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Low Temperature Synthesis of Anatase TiO_2 Nanoparticles and its Application in Nanocrystalline Thin Films

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Abstract. The nano-sized TiO_2 is an important material based on its application for solar cells. The low-cost synthesis of nano-sized TiO_2 is of high demand for commercial purposes. Synthesis of TiO_2 nanoparticles was achieved via the low-temperature Sol-gel method. Surface morphology was confirmed from SEM analysis, which showed that particle size is in the range of nanometer with no aggregation, The XRD results confirm the formation of anatase phase with high crystallinity. Furthermore, as prepared nano-sized TiO_2 particles were developed as sol-gel ink which was later deposited by spin coating on glass substrate with controlled spinning speed thereafter structural and optical properties were characterized by UV-vis spectroscopy, electrochemical impedance spectroscopy and DSC-TGA. The low-cost synthesis of TiO_2 nanoparticles with highly conductive thin films can be used as a potential material for future dye-sensitized solar cells

Introduction

The technique through which an outcome is fabricated has a prominent influence on its properties. Solution process method is a robust way to produce high purity products for a wide variety of applications and make various revolutionary developments is the field of nanotechnology [1-2]. Nowadays the modern processes of synthesizing metal oxide nanostructures are mainly involved in Solution process which requires an inorganic precursor followed by the preparation of gel with semi rigid mass, through a series of reactions [3-4].

Low temperature synthesis of metal oxide nanoparticles by Solution process is a low-cost technique for the fabrication of powders and coatings [5-6]. Solution Processed synthesis of TiO_2 nanoparticles has been studied extensively because of its wide application including protective coatings, white pigments for paints, cosmetics, fillers, piezoelectric devices, catalysts, as well as its chemical stability, with suitable band gap energy and biocompatibility [6-13]. TiO_2 conductive thin films also can be used as a parameter for Dye Sensitized Solar Cell (DSSC) to enhance its performance rate [14].

The usually TiO_2 is existing in three different crystalline phases such as brookite, rutile, and anatase. Among these phases, anatase and rutile crystalline phase are most widely used in the application of anticorrosive coatings, antireflection films, photocatalysis and solar cell [15-18]. In lower temperature applications, anatase and brookite phases are more stable but both will change to the rutile phase at certain temperature [19]. Anatase phase is found as mineral forms of TiO_2 and mostly researchers tend to utilize anatase TiO_2. Due to the effective photocatalytic activity, anatase crystalline TiO_2 is mostly used in photo-catalysis applications because of better response to ultraviolet photons and larger band gap as compared to brookite and rutile phases. The current fabrication techniques employed for TiO_2 thin films by solution process for solar cell applications are usually some sort of casting method such as doctor-blading and spin-coating for lab scale [20].

In the present study, we demonstrated the synthesis of TiO_2 nanoparticles by simple solution method. For application of TiO_2 nanoparticles for photovoltaic devices, it is important to understand the structural and optical properties of TiO_2 nanoparticles nanofilms. For that, we formulated ink of as-synthesized TiO_2 nanoparticles and deposited as a thin film on the glass substrate by low cost spin coating to investigate structural and optical properties in detail.

Experimental Details

Chemicals. Titanium isopropoxide (TTIP), Ethanol, Acetone, Potassium Iodide, FTO glass, were used as received without further purification.

Synthesis of TiO_2 Nanoparticles. The "A" solution was made by mixing TTIP and absolute ethanol in a volume of 20ml and 30ml, respectively. The "B" solution was made by mixing acetone and absolute ethanol in a volume of 7.5ml and 15ml, respectively. The titanium dioxide sol-gel was prepared by sequentially premixing the "B" solution into the "A" solution and stirred at room temperature for 10 min to form sol 1. The mixture of the solutions was stirred at room temperature for 90 min to form an insoluble gel followed by centrifugation of as-synthesized mixture at 3000 rpm for 30 min and washing with ethanol for 3 times. The TiO_2 nanoparticles were further dried at 80^{o}C for 12 h in order to characterize X-ray Diffraction (XRD).

Synthesis of TiO_2 Nanoparticles based Nanofilms. The as-synthesized TiO_2 Nanoparticles were formulated as an ink by taking the TiO_2 powder 2 grams and dissolve mixed solvents of deionized (DI) water: Ethylene glycol: Glycerol = 50:25:25 vol %. For the deposition of TiO_2 nanofilms, quartz glass substrates were cleaned by sonication in DI-water, acetone and ethanol for 15 min each, sequentially. As formulated TiO_2 ink was then dropped onto glass substrate and spin-coated at 3000 rpm for 30 seconds. The films were dried at 100^{o}C for 10 min on a hotplate to evaporate solvents and remove residuals.

Results and Discussion

Structural Properties of TiO_2 based Nanofilms. Fig. 1 demonstrated a typical XRD spectrum of the as-synthesized TiO_2 nanoparticles. The peaks of the TiO_2 powder samples are identified to dominating (101), (004), (200) and (211) crystal planes. All diffraction typical peaks are distinct and can be perfectly corresponded to the anatase TiO_2 (JCPDS-21-1272) [21]. It can be seen from figure that no peaks for other impurities or other crystal phases are observed, which confirms that the as-grown TiO_2 nanoparticles are high crystalline.

Fig. 2 (a, b) shows the top and cross-sectional FESEM images of TiO_2 nanofilms deposited on the quartz glass substrate. The surface of the TiO_2 film was observed as completely dense, uniform, and smooth in Figure 2(a). It is also noted that the TiO_2 nanofilm has fully covered and good adhesion of films on the glass substrate. In addition, a large number of rounded grains with the film thickness of ~150 nm were observed in a cross-sectional SEM image of TiO_2 film (Fig. 2(b)).

Optical Properties of TiO_2 Nanoparticles based Nanofilm. The optical properties of TiO_2 nanofilm which were prepared on quartz substrate have been studied in this work and shown in Figure 3. UV-vis absorption spectrum TiO_2 nanofilm sample clearly showing (figure 3(a)) low absorption in the visible and infrared regions; however, the absorption in the ultraviolet region is high. The bandgap of TiO_2 nanofilm is calculated by extrapolating the absorption edge onto energy axis. Figure 3(b) shows plots of $(\alpha h\upsilon)^2$ versus photon energy and optical bandgap of TiO_2 nanofilm was found to be 3.46 eV. It is worth noting that resulted absorption spectrum and bandgap calculation of TiO_2 nanofilm was in agreement with the pure TiO_2 which was obtained by other researchers [22-23].

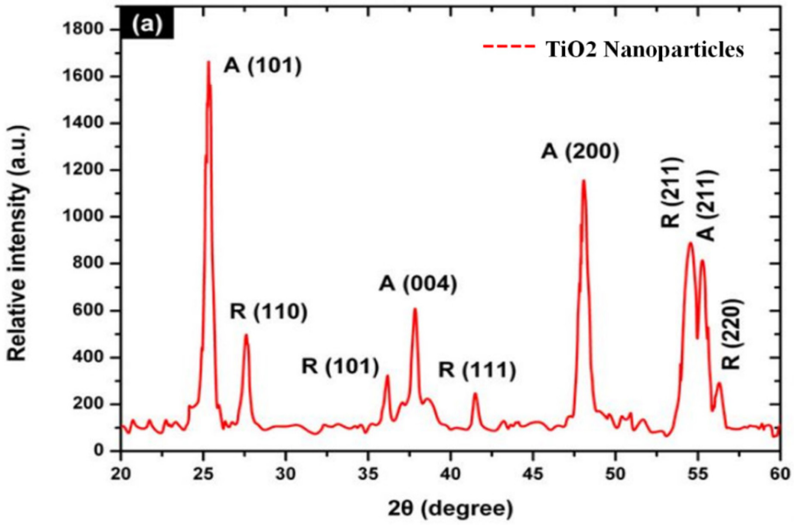

Fig. 1. XRD patterns of TiO_2 nanoparticles

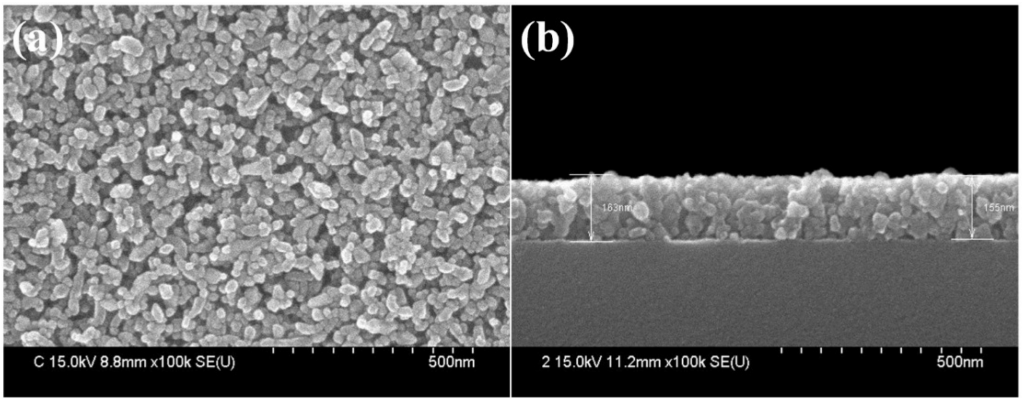

Fig. 2. FESEM images of TiO_2 nanofilm (a) Cross-section and (b) surface view deposited on the quartz glass substrate

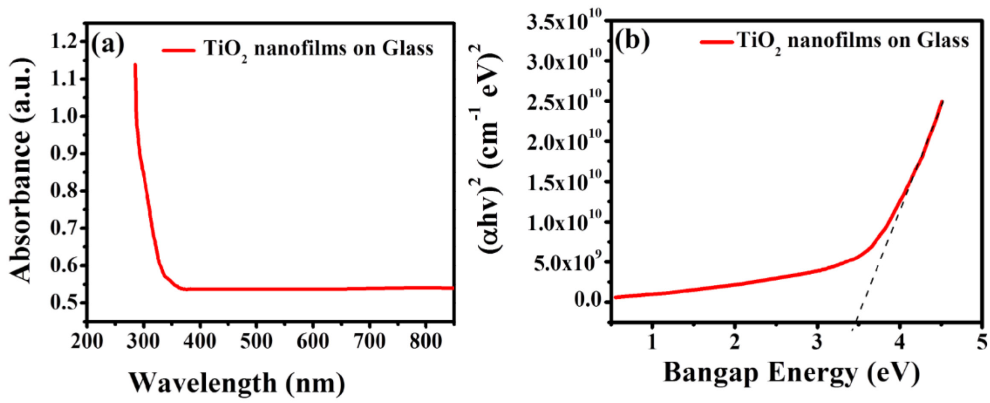

Fig. 3. (a) UV-vis absorption spectra and (b) bandgap calculation of TiO2 nanofilm deposited on the quartz glass substrate

Electrical Measurement of TiO_2 Nanoparticles based Nanofilms. Electrical characteristics of TiO_2 nanofilm were measured using a probe station and a semiconductor parameter analyzer. Fig. 4 show the I-V characteristics of the TiO_2 nanofilms deposited on the quartz glass substrate for the applied bias voltage in the range between −20V and +20V. As it can be seen from linear scale of I-V curve, TiO_2 nanofilm is displaying a conductive state when a forward bias voltage is applied and however linear relationship of the characteristics reveals that the contact is ohmic in nature of TiO_2 nanofilm [24].

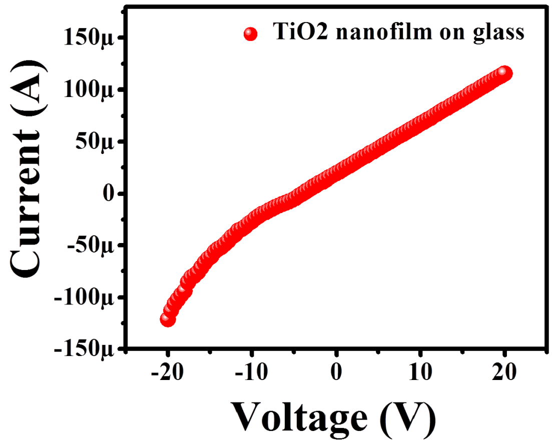

Fig. 4. I-V characteristics of TiO2 nanofilm deposited on the quartz glass substrate

Conclusions

In conclusion, the TiO_2 nanoparticles have been successfully synthesized via low-temperature solution process. XRD analysis indicated that as-prepared TiO_2 nanoparticles were pure anatase crystalline phase and uniformly dispersed. Moreover, TiO_2 nanoparticles were further developed as an ink using mixed solvents of water, ethylene glycol and glycerol. FESEM micrographs confirmed that as-deposited TiO_2 nanoparticles nanofilms were smooth, dense without any cracks and possess good adhesion with substrate. In addition, the achieved optical and electrical properties of TiO_2 nanoparticles nanofilms can be paternally used for photovoltaic applications.

References

[1] E. Moncada, R. Quijada, J. Retuert, Nanoparticles prepared by the sol–gel method and their use in the formation of nanocomposites with polypropylene, Nanotechnol., 18 (2007) 335606 - 613.

[2] X. Yu, T. J. Marks, A. Facchetti, Metal oxides for optoelectronic applications, Nat. Mater., 15 (2016) 383–396.

[3] R. Sui, P. Charpentier, Synthesis of Metal Oxide Nanostructures by Direct Sol–Gel Chemistry in Supercritical Fluids, Chem. Rev., 112 (2012) 3057–3082.

[4] I. A. Rahman, V. Padavettan, Synthesis of Silica Nanoparticles by Sol-Gel: Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer Nanocomposites, J. Nanomater., 2012 (2012) 132424-39.

[5] S. Tripathy, D. S. Saini, D. Bhattacharya, Synthesis and fabrication of MgAl2O4 ceramic foam via a simple, low-cost and eco-friendly method, J. Asi. Cera. Soci., 4 (2016) 149-154.

[6] V. Vohra, W. Mroz, S. Inaba, W. Porzio, U. Giovanella, F. Galeotti, Low-cost and green fabrication of polymer electronic devices by push-coating the polymer active layers, ACS Appl. Mater. Interf., 9 (2017) 25434–25444.

[7] C. Chen, Y. Wang, G. Pan, Q. Wang, Gel-sol synthesis of surface-treated TiO_2 nanoparticles and incorporation with waterborne acrylic resin systems for clear UV protective coatings, Journal of Coatings Technol. Resear., 11 (2014) 785–791.

[9] B. A. van Driela, P. J. Kooymand, K. J. van den Bergb, A. Schmidt-Otte, J. Dikc, A quick assessment of the photocatalytic activity of TiO_2 pigments — From lab to conservation studio, Microche. J., 126 (2016) 162-171.

[10] P. Lu, S. C. Huang, Y. P. Chen, L. C. Chiueh, D. Y. C. Shih, Analysis of titanium dioxide and zinc oxide nanoparticles in cosmetics, Journal of Food and Drug Analysis 23 (2015) 587-594.

[11] M. Tanahashi, Development of Fabrication Methods of Filler/Polymer Nanocomposites: With Focus on Simple Melt-Compounding Based Approach without Surface Modification of Nanofillers, Mater., 3 (2010) 1593-1619.

[12] M. Eslamian, Inorganic and Organic Solution-Processed Thin Film Devices, Nano-Micro Lett., 9:3 (2017) 1-23.

[13] N. S. Khalid, F. I. M. Fazli, N. K. A. Hamed, M. L. M. Napi, S. C. Fhong, M. K. Ahmad, Biocompatibility of TiO_2 Nanorods and Nanoparticles on HeLa Cells, Sains Malaysiana 45 (2016) 1675–1678.

[14] M. M. Rashad, A. E. Shalan, M. L. Cantú, M. S. A. Abdel-Mottaleb, Enhancement of TiO_2 nanoparticle properties and efficiency of dye-sensitized solar cells using modifiers Authors Authors and affiliations, Appl. Nanosci., 3 (2013) 167-174.

[15] Y. Lu, S. Guan, L. Hao, H. Yoshida, Review on the Photocatalyst Coatings of TiO_2: Fabrication by Mechanical Coating Technique and Its Application, Coat.,5 (2015) 425-464.

[16] T. Busani1, R. A. B Devine, Dielectric and infrared properties of TiO_2 films containing anatase and rutile, Semicond. Sci. Technol., 20 (2005) 870–875.

[17] W. Siah, H. O. Lintang, M. Shamsuddin, L. Yuliati, High photocatalytic activity of mixed anatase-rutile phases on commercial TiO_2 nanoparticles, IOP Conf. Series: Mater. Sci.Eng., 107 (2016) 012005.

[18] N. G. Park, J. V. Lagemaat, A. J. Frank, Comparison of Dye-Sensitized Rutile- and Anatase-Based TiO_2 Solar Cells, Journal of Phy. Chem, B, 104 (2000) 8989-8994.

[19] K. Fischer, A. Gawel, D. Rosen, M. Krause, A. A. Latif, J. Griebel, A. Prager, A.Schulze, Low-Temperature Synthesis of Anatase/Rutile/Brookite TiO_2 Nanoparticles on a Polymer Membrane for Photocatalysis, Catal., 7 (2017) 1-14.

[20] S. Saehana, R. Prasetyowati, M. I. Hidayat, P. Arifin, Khairurrijal, M. Abdullah, Efficiency Improvement in TiO_2-Particle based Solar Cells after Deposition on Metal in Spaces between Particles, International Journal of Bas.Appl. Sci., 6 (2011) 15-28.

[21] W. Li, R. Liang, A. Hu, Z. Huanga, Y. N. Zhou, Generation of oxygen vacancies in visible light activated one-dimensional iodine TiO_2 photocatalysts, RSC Adv., 4 (2014) 36959–36966.

[22] D. L. Domtau1, J. Simiyu, E. O. Ayieta, B. Muthoka1, J. M. Mwabora1, Optical and Electrical Properties Dependence on Thickness of Screen-Printed TiO_2 Thin Films, J. Mater.s Phy. Chem., 4 (2016) 1-3.

[23] J. Xu, X. Xiao, A. L. Stepanov, F. Ren, W. Wu, G. Cai, S. Zhang, Z. Dai1, F. Mei, C. Jiang, Efficiency enhancements in Ag nanoparticles-SiO2 -TiO_2 sandwiched structure via plasmonic effect-enhanced light capturing, Nanosc. Res. Lett., 8:73 (2013) 1-5.

[24] R. Kaur, B. Pal, Plasmonic Coinage Metal-TiO_2 Hybrid Nanocatalysts for Highly Efficient Photocatalytic Oxidation under Sunlight Irradiation, New J.Chem., 39 (2015) 5966-5976.