as the precursor and 37 % hydrochloric acid (HCl) as the catalyst for suspension were used (Both MERCK, Germany) in addition to deionized water as the diffracting environment[19]. Nano-rods of TiO_2 were then fabricated by template-assisted electrophoresis deposition. For the purpose of growing one-dimensional nanostructures, polycarbonate templates having diameter of 180 nm were spattered by a thin film of gold in one side to be rendered electric conductor (cathode) while the second electrode (anode) was made of pure platinum with area of 4 cm^2. These electrodes were placed in parallel with constant voltage 0f 0.5-1 v/cm being applied for 80 min. For instant current measurements, *Fluke289* digital multimeter was utilized with the ability to be connected to computer. Chrono-amperometry curves were investigated to study different steps of filling voids and growth of one-dimensional nanostructures. At the end of electrophoresis, nanostructures grown were dried at 120 ºC and annealed at 530 ºC for 50 min in order to get stoichiometric chemical composition with desired crystal structure. Morphology and phase structure of the nano-rods were evaluated by SEM, FESEM and XRD techniques.

RESULTS AND DISCUSSION

Fig. 1 illustrates FTIR analysis of TiO_2 sol. Peak of OR group for titanium isopropoxide, which is precursor of the Ti sol, appears in the range of 1085-1050 cm^{-1}. Since no peak is observed in this range, it can be argued that all OR groups of titanium isopropoxide are replaced with OH groups of water and complete transformation of the initiator to TiO_2 has been implemented by the hydrolysis reaction. One peak observed at 1636 cm^{-1} is characteristics of the expanding oscillation of H-O-H bind while the peak seen at 3431 cm^{-1} is indicative of

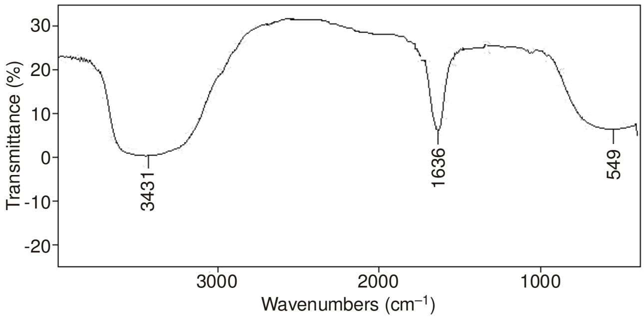

Fig. 1. FTIR spectrum of TiO_2 sol

the surface oscillation of O-H groups (in the range of 3650-3200 cm^{-1}). One wide peak in the range of 900-500 cm^{-1} belongs to Ti-O-Ti bind in the sol[20]. SEM micrograph of TiO_2 nano-rods growth in polycarbonate templates through sol-electrophoresis is depicted in Fig. 2. For resolution of the images, a thin film of gold was coated on surface. As observed herein, TiO_2 nano-rods are grown completely in parallel direction and structured completely arranged which is known as the advantages of using template-assisted growing methods. Fig. 3 exhibits FESEM images after complete removal of the template at 530 ºC. It can be concluded that the developed nano-rods bear similar diameter along it's entire length. Their surface is rather plane, they have tetragonal structure which reveals crystal structure of the nano-rods grown after heat treatment and template removal. This fact was in good agreement with the results earned from XRD analysis. X-Ray diffraction pattern of TiO_2 nano-rods synthesized and annealed at 120 ºC (drying) and 530 ºC is illustrated in Fig. 4. As obvious in XRD patterns of the synthesized TiO_2 nano-rods, nano-structures have a completely amorphous structure after growth which experiences a phase transformation to anatine at 120 ºC. As can be observed in X-ray spectrum of the nano-rods at 530 ºC, a mix of anatine and rutile phases is available at this temperature.

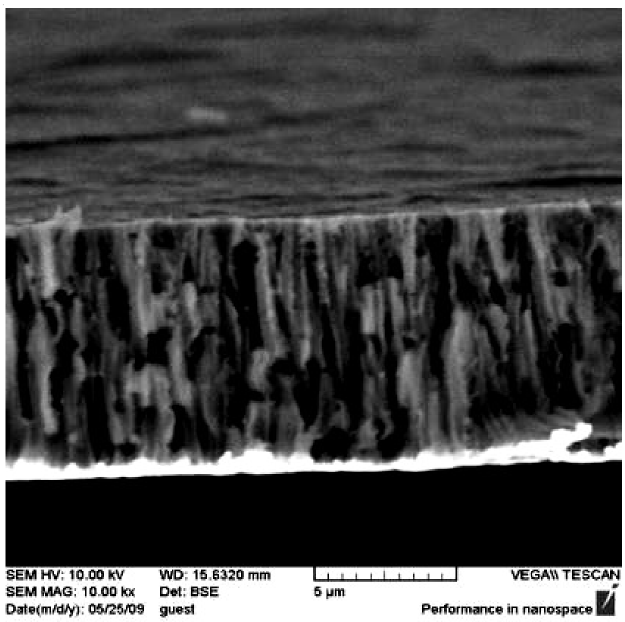

Fig. 2. SEM micrographs of TiO_2 nano-rods grown within polycarbonate template

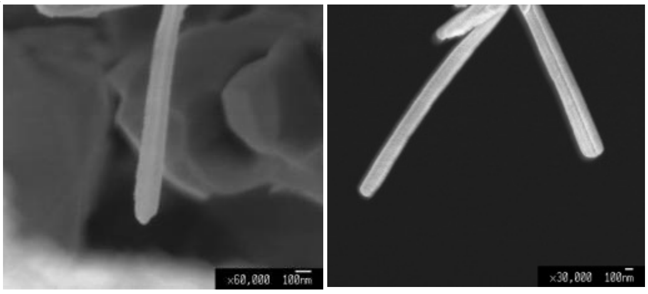

Fig. 3. SEM micrographs of TiO_2 nano-rods after annealing at 530 ºC in two different magnifications of 60,000 X (left) and 30,000 X (right)

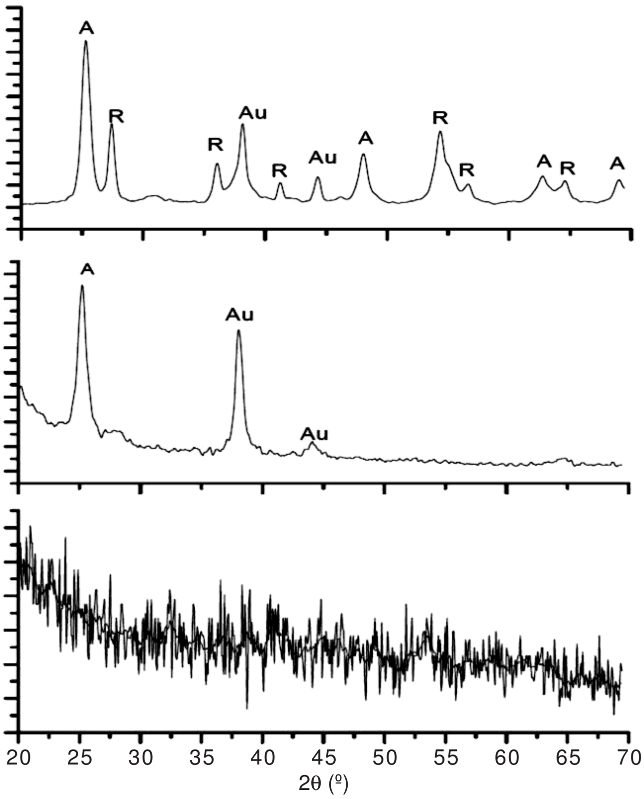

Fig. 4. XRD patterns of TiO_2 nano-rods synthesized and annealed at 120 ºC and 530 ºC for 50 min

Conclusion

Microscopic investigations have revealed that the TiO_2 nano-rods grown in polycarbonate templates using electrophoresis deposition from aqueous-based sol show uniform diameter throughout the nanostructure with a completely plain surface. XRD analysis of the TiO_2 nano-rods grown in polycarbonate templates by electrophoresis deposition from aqueous-based sol implies that phase structure of the nanorods exposed to drying at 120 ºC was a mix of anatine and brokite whereas those annealed at 530 ºC for 50 min introduced a mix of anatine and rutile. This study has clarified that the combination of two methods of sol-gel and electrophoresis deposition are much advantageous over other methods considering temperature of reaction and quality of the nanostructure.

REFERENCES

1. H. Jia, Z. Zheng, H. Zhao, L. Zhang and Z. Zou, *Mater. Res. Bull.*, **44**, 1312 (2009).
2. Y. Li, M. Guo, M. Zhang and X. Wang, Hydrothermal Synthesis and Characterization of TiO_2 Nanorod Arrays on Glass Substrates (2009).
3. K. Pan, Q. Zhang, Q. Wang, Z. Liu, D. Wang, J. Li and Y. Bai, *Thin Solid Films*, **515**, 4085 (2007).
4. K. Asagoe, S. Ngamsinlapasathian, Y. Suzuki and S. Yoshikawa, *Cent. Eur. J. Chem.*, **5**, 921 (2007).
5. X. Zhang, A. Jianhong, P. Lee, D.D. Sun and J.O. Leckie, *J. Memb. Sci.*, **313**, 44 (2008).
6. L. Francioso, A.M. Taurino, A. Forleo and P. Siciliano, *Sens. Actuators B*, **130**, 70 (2008).
7. Z. Zhang, C. Wang, R. Zakaria and J.Y. Ying, *J. Phys. Chem. B*, **102**, 10871 (1998).
8. Y. Wu, H. Yan, M. Huang, B. Messer, J.H. Song and P. Yang, *Chem. Eur. J.*, **8**, 1260 (2002).
9. S.K. Pradhan, P.J. Reucroft, F. Yang and A. Dozier, *J. Crystal Growth*, **256**, 83 (2003).
10. A.M. Morales and C.M. Lieber, *Science*, **279**, 208 (1998).
11. Y.X. Zhang, G.H. Li, Y.X. Jin, Y. Zhang, J. Zhang and L.D. Zhang, *Chem. Phys. Lett.*, **365**, 300 (2002).
12. A.S. Attar, M.S. Ghamsari, F. Hajiesmaeilbaigi, Sh. Mirdamadi, K. Katagiri and K. Koumoto, *J. Mater. Sci.*, **43**, 5924 (2008).
13. W. Wook, S. Park, K.J. Kim and C. Shin, *J. Mater. Sci.*, **36**, 4299 (2001).
14. T. Wen, J. Zhang, T.P. Chou, S.J. Limmer and G. Cao, *J. Sol-Gel Sci. Technol.*, **33**, 193 (2005).
15. H. Jia, Z. Zheng, H. Zhao, L. Zhang and Z. Zou, *Mater. Res. Bull.*, **44**, 1312 (2009).
16. W. Wook, S. Park, K.J. Kim and C. Shin, *J. Matter. Sci.*, **36**, 4299 (2001).
17. M.R. Mohammadi, M.C. Cordero-Cabrera, M. Ghorbani and D.J. Fray, *J. Sol-Gel. Sci. Techn.*, **40**, 15 (2006).
18. G. Cao, *J. Phys. Chem.*, **B108**, 19921 (2004).
19. R.N. Basu, C.A. Randall and M.J. Mayo, *J. Am. Ceram. Soc.*, **84**, 33 (2001).
20. Vu Trung, M. Pavlik, N. Hebestreit and J. Pfleger, *Electrochim. Acta*, **51**, 1117 (2005).