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Morphology Effect of Anodized TiO_2 Nanotubes Active Anodes on Dye Sensitive Solar Cell

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Anodized TiO_2 nanotubes have recently became one of the favourable active anodes in making dye sensitive solar cell. This work investigate the effect of morphological properties of the anodized TiO_2 on the electrical conversion efficiency (η %) of the dye sensitive solar cells fabricated using N_3 commercial dye, polymers blend (KI/PEO/PMMA) as electrolyte and electro-polymerized polyaniline on fluorine-doped tin oxide glass as counter electrode. Different morphological TiO_2 were produced *via* anodizing of the Ti foil in ethylene glycol containing 0.5 % NH_4F and 4 mL deionized water, at different anodizing potentials; namely 10, 20, 30, 40, 50 and 60 v for 1 h at room temperature. The deposited anodized TiO_2 nanotubes layers extensively characterized using scanning electron microscope. The calculated (η %) ranged between 0.370 and 2.126 %, the relation between these values and the tubes parameters were discussed.

Keywords: Dye sensitive solar cells, Gel polymer electrolyte, TiO_2 nanotubes, Counter electrode.

INTRODUCTION

Dye-sensitized solar cells (DSSCs) have pulled a great consideration because they are financially savey and earth amicable with efficiencies practically identical to those of the customary silicon-based cells [1]. A dye sensitive solar cell is composed of a dye adsorbed nanoporous TiO_2 strata on a indium-tin oxide (ITO) or fluorine-doped tin oxide (FTO) glass substrate, redox electrolytes and a counter electrode [2]. Unidirectional charge flow with no electron leakage at the interfaces is essential for high energy-conversion efficiency. Then, researchers started to survey the use of ordinal TiO_2 in dye sensitive solar cells; this includes TiO_2 nanowires, nanorods and anodized TiO_2 nanotubes (ATNTs) which may be an interesting process to improve electron transport through the film. For the formation of an efficient dye sensitive solar cell, photoanode materials with various morphologies such as nanoparticles [3], ordered mesostructured materials [4], one-dimension structured materials (nanorod, nanowire and nanotube) have been extensively explored [5,6]. It is now well-accepted that a high-efficiency photoelectrode for dye sensitive solar cells requires not only a high surface area for the loading of large amounts of dye molecules but also a tailored microstructure for light harvesting and fast electron transport [7]. In previous years, more and more attentions have been paid to the polymeric materials due to their potential applications in solid state batteries, fuel cell, smart windows, sensors and electrochemical devices [8]. Numerous researchers have worked on various host polymers *e.g.*, polyethylene oxide (PEO), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC) and polyvinyl acetate (PVA). Among various homopolymers studied, polyethylene oxide exhibits stellar ion transport properties as a result of its high concentration of electron pairs and rapid segmental dynamics. Polyethylene oxide attains a high degree of crystallinity, approximately 60 %, at room temperature. Polymer blends display a practical and efficient way to fulfill novel requirements for material properties and applications [9,10]. The addition of salt to the polymer provides mobile ions and the polymer host chains play a critical role in ionic transport process of the polymer electrolytes. For these reasons, we chose polymer blend as electrolyte for all 6 assembled cells in this research.

Among the known materials used in making the catalyzed counter electrodes [11], polyaniline coated FTO glass was candidates to serve as counter electrode [12]. It is well-known that there were two types of electrolytes used to produce anodized TiO_2 nanotubes and the two should contain fluoride ions, the first is aqueous and the second is non-aqueous. It is also known that the first type produces short TiO_2 nanotubes (> 1 μ) while the second can grow very longer [13-18]. In this work, non-aqueous route were chosen to produce different morphological anodized TiO_2 nanotubes with length more than one microns to serve as photoanode in the dye sensitive solar cells.

EXPERIMENTAL

All materials used as received, polyethylene oxide (PEO, Sigma-Aldrich) with an average molecular weight of 100,000, polymethylmetacrylate (PMMA Sigma-Aldrich,) with average molecular weight of 996,000, dimethyl sulfoxide (Sigma-Aldrich) used as solvent, potassium iodide (BDH) and iodine (BDH), Ti foil (99.5 % purity, Alfa Aesar), Pt foil (99.9 %, Alfa Aesar), ethylene glycol (99.8 %, BDH), ammonium fluoride (98 %, Aldrich), aniline monomer (purity 99.4 %, BDH), N_3 dye (Solaronix SA), sulfuric acid (99.8 %, BDH).

Preparation of dye sensitive solar cell electrolyte: Polymers blend electrolyte was prepared with KI. First, we dissolve potassium iodide (30 % wt.) in 5 mL of DMSO in a glass bottle by using stirrer and heat to 65 °C and then added the two polymers; PEO and PMMA. One by one with weight ratio 70/30 % and stirred for one h till being a gel. The polymers blend was allowed to cool down to room temperature and subsequently, iodine chips were added. Finally, the mixture was again constantly magnetically stirred (24 h) to obtain a homogeneous gel electrolyte. The polymer electrolyte was then transferred into a desiccator for further drying. The gel electrolyte was prepared and studied under controlled temperature and humidity conditions (25 °C and RH about 50 %).

Synthesis of anodized TiO_2 nanotubes (ATNTs) electrode: Highly ordered TiO_2 nanotube arrays grown on titanium foil by an anodization procedure in a two electrode electrochemical plexiglass cell (Fig. 1), this anodizing system consists of electrochemical cell made of homemade plexiglass cell, two electrodes (cathode and anode) and DC-power supply. During anodization the current (mV throw 1 Ω resistance) and the voltage were recorded continuously using two channels millvoltmeter XY recorder (siemense8800), extra Avometer was used to measure anodizing potential. The electrochemical processes were performed at 20 °C, the temperature of the electrolyte maintained within ± 1 °C with cooling and heating water bath circulator with a thermo couple sensor. The distance between the anode and cathode was 30 mm.

Titanium foil for rectangular dimensions of (2 cm × 2.5 cm) with 0.25 mm thick was used as anode, the platinum foil used as cathode. A thin TiO_2 nanotube array layer was created by anodizing the Ti foil in a solution of ethylene glycol containing 0.5 % ammonium fluoride and 4 mL deionized water. Anodization was accomplished at different voltages in the range between 10 to 60 V, the anodizing duration was 1 h in all experiments. After the end of the anodizing period, the anodized foil was rinsed with deionized water and then with ethanol, dried under a flow of nitrogen gas and annealed at 450 °C for 30 min in air. All produced anodized TiO_2 nanotubes were examined using scanning electron microscope (Zeiss Ultra 60 FE-SEM).

Preparation of polyaniline (PANI)/FTO electrode: Polyaniline (PANI) films were instue deposited on a conducting FTO glass to serve as counter electrode for dye-sensitized solar cell (DSSC), by cyclic potentiodynamic procedure using advanced potentiostat (MLab200, Bank Elek.GmBH) as shown in Fig. 2, the electrolyte composed of 0.1 M aniline monomer and 0.3 M sulfuric acid, the voltage scan range was (-100 to 1500 mV) with a scan rate of 30 mV/sec and cycle repetitions of 6.

Fabrication of dye sensitized solar cells: TiO_2 nanotube electrodes were immersed in an ethanolic solution of N_3 dye (Solaronix SA) for 24 h, the electrodes then have been taken out from the dye solution and washed with acetone to remove unabsorbed dye. Dye sensitive solar cells were assembled using the prepared photoanodes and counter electrodes and fixed both electrodes facing each other using a clips binder. The space between two electrodes was obtained by using two sides scotch tape as a spacer and sealed after putting a small amount of electrolyte over photoanodes.

RESULTS AND DISCUSSION

SEM examination of anodized TiO_2 nanotubes: The SEM images revealed a small effect of the anodizing potential on the inner tube diameters at all voltages, they are around 75 nm. The tube wall thickness increased with increasing the anodizing potentials up to 30 V, then deceased with increasing

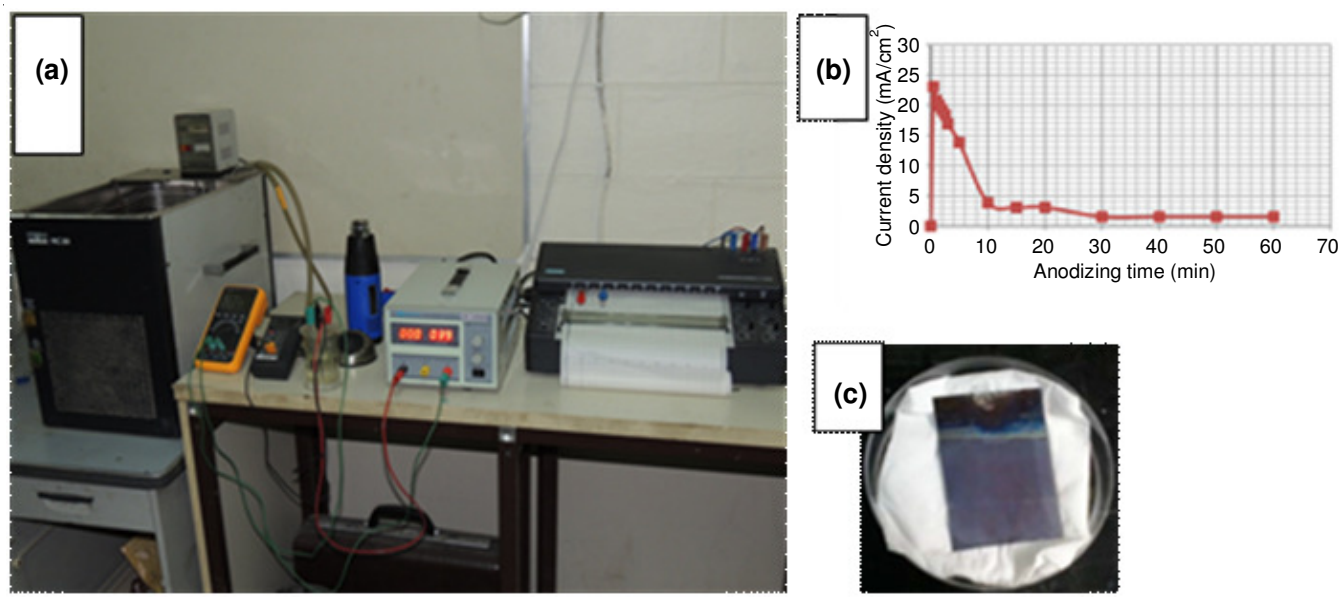

Fig. 1. (a) Ti anodizing apparatus, (b) sample profile of the current-time plot of Ti anodizing process, (c) Ti/TiO_2 nanotubes photoanode

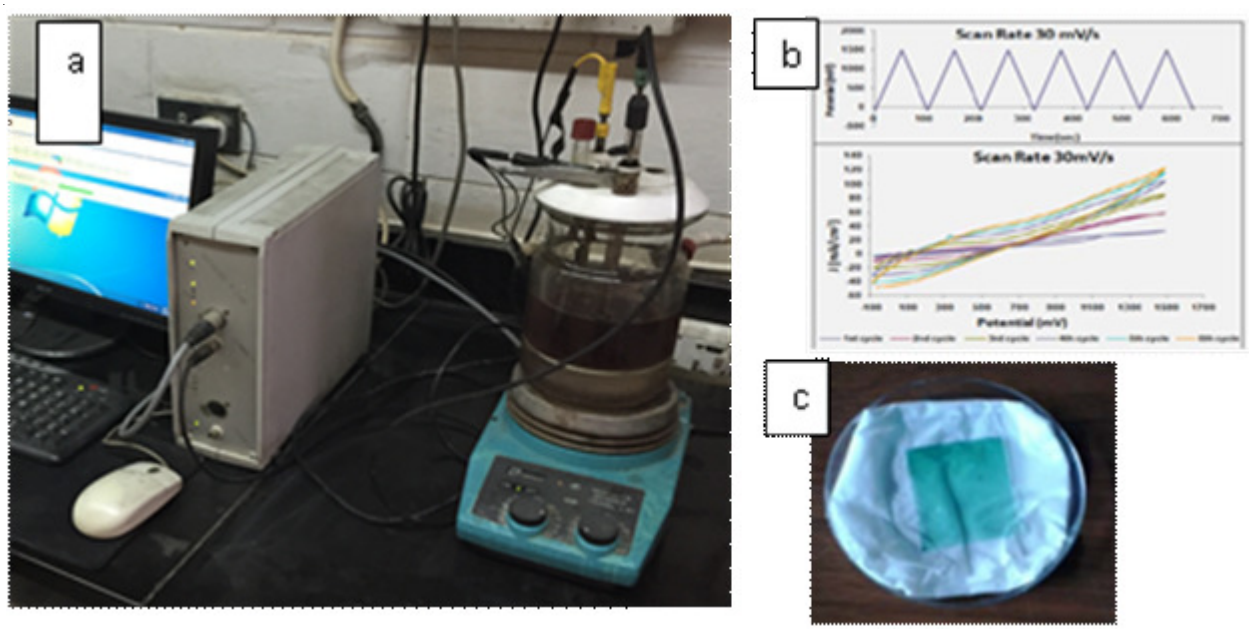

Fig. 2. (a) Apparatus used in the electropolymerization of aniline monomer, (b) electropolymerization cyclic voltagram, (c) PANI/FTO counter electrode

potential up to 60 V. On the other hand, the tubes length which were estimated over TiO_2 bundles due to artificially scratches made on the template surface increased with increasing potentials and reached 8000 nm at 60 V (Fig. 3). Fig. 3 also shows the current time profile of the anodizing process. The average values of all tubes parameters are listed in Table-1.

Photovoltaic performance of TiO_2 nanotube (TNT) dye sensitive solar cells: It assured that the photovoltaic properties of dye sensitive solar cells largely depend on the film thickness. Fig. 3 shows the current-voltage photovoltaic performance curves of dye sensitive solar cells based on the nanotube TiO_2 (TNT) electrode anodization at different voltages, 10, 20, 30, 50 and 60 volts, under AM 1.5 illumination (100 mW/cm^2) at room temperature.

Current–voltage (I–V) characteristics plots of six dye sensitive solar cells were established using two electrodes potentiostat under a standard air mass (AM 1.5) with Zenon lamp illumination at 100 mW/cm^2 as shown in Fig. 4.

The fill factor (FF) is defined as the ratio of maximum power output to the product of V_{OC} and J_{SC}, ($FF = J_{max} \times V_{max}/J_{sc} \times V_{oc}$) where J_{max} and V_{max} are the current density and voltage at maximum power output, J_{sc} is the short circuit current (V = 0)

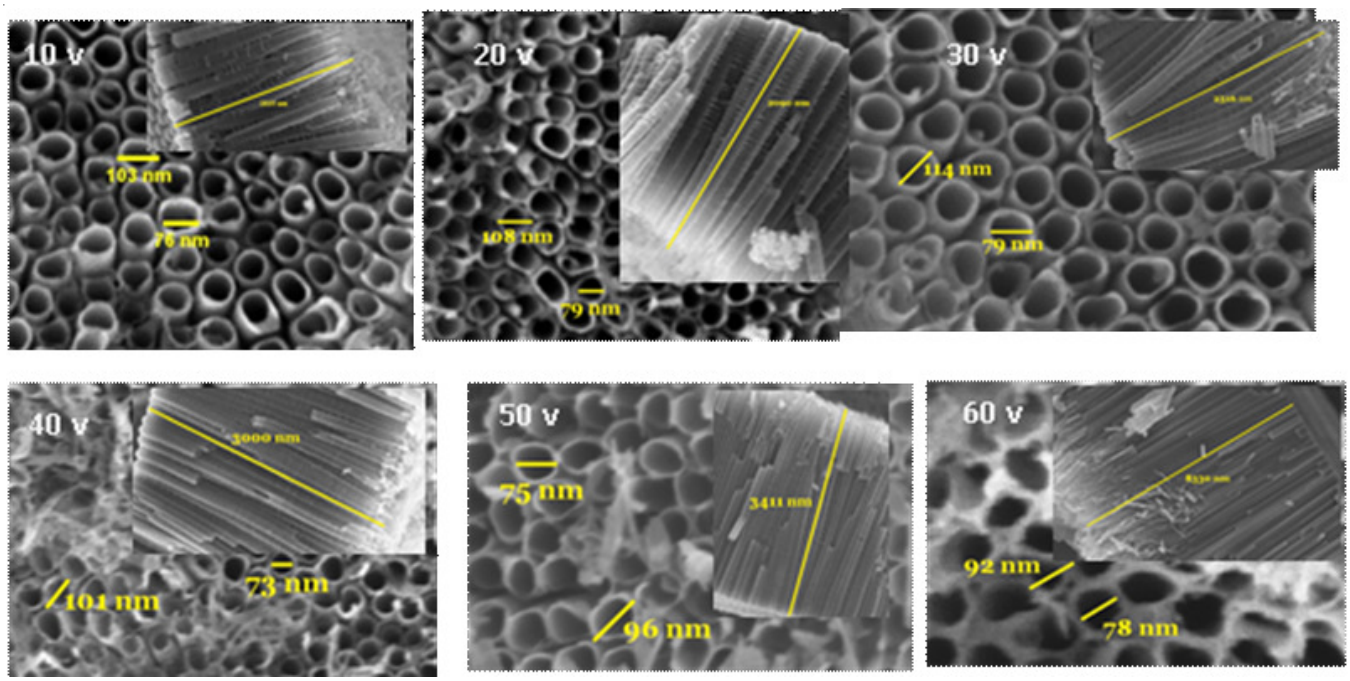

Fig. 3. SEM images show the outer, inner diameters and tubes length for the produced TiO_2 nanotubes by anodizing of the Ti foil in ethylene glycol containing/0.5 % NH_4F/4 mL deionized water at different anodizing potentials for 1 h at room temperature

TABLE-1
CALCULATED TUBES LENGTH, CELL DIAMETER, INNER DIAMETER AND TUBE WALL THICKNESS FOR THE PRODUCED TiO_2 NANOTUBES BY ANODIZING OF THE TI FOIL IN ETHYLENE GLYCOL CONTAINING/0.5 % NH_4F/4 mL DI WATER AT DIFFERENT ANODIZING POTENTIALS FOR 1 h AT ROOM TEMPERATURE

Anodizing potential (volt)	Tubes length (nm)	Outer diameter (nm)	Inner diameter (nm)	Tube wall thickness (nm)
10	1835	103	76	13.5
20	2090	108	79	14.5
30	2316	114	79	17.5
40	3000	101	73	14.0
50	3411	96	75	11.5
60	8330	92	78	7.0

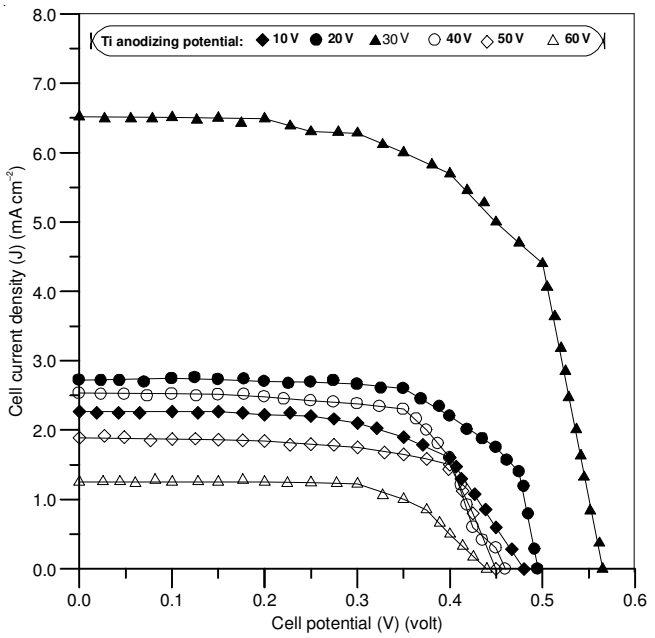

Fig. 4. J-V plots of the DSSC's composed of different anodized TiO_2 nanotubes grown on Ti foil as photo-anode with polyaniline coated FTO as counter electrode using gel electrolyte of (70 % PEO:30 % PMMA-30 % KI-I_2)

and V_{oc} is the open circuit voltage (J = 0). The power conversion efficiency (η %), is defined as the ratio of maximum power output (P_{max}) to the power of the incident light (P_{in}); $\eta = P_{max}/P_{in} = J_{sc} \times V_{oc} \times FF/P_{in} \times 100$ [19]. All the measured and calculated cells parameters are listed in Table-2.

The results reflected a strong relation between tubes length and the power conversion efficiency (η %). It is found that the electrical conversion efficiency (η %) increased with increasing the tubes length until reaching the value of (2.126 %) using TiO_2 photoanode with length of (2316 nm) fabricated by Ti foil anodizing at voltage of 30 V, after this value the trend is reversed and finally the longer nanotubes showed the less conversion efficiency (0.37 %) in which air perhaps trapped in during infiltration of the dye solution and redox electrolyte.

The pore diameter (or tube inner diameter) and intertube spacing have a significant influence on surface roughness factor and porosity of nanotube arrays, thus affecting the performance of dye-sensitized solar cells. But in present case, the tubes diameters seems to be have no effect on η % because all produced photoanodes have nearly similar diameters (around 75 nm). On the other hand, η % increased always with increasing tubes wall thickness which may be attributed to the enhancing dye loading properties.

The J_{sc} changes is predominantly related to the changes in injection current from excited dyes to the conduction band of TiO_2, arising from the surface area and film thickness. The decrease of V_{oc} implies that the conduction band edge of TiO_2 shifts positively, assuming that both the energy planes of the dye and the standard reduction potential of I^{3-}/I^- do not vary irrespective of film thickness [19]. The V_{oc} decreases can be related to the enhancement of the above-mentioned back electron transfer. Increasing the surface area of the electrode with increasing the film thickness mostly likely leads to an increase in the number of trapping surface states, through which the back electron transfer would be facilitated, resulting in a lowering of the V_{oc} [20]. The variations of J_{sc} and η are similar, indicating that the η increase is mainly due to the J_{sc} increase. The lower V_{oc} and J_{sc} exhibited by the cell utilizing the anodized photoanode with (60 V) are probably due to the smaller number of photoelectrons injected into the conduction band of the TiO_2 nanotubes. As reported earlier, the relatively lower quantity of adsorbed dye on TNT-TiO_2 film probably results from the disordered structure as well as the random agglomeration of TiO_2 tubes and finally leading to the reduction of effective adsorption area of TNT-TiO_2 film [21].

Conclusion

Different morphologies of anodized TiO_2 nanotubes were produced by applying different anodizing potentials namely; 10, 20, 30, 40, 50 and 60 V, the anodized Ti foils serve as photoanodes in making dye sensitive solar cells, the effect of the tubes length showed two different reversed trends relation with the electrical conversion efficiency (η %); the first was positively related trends until reaching the length of 2316 nm and the second was negatively trends going to length of 8300 nm. Increasing the tubes wall thickness always leads to increasing the electrical conversion efficiency (η %).

TABLE-2
PHOTOVOLTAIC PARAMETERS FOR THE DYE SENSITIVE SOLAR CELLS MADE OF USING DIFFERENT MORPHOLOGY ANODIZED TiO_2 NANOTUBES

Ti anodizing potential (volt)	J_{sc} (mA cm^{-2})	V_{oc} (volt)	J_{max} (mA cm^{-2})	V_{max} (volt)	Fill factor (FF)	η (%)
10	2.267	0.480	1.98	0.391	0.711	0.774
20	2.720	0.495	2.11	0.425	0.666	0.896
30	6.520	0.565	4.43	0.480	0.577	2.126
40	2.530	0.460	2.22	0.411	0.784	0.912
50	1.890	0.450	1.52	0.375	0.670	0.570
60	1.253	0.440	0.88	0.421	0.672	0.370

REFERENCES

1. C.H. Lee, S.W. Rhee and H.W. Choi, *Nano. Res. Lett.*, **7**, 48 (2012); https://doi.org/10.1186/1556-276X-7-48.
2. H. Kim, H. Choi, S. Hwang, Y. Kim and M. Jeon, *Nano. Res. Lett.*, **7**, 53 (2012); https://doi.org/10.1186/1556-276X-7-53.
3. T.H. Meen, W. Water, W.R. Chen, S.M. Chao, L.W. Ji and C.J. Huang, *J. Phys. Chem. Solids*, **70**, 472 (2009); https://doi.org/10.1016/j.jpcs.2008.12.002.
4. L. Hu, S. Dai, J. Weng, S. Xiao, Y. Sui, Y. Huang, S. Chen, F. Kong, X. Pan, L. Liang and K. Wang, *J. Phys. Chem. B*, **111**, 358 (2007); https://doi.org/10.1021/jp065541a.
5. J. Jiu, S. Isoda, F. Wang and M. Adachi, *J. Phys. Chem. B*, **110**, 2087 (2006); https://doi.org/10.1021/jp055824n.
6. K. Shankar, J. Bandara, M. Paulose, H. Wietasch, O.K. Varghese, G.K. Mor, T.J. LaTempa, M. Thelakkat and C.A. Grimes, *Nano Lett.*, **8**, 1654 (2008); https://doi.org/10.1021/nl080421v.
7. H. Xu, X. Tao, D.T. Wang, Y.Z. Zheng and J.F. Chen, *Electrochim. Acta*, **55**, 2280 (2010); https://doi.org/10.1016/j.electacta.2009.11.067.
8. A. Dey, S. Karan, A. Dey and S.K. De, *Mater. Res. Bull.*, **46**, 2009 (2011); https://doi.org/10.1016/j.materresbull.2011.07.008.
9. S.K. Lim, J.W. Kim, I. Chin, Y.K. Kwon and H.J. Choi, *Chem. Mater.*, **14**, 1989 (2002); https://doi.org/10.1021/cm010498j.
10. X.H. Flora, M. Ulaganathan and S. Rajendran, *Int. J. Electrochem. Sci.*, **7**, 7451 (2012).
11. B.-K. Koo, D.-Y. Lee, H.-J. Kim, W.-J. Lee, J.-S. Song and H.-J. Kim, *J. Electroceram.*, **17**, 79 (2006); https://doi.org/10.1007/s10832-006-9941-x.
12. J. Zhang, T. Hreid, X. Li, W. Guo, L. Wang, X. Shi, H. Su and Z. Yuan, *Electrochim. Acta*, **55**, 3664 (2010); https://doi.org/10.1016/j.electacta.2010.01.115.
13. R. Beranek, H. Hildebrand and P. Schmuki, *Electrochem. Solid-State Lett.*, **6**, B12 (2003); https://doi.org/10.1149/1.1545192.
14. H.A. Hamedani, S.W. Lee, A. Al-Sammarraie, Z.R. Hesabi, A. Bhatti, F.M. Alamgir, H. Garmestani and M.A. Khaleel, *ACS Appl. Mater. Interfaces*, **5**, 9026 (2013); https://doi.org/10.1021/am402203m.
15. J.M. Macak, L.V. Taveira, H. Tsuchiya, K. Sirotna, J. Macak and P. Schmuki, *J. Electroceram.*, **16**, 29 (2006); https://doi.org/10.1007/s10832-006-3904-0.
16. S. Yoriya, G.K. Mor, S. Sharma and C.A. Grimes, *J. Mater. Chem.*, **18**, 3332 (2008); https://doi.org/10.1039/b802463d.
17. J. Zhao, X. Wang, R. Chen and L. Li, *Solid State Commun.*, **134**, 705 (2005); https://doi.org/10.1016/j.ssc.2005.02.028.
18. A. Hochbaum and P. Yang, *Chem. Rev.*, **110**, 527 (2010); https://doi.org/10.1021/cr900075v.
19. D. Song-Yuan and W. Kong-Jia, *Chin. Phys. Lett.*, **20**, 953 (2003); https://doi.org/10.1088/0256-307X/20/6/351.
20. M.G. Kang, K.S. Ryu, S.H. Chang, N.G. Park, J.S. Hong and K.-J. Kim, *Bull. Korean Chem. Soc.*, **25**, 742 (2004); https://doi.org/10.5012/bkcs.2004.25.5.742.
21. L. Sun, S. Zhang, X. Sun and X. He, *J. Nanosci. Nanotechnol.*, **10**, 4551 (2010); https://doi.org/10.1166/jnn.2010.1695.