Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2014, Article ID 831752, 14 pages
http://dx.doi.org/10.1155/2014/831752

Review Article

Anodic Oxidation Synthesis of One-Dimensional TiO_2 Nanostructures for Photocatalytic and Field Emission Properties

Qiang Zhang, Lisha Ma, Minghui Shao, Jinzhao Huang, Meng Ding, Xiaolong Deng, Xianqi Wei, and Xijin Xu

School of Physics and Technology, University of Jinan, 336 Nanxin Zhuang West Road, Jinan, Shandong 250022, China

Correspondence should be addressed to Xijin Xu; sps_xuxj@ujn.edu.cn

Received 18 January 2014; Accepted 12 February 2014; Published 17 March 2014

Academic Editor: Xiang Wu

One-dimensional (1D) TiO_2 micro/nanostructures have received more and more attentions because of their potential applications in environmental issues. This paper reviews the most recent activities in TiO_2 nanostructures with an emphasis on the authors' own results especially on those synthesized using anodic oxidation method. The review begins with a survey of the effects of fabrication methods and the experiment conditions on the obtained TiO_2 nanostructures, and then focuses on their 1D nanostructures, including the syntheses, characterizations, formation mechanisms, photocatalytic, and field emission properties. Finally, we conclude this review with the perspectives and outlooks on the future developments in this field.

1. Introduction

Semiconductor nanomaterials have attracted great interests due to their potentials in understanding fundamental physical concepts and constructing nanoscale devices [1–4]. As an important semiconductor material, TiO_2 nanostructures have been widely explored in the field of photocatalysis, dye-sensitized solar cells, sensing [5–8], self-cleaning, photolysis of water, and energy storage [9–20]. Many kinds of nanostructured TiO_2 materials including spheroidal nanocrystallite [21], nanoparticles [22, 23], elongated nanotubes [24], nanosheets [25], nanorods [26, 27], nanocolumn arrays [28], and nanofibers [29] have been synthesized, and these nanostructures have been effectively produced by a variety of methods including template method [30–32], sol-gel methods [33–35], hydrothermal processes [35–37], and anodic oxidation method [38]. Among these methods, anodic oxidation method has become one of the most popular methods because of its high controllability, especially for their abilities on the fabrication of 1D TiO_2 nanostructures. 1D TiO_2 nanostructures, such as nanotubes and nanorods, have dramatically improved their intrinsic photocatalytic properties compared to other forms of TiO_2 [39–51] due to their high surface-to-volume ratios, high surface areas, and highly ordered arrangements.

This paper reviews the most recent research activities in 1D TiO_2 nanostructures, with an emphasis on the authors' own results, and on those prepared using anodic oxidation method.

2. Synthesis Routes towards 1D TiO_2 Nanostructures

2.1. Template Method. In this method, TiO_2 nanoarchitectures, such as nanowires, nanotubes, and nanorods, were grown in the nanoholes of the templates such as in aluminum oxide templates (AAM), the polymer templates, porous silicon templates, the protein templates, and metal materials templates [52–55]. Porous AAM with ordered nanohole arrays and polymer template are the common templates to fabricate TiO_2 nanoarchitectures using electrochemical deposition, sol-gel method, sol-gel-polymerization techniques, and followed by the calcination, acid, or alkali to remove these template. Template method possesses obvious advantages, such as simplicity, low cost, and low demand

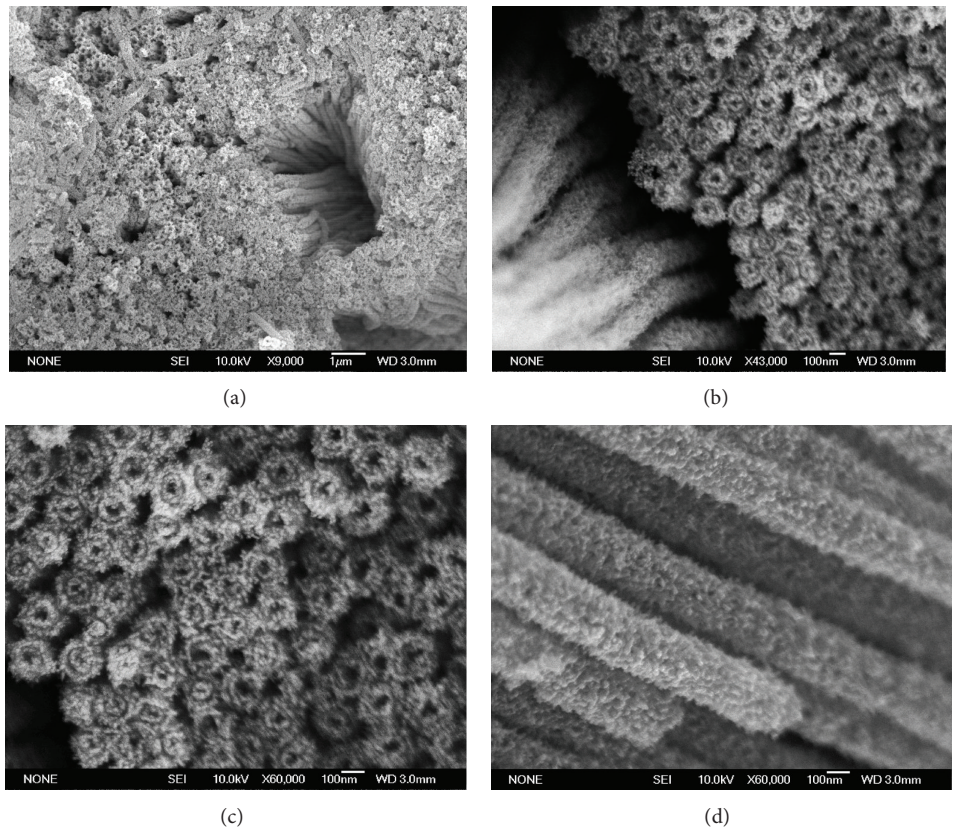


FIGURE 1: SEM images of TIT TiO_2 nanostructures at a low magnification ((a), (b)), and the corresponding enlarged top-view image (c) and side-view image (d).

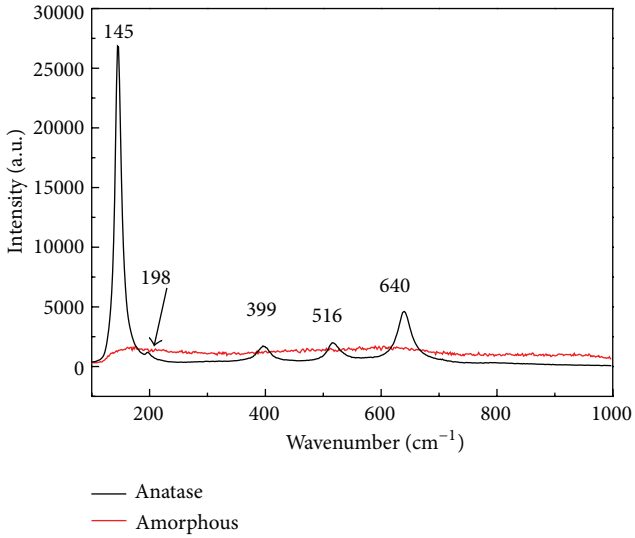


FIGURE 2: Raman spectra of amorphous and anatase TIT TiO_2 nanostructures.

of raw materials and device; however, it also has many limitations: the preparation process is very complex, the obtained nanoarchitectures depend entirely on the size and shape of the template, and the posttreatment process of the templates tends to damage the morphologies of the nanoarchitectures.

2.2. Hydrothermal Method. Hydrothermal processes use a special closed reaction vessel, in which aqueous solution is used as the reaction medium, to create a high temperature, high pressure reaction environment by heating the reaction vessel to a certain temperature.

Zhu et al. [56] synthesized TiO_2 nanotubes for the first time with the inner diameter of about 5 nm, outer diameter about 8 nm, and length about 100 nm using hydrothermal processes in 1998. Many researchers developed the method and many different TiO_2 architectures (nanotubes, nanorods, and nanoribbons) were successfully fabricated by adjusting the precursors and experimental conditions. Miyauchi and Hiromasa [57] sputtered 200 nm thick titanium films on the surface of the corundum by cathodic sputtering under argon atmosphere, then the corundum with Ti film was placed into the NaOH aqueous solution, and finally they obtained the highly hydrophilic, transparent, neatly arranged TiO_2 nanotube arrays.

2.3. Electrochemical Anodic Oxidation Method. Electrochemical anodic oxidation method has been the foremost technique to fabricate TiO_2 nanotube arrays in an F^- containing solution. It is generally considered that three steps were

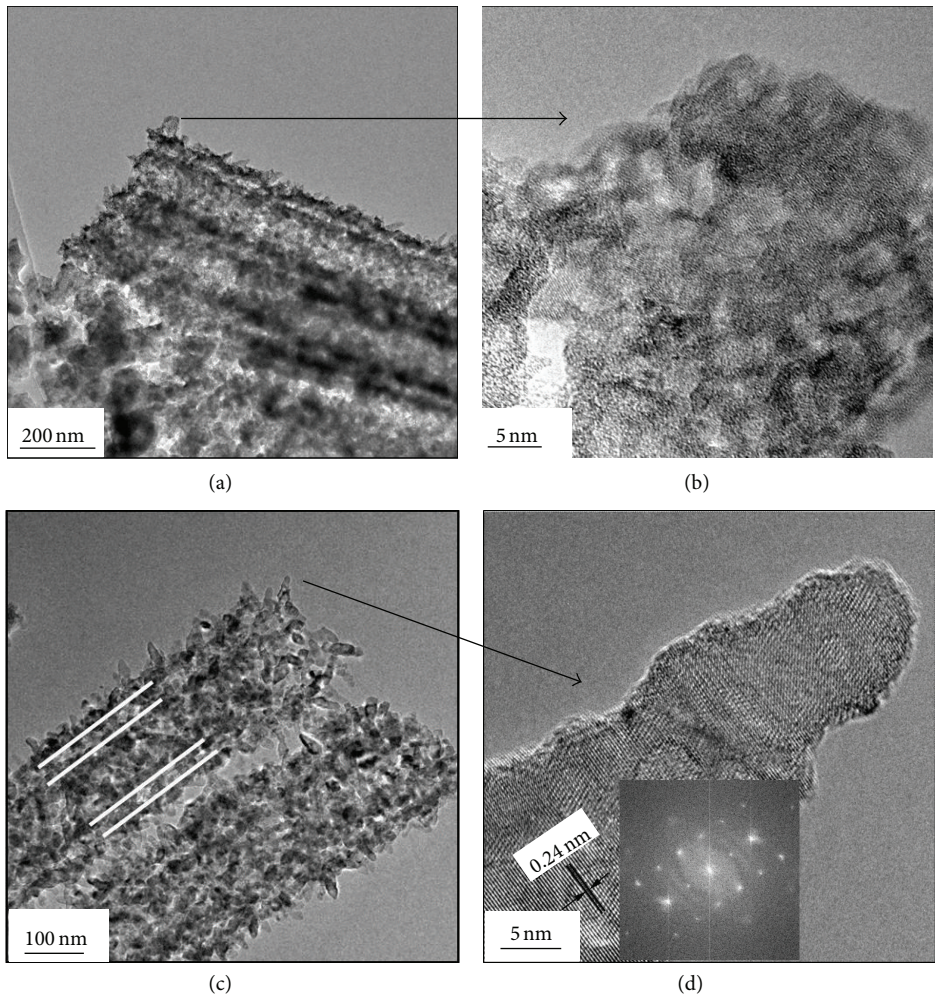


Figure 3: (a) TEM image, (b) HRTEM image for the as-grown TIT TiO_2 nanostructures; (c) TEM images and (d) HRTEM image and corresponding FFT pattern (d inset).

involved. First, Ti was dissolved in F^- containing acidic electrolytes and large amounts of Ti^{4+} were produced; second, the intensity of electric field exerted on the layer gradually increased with the formation of oxide layer on the surface, TiO_2 barrier layer was partically etched, and many irregular pits were formed; third, more H^- anions were gathered at the bottom of the micropores, and the TiO_2 at the bottom were more easily dissolved and the Ti substrate exposed. Then the titanium substrates contacted with the electrolytes and the above three processes repeatedly occurred; eventually TiO_2 nanotube arrays were formed.

3. Influence Factors in Anodic Oxidation Method

3.1. Anodizing Potential. The oxidation potential is an important factor to form the nanotube arrays. The highly ordered TiO_2 nanotube arrays can be formed at the right potential range, which is generally called potential window [58]. When the oxidation potential is lower than the potential window, only nanoporous film is formed on the Ti film; however, when the potential is too high, a sponge oxide layer [59, 60] is formed. The potential window generally ranges from 10 V to 40 V. The upper limit of the potential window can reach 220 V in some special solution system. With the increase in oxidation potential, the diameters TiO_2 nanotubes increase dramatically.

3.2. Potential Rising Rate. Potential rising rate (PRR) means the rising rate for the applied potential to the predetermined one from the open circuit potential in anodic oxidation process. The PRR affects the morphologies of oxide layer greatly; if it is too large, the disorder porous TiO_2 layers are formed. The PRRs are different in different solutions, and it is generally larger in the organic solutions than that in aqueous solutions.

3.3. The Oxidation Time. The oxidation time (OT) is another important factor for the nanotube formation. If the OT is too short, the electrochemical reaction has not yet reached a final equilibrium state, then the resulting product is a disordered porous oxide layer, and no ordered TiO_2 nanotube arrays

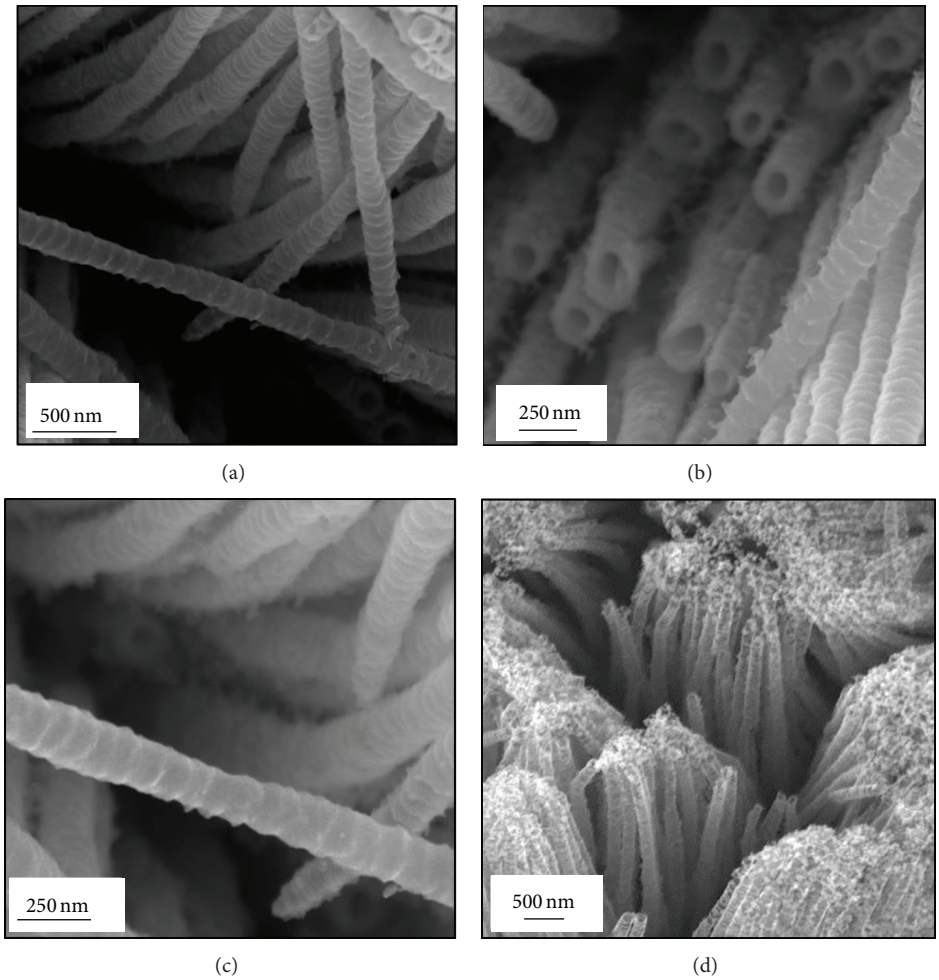


Figure 4: SEM images of ridged TiO_2 nanotubes at (a) low-magnification, and the corresponding enlarged (b) top-view and (c) side-view images for the as-grown nanotubes. (d) Low-magnification SEM image of annealed nanotubes.

can be formed. When the OT is too long, the tubes' top and bottom will collapse due to excessive corrosion, and the wires [61] or porous walls [62] will be formed, so an appropriate OT is important for the tube formation.

3.4. PH and Concentrations of F^-. The impacts of pH and concentrations of F^- determine the final morphologies to a certain extent in the dissolution process. When the pH is lower and F^- concentrations are higher than those of the electrolyte solution, the dissolution rate will be faster, so the electrolyte solutions with acidic or weakly alkaline ($pH \leq 8.4$) are generally chosen for the formation of ordered TiO_2 nanotube arrays. With the lower pH, the oxidation time is short; and with the higher pH, the oxidation time needed will be longer for the tube formation. Furthermore, if the F^- concentration is too low, it is impossible to obtain TiO_2 nanotube arrays; if the F^- concentration is too high; the reaction is too severe to form TiO_2 nanotube arrays.

3.5. Solution. Aqueous solution and the organic solution are used in the fabrication of TiO_2 nanotube arrays by anodic oxidation method. Generally, the TiO_2 architectures dissolve faster in aqueous solutions than that in organic solution. Compared with aqueous solution, TiO_2 nanotubes arrays prepared in organic solution have uniform shape and are very regular, and the extra-long tubes with smooth surface can be obtained.

4. Synthesis, Characterization, and Properties of Different TiO_2 Nanoarchitectures

Recently, various TiO_2 nanoarchitectures have been fabricated; microstructured-TiO_2 nanotubes were synthesized using a LUCE laser source, processing the Ti substrates in an electrolyte for 2 h at room temperature [63]. Bamboo-type TiO_2 nanotubes were electrochemically prepared by controlling anodization of Ti in an electrolyte consisting of 0.2 $mol \cdot L^{-1}$ HF in ethylene glycol [64–66], and bamboo leaf-like structured TiO_2 layer on TiO_2 nanotube arrays was synthesized via simple electrochemical anodization with wet chemistry pretreatment [67]. Furthermore, thick anatase TiO_2 mesosponge layers were synthesized by voltage-step

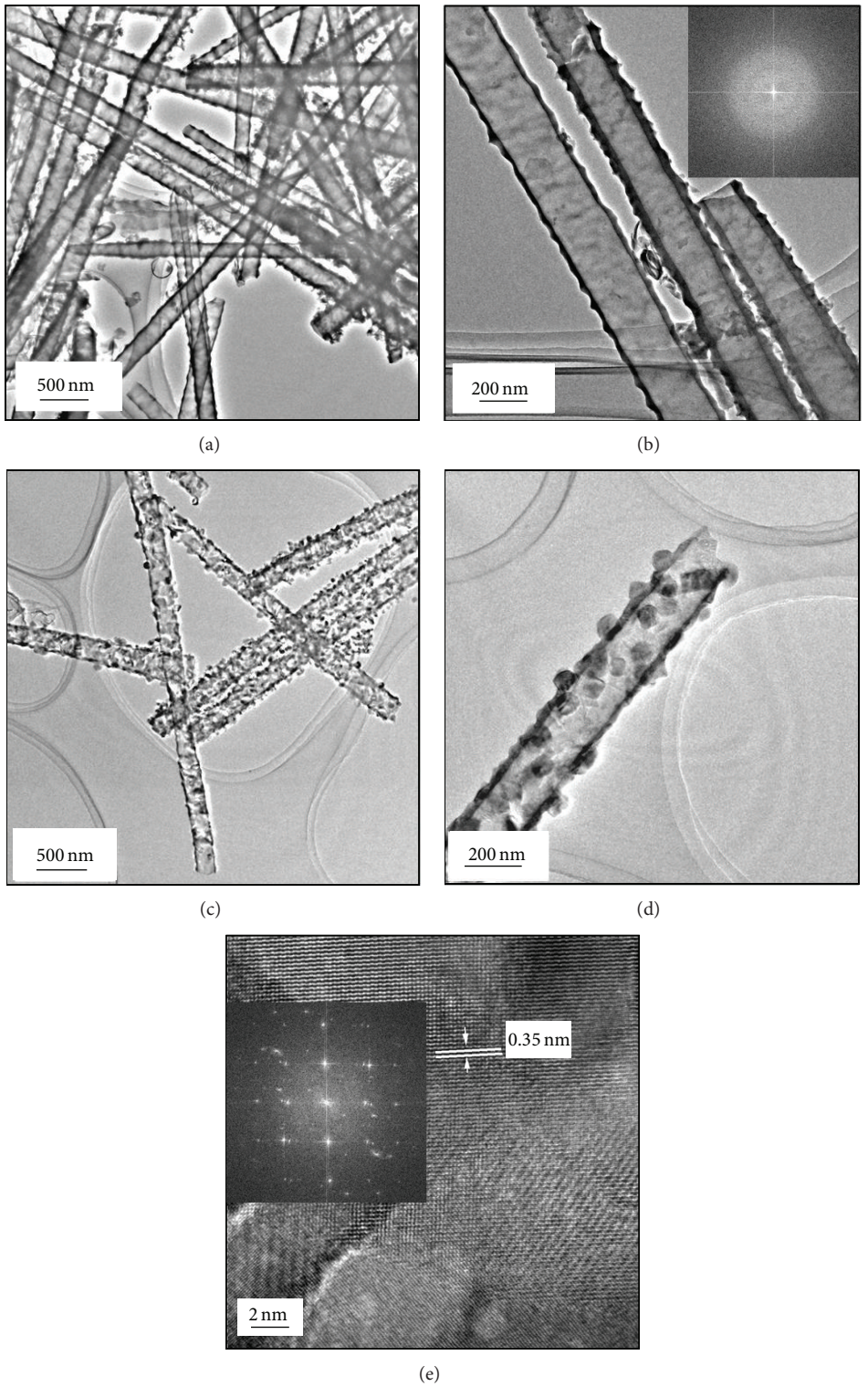


FIGURE 5: TEM images of ridged TiO_2 nanotubes: (a) TEM image, (b) enlarged TEM image, and corresponding FFT pattern (inset) for the as-grown samples; and ((c), (d)) TEM and (e) HRTEM images and corresponding FFT patterns (inset).

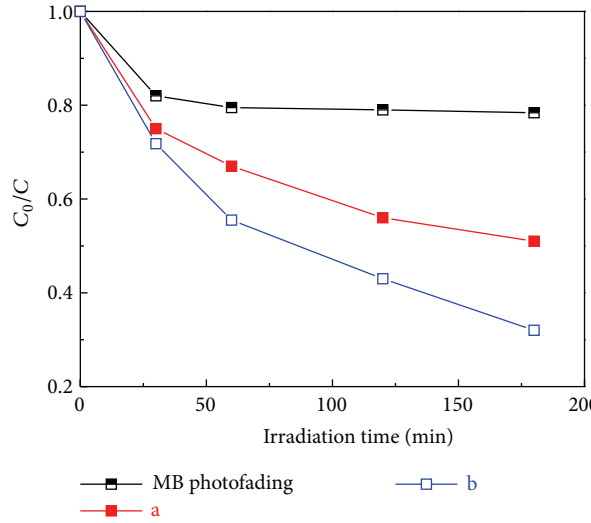


Figure 6: Photodegradation efficiency of MB: (a) as-grown amorphous ridged TiO_2 nanotubes and (b) annealed anatase nanoparticle decorated TiO_2 nanotubes. (The black line for the MB photofading is selected from ref 24 for comparison).

anodization of a Ti metal foil at 50 V for 48 h in a 10 wt% K_2HPO_4-containing glycerol electrolyte followed by a chemical etch in 30 wt% H_2O_2 [68]; highly ordered TiO_2 nanolace was synthesized in an organic electrolyte with Ti pressed together with a Cu plate against an O-ring in an electrochemical cell [69]. Large-diameter multipodal TiO_2 nanotubes were synthesized via processing the TiO_2 nanotubes into 0.1 M HCl acid for an hour [70], and conical-shaped TiO_2 nanotube arrays were prepared using anodic oxidation of Ti foil at 80 V in a 3 : 97 (v/v) mixture of H_2O_2 and ethylene glycol solution containing 0.5 wt% NH_4F at 20°C [71]; multibranched TiO_2 nanotubes were controllably fabricated via a two-step anodization method [72]. Other TiO_2 nanotubes have been successfully synthesized via various methods.

In this section, we will present recent progresses achieved by us in relation to the synthesis, characterizations, and properties of TiO_2 nanostructure by oxidation method.

4.1. Tube-in-Tube TiO_2 Nanotubes with Porous Walls [62]. In our previous work, we successfully fabricated tube-in-tube (TIT) TiO_2 nanostructures as shown in Figure 1, which have coarse, porous walls increasing the surface areas compared with the conventional TiO_2 nanotubes. The TIT TiO_2 nanostructures cover the entire substrate surface, and the enlarged scanning electron microscopy (SEM) images (Figures 1(b) and 1(c)) clearly show numerous TIT TiO_2 nanotube-like structures with the outer tube diameter within the array are of about 200 nm (Figures 1(b) and 1(c)). The nanotubes lateral profiles are coarse (Figure 1(d)), which means they have a larger contact surface area compared to conventional structures.

The as-fabricated TIT nanostructures are amorphous and the crystallinity is improved when the thermal annealing process was carried out at 550°C. It can be seen that the nanostructures crystallize in an anatase phase after the heat treatment, which are confirmed by Raman spectroscopy (Figure 2). TEM and HRTEM images (Figure 3) show that the nanostructures have uniform diameters throughout their lengths. The TIT morphologies are preserved after the thermal treatment.

4.2. Ridged TiO_2 Nanotubes [61]. Ridged TiO_2 nanotubes were fabricated and their growth mechanism together with their structures and morphology transformations is analyzed. The nanotubes turn into an anatase phase from the amorphous state after an annealing process. It should be mentioned that the annealed nanotubes become decorated with nanoparticles opposed to the starting ridged tube surfaces as shown in Figure 4.

From the TEM observations, the as-prepared TiO_2 nanotubes have the ridged surface structures (Figures 5(a) and 5(b)), and it is amorphous confirmed by the FFT in Figure 5(b). However, the annealed nanotubes change into nanoparticle-decorated morphologies (Figures 5(c) and 5(d)), and the ridged structures disappear. Furthermore, the annealed ones become anatase (Figure 5(e)), with spacing between the lattice fringes being ca 0.35 nm (JCPDS card Number 21-1272).

The photocatalytic activities (Figure 6) show that the crystalline nanotubes with nanoparticle-decorated morphologies have a stronger photocatalytic activity than the amorphous samples.

We have carried out FE measurements on the dependence of the FE properties on the distances between the anodes and the samples. It is observed that the E_{to} decreases from 96.2 to 34 V μm^{-1} during a voltage increase when the distance increases from 10 to 25 μm and β increase (61.8, 115.6, 214.2, and 255.5 for d = 10, 15, 20, and 25 μm, resp.) (Figure 7).

4.3. Anatase TiO_2 Nanotubes with Rod-Formed Walls [73]. Besides the TIT nanostructures, the TiO_2 nanostructures with rod-formed single walls (RWTN) (Figure 8) were also

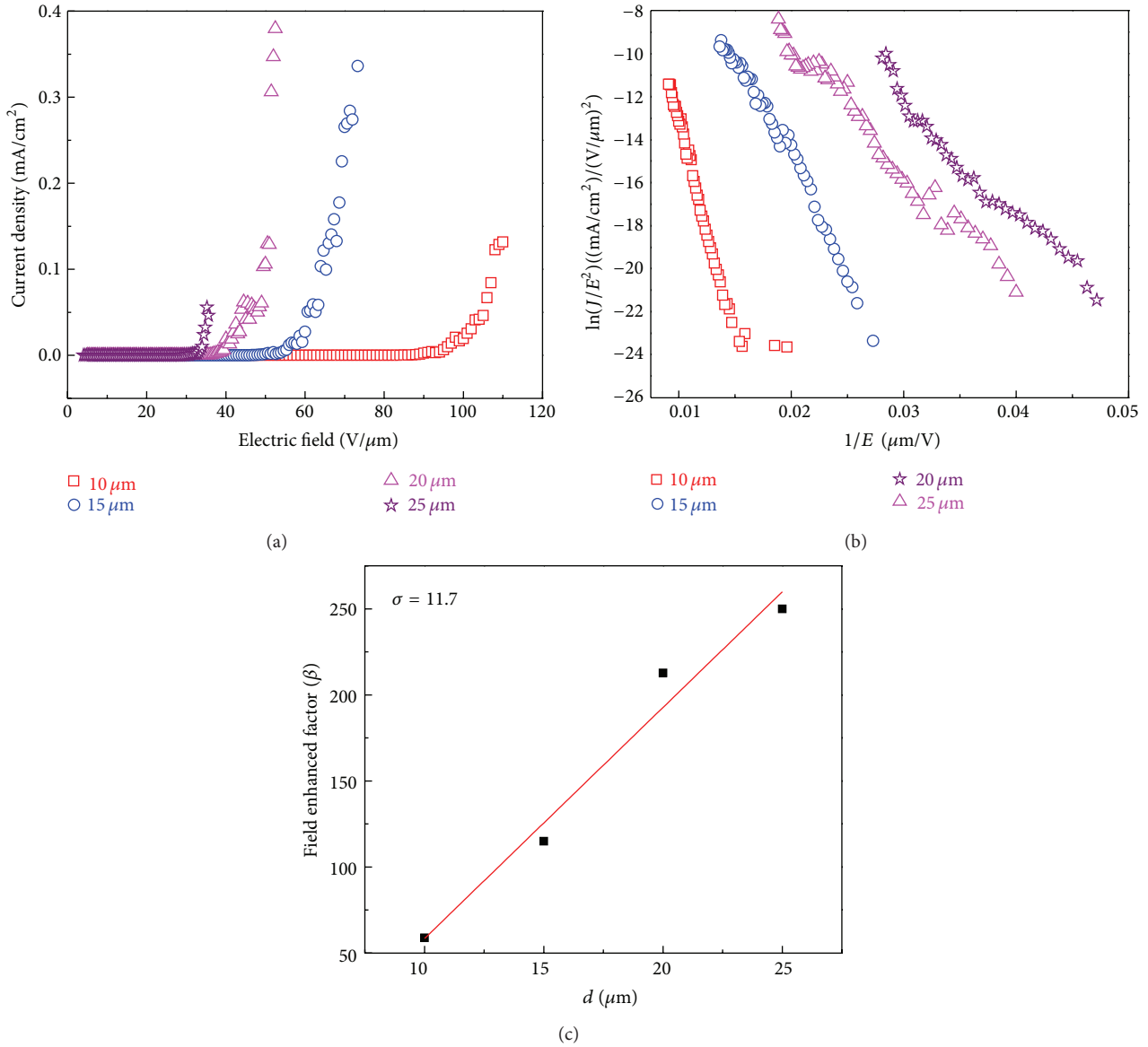


FIGURE 7: (a) J-E plots and (b) corresponding F-N plots for nanoparticle-decorated TiO_2 nanotubes at a different sample-anode separation, d; (c) the variation in field enhancement factor (β) with a distance (d); (d) stable emission current recorded from ridged nanotubes.

fabricated. The fabrication of RWTN nanostructures is similar to the process of TIT [62]. In brief, the pretreated Ti foils were anodized at a constant potential of 40 V for 72 h in the mixture of HF and DMSO and followed by the annealing process at 550°C for 3 h.

The SEM results show that the nanostructures have a porous structure and the tube walls are coarse. Compared to TIT, RWTN nanostructures are single-walled with the rod-formed morphologies and coarse walls characteristics (Figures 8(a)–8(d)), which endow them larger surface areas compared with the conventional TiO_2 nanotubes. The rods with the length of about 20 nm constitute the tube walls, and the outer and inner diameters are of about 200 nm (Figures 8(e) and 8(f)) and 100 nm, respectively.

TEM images of a single RWTN (Figures 9(a) and 9(c)) show that the outer diameter is about ~200 nm, and the tube walls are assembled by many small nanorods (Figure 9(c)) with the length of about 20 nm. HRTEM image (Figure 9(b)) shows the lattice fringe separation of ~0.35 nm, corresponding to the [101] zone axis lattice orientation. FFT pattern (inset) further confirms that the crystalline structure grows along the [101] direction. EDS (Figure 9(d)) indicates that the RWTN consists of Ti and O in a stoichiometric 1 : 2 composition.

Field-emission properties (Figure 10) were studied and the results showed that the annealed RWTN arrays have a better FE property, with a lower turn-on field of 96.8 V μm^{-1} and higher field-enhancement factors β (120.9) than those of

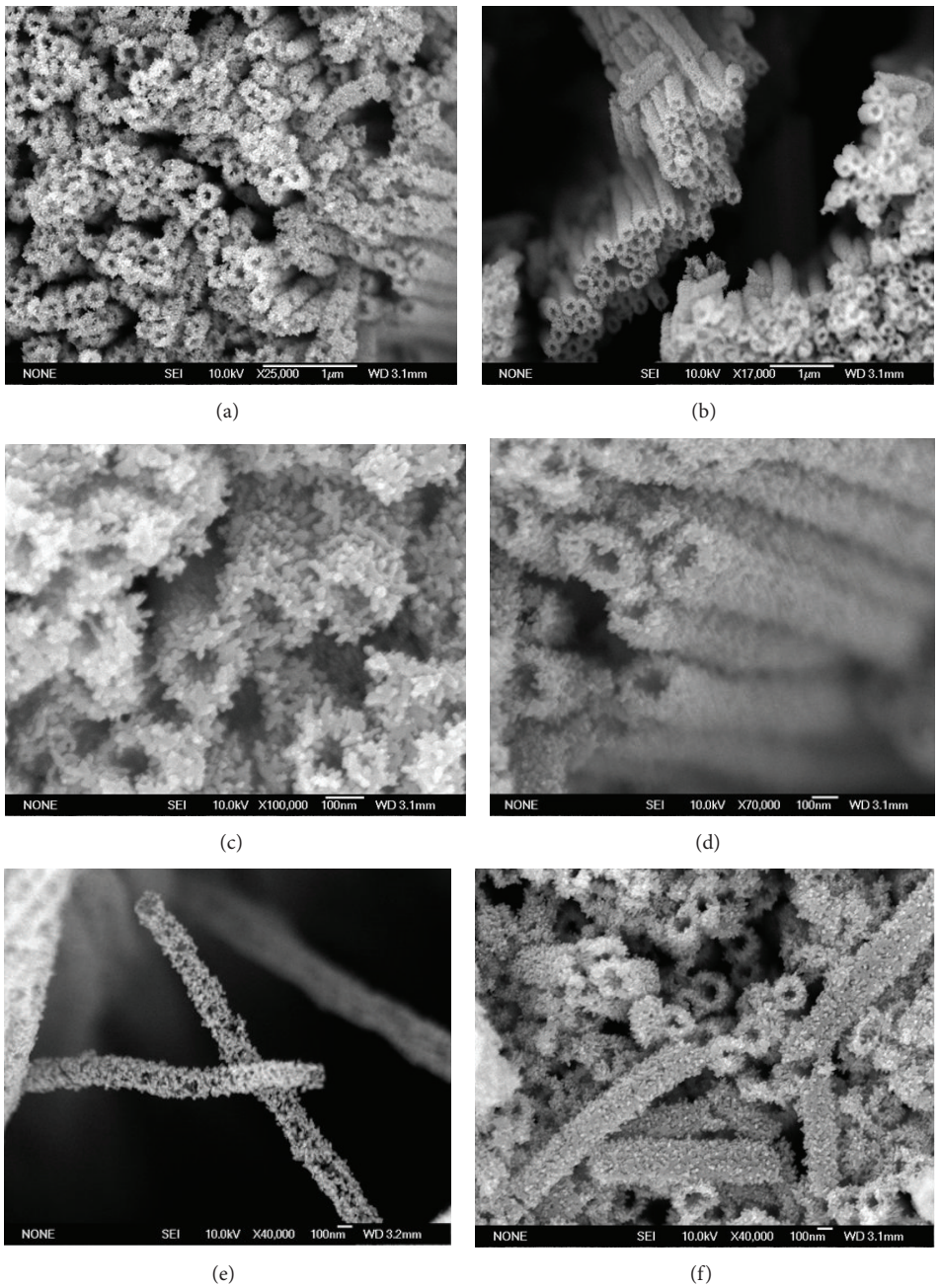


Figure 8: Typical field-emission SEM images of rod-formed walls TiO_2 nanostructures: (a), (c), top view and (b), (d); SEM images of two separate nanotubes (e) and tiled nanotubes on the nanoarrays (f).

the as-prepared arrays (102.5 V μm^{-1} for turn-on voltage, 86.7 for β). The F-N plots (Figure 10(b)) exhibit approximately linear relationship, indicating that the electron emission from as-prepared and annealed RWTN nanostructures follows the F-N behavior.

4.4. TiO_2 Nanorods and Porous Layers [74]. By adjusting the anodized time, we successfully fabricated TiO_2 with different morphologies, such as nanotubes, nanorods, and porous layers with one-step anodization. In this case, Ti sheets and Ti films on the Si substrates were used, which were anodized in 0.5% HF solution and the anodization is conducted using a 20 V DC voltage at 25°C. Different anodization time (such as 10 min, 30 min, and 60 min) was used for the TiO_2 nanostructures with different morphologies, respectively, and 20 min for the Ti film on the Si substrate.

XRD patterns (Figure 11) of synthesized nanostructures under different anodic oxidation conditions show that Ti peaks dominate, caused by the Ti substrates. The main reasons is the poor crystallinities of the TiO_2 nanostructures, as mentioned in our previous reports on the TIT and ridged nanotubes [61, 62]. However, the Raman results prove the

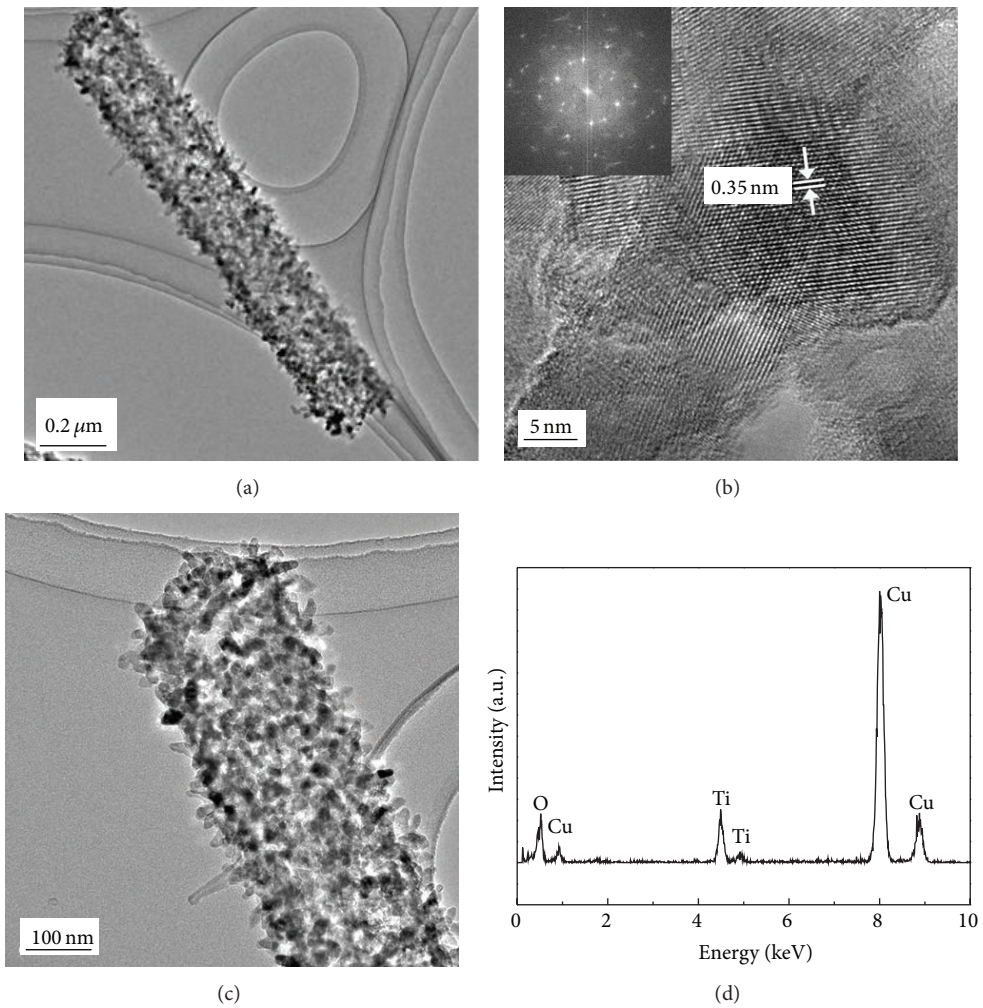


FIGURE 9: TEM images of the RWTN with low (a) and high (c) magnification; (b) HRTEM image and corresponding FFT pattern; (d) EDS spectrum of the nanostructure.

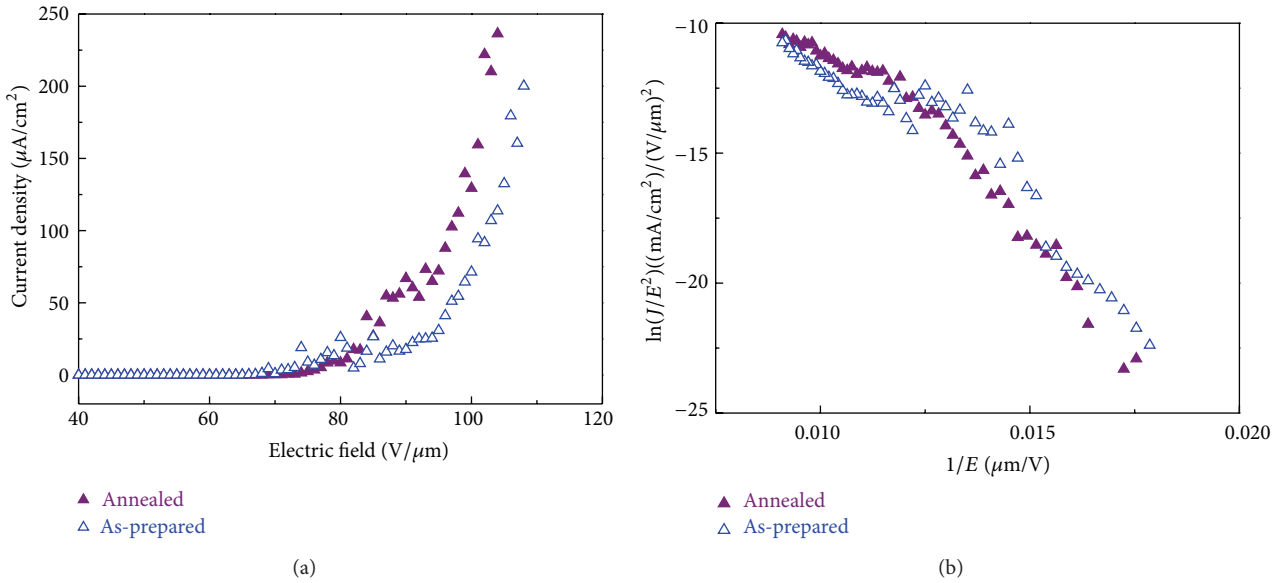


FIGURE 10: Field-emission properties (a) and the corresponding Fowler-Nordheim plots (b) of as-grown and annealed nanostructures (at a working distance of 10 mm).

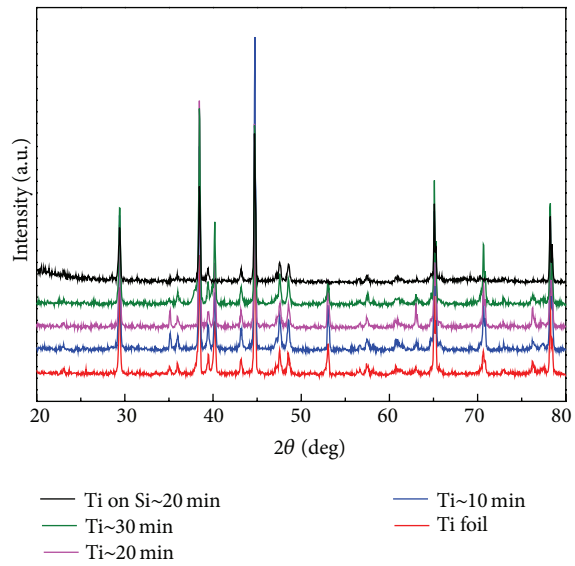


Figure 11: XRD patterns of nanostructures under different experimental conditions.

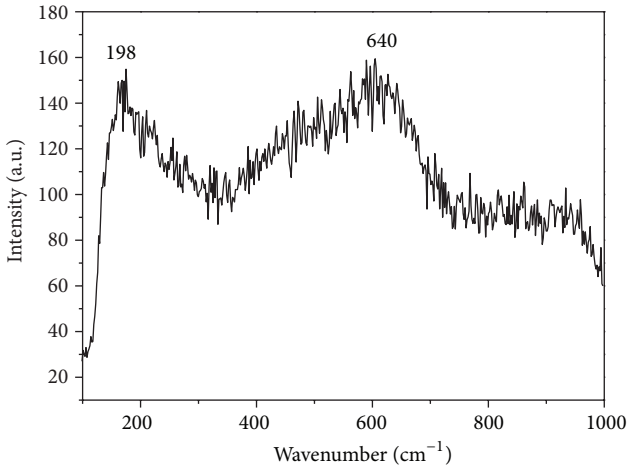


Figure 12: Raman spectrum of the sample anodized for 60 minutes.

formation of anatase TiO_2 (Figure 12), as the anatase TiO_2 phase at 198, and 640 cm^{-1} [75] can be clearly observed.

The SEM images of TiO_2 nanostructures under different anodization time (Figure 13) show that the tubular nanostructure is formed on the surface of the Ti sheet when the time is 10 min, when the oxidation time is extended to 30 min and 60 min, the synthesized samples are rod-like nanostructure, and the length of the rod is increased with the increasing anodization time (Figures 13(b) and 13(c)). This is first report on the synthesis TiO_2 nanorod structure by the simple anodic oxidation method.

Meanwhile, the porous TiO_2 layers were also fabricated when Ti films on Si substrate were anodized (Figure 14), which were different to the morphologies of discrete TiO_2 nanotubes and rod-like structures. The main reason is that the Ti films deposited on the Si substrate are not so compact; then the "soft" parts are easy to be anodized and finally these special morphologies were formed in the anodization process.

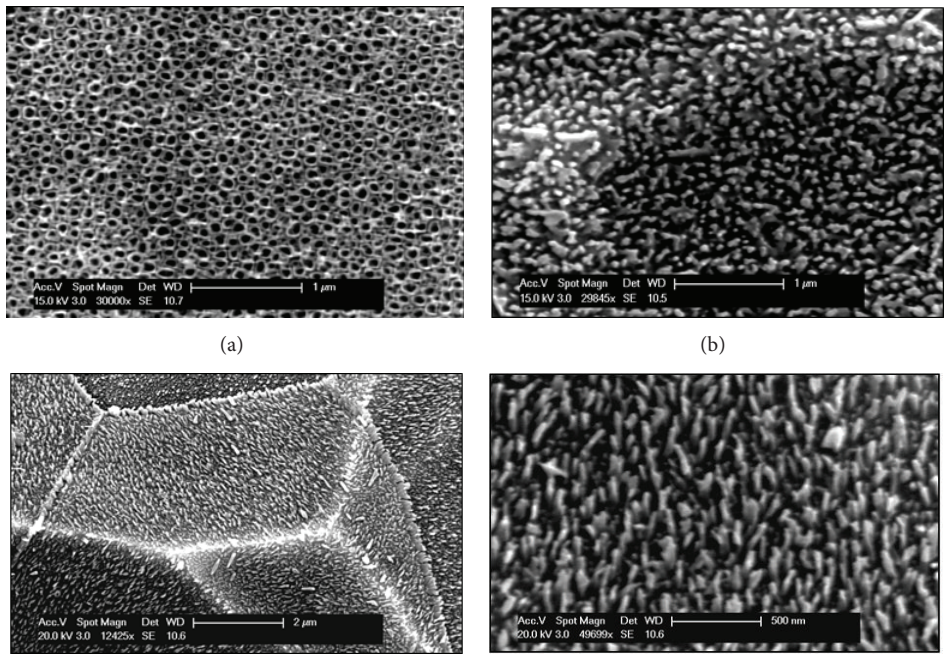
5. Conclusion and Outlook

In conclusion, this paper briefly reviews the authors' recent efforts with respect to the TiO_2 nanoarchitectures syntheses using anodic oxidation method. TiO_2 nanotubular structures were synthesized in different electrolytes and its field emission; photocatalytic properties are briefly discussed. The fascinating achievements towards the practical applications of TiO_2 nanotubular structures should inspire more and more research efforts to address the remaining challenges in the fundamental and technological fields.

Of course, we know this brief review is unable to cover all the progresses, but we do hope this paper can offer some help to the researchers in this field. The investigation of these TiO_2 nanostructures will be continuously exciting and highly rewarding. Undoubtedly, more and more innovations and developments will happen toward their practical applications and many issues need to be solved before that.

(1) Much more challenges still exist to develop stable, efficient, and low-cost anodic oxidation technology to synthesize high-performance TiO_2 nanoarchitectures; the existing problems include the choice of the electrolytes, the time of anodic oxidation, the stability, and the crystalline of the nanostructures.

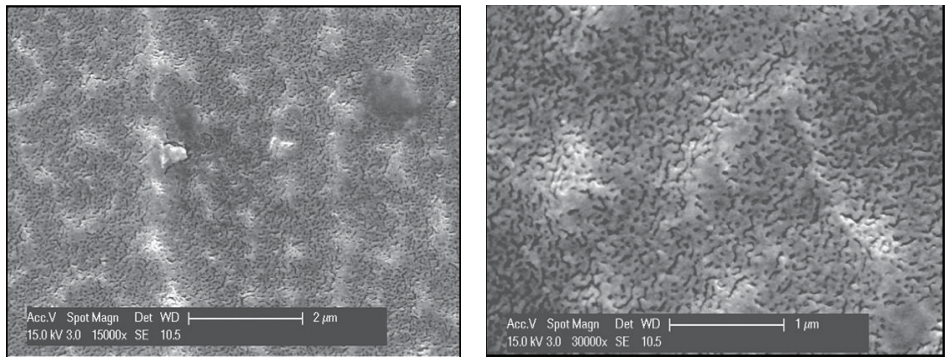
(2) Doping and composites of the TiO_2 nanotubular structures have become an important route for strengthening the performance in many possible applications. Different doping of these nanostructures, such as metal, oxide, sulfide, and element, could improve the electrical, optical, and photocatalytic properties.



(a) (b)

(c) (d)

Figure 13: SEM images of TiO_2 nanostructures under different anodizing times, (a) 10 min (b) 30 min, (c) and (d) are the SEM images with the low and high magnifications, respectively, for 60 min.



(a) (b)

Figure 14: SEM images of porous TiO_2 layer on Si substrate with the low (a) and (b) high magnification.

(3) Sensitivity, selectivity, and stability of the TiO_2 nanotubular photoelectric device and photocatalysts will require significant improvements in order to meet the great demands in a variety of fields.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

Thanks are due to University of Jinan (UJN) for the support on new staff, and the project supported by the Taishan Scholar (no. TSHW20120210), the National Natural Science Foundation of China (Grant nos. 11304120 and 61106059), the Encouragement Foundation for Excellent Middle-aged and Young Scientist of Shandong Province (Grant nos. BS2012CL005, BS2011NJ003, and BS2013CL020), the Science-Technology Program of Higher Education Institutions of Shandong Province (Grant no. J11LA10), and the Research Foundation of University of Jinan (Grant no. XKY1127).

References

[1] H. Zeng, X. Xu, Y. Bando et al., "Template deformation-tailored ZnO nanorod/nanowire arrays: full growth control and optimization of field-emission," *Advanced Functional Materials*, vol. 19, no. 19, pp. 3165–3172, 2009.

[2] T. Zhai, X. Fang, Y. Bando et al., "Characterization, cathodolutumescence, and fieldemission properties of morphology-tunable CdS micro/nanostructures," *Advanced Functional Materials*, vol. 19, no. 15, pp. 2423–2430, 2009.

[3] X. Xu, G. Fei, W. Yu, X. Wang, L. Chen, and L. Zhang, "Preparation and formation mechanism of ZnS semiconductor nanowires made by the electrochemical deposition method," *Nanotechnology*, vol. 17, no. 2, pp. 426–429, 2006.

[4] M. Chang, X. L. Cao, X. Xu, and L. Zhang, "Fabrication and photoluminescence properties of highly ordered ZnS nanowire arrays embedded in anodic alumina membrane," *Physics Letters, Section A: General, Atomic and Solid State Physics*, vol. 372, no. 3, pp. 273–276, 2008.

[5] O. K. Varghese, D. Gong, M. Paulose, K. G. Ong, E. C. Dickey, and C. A. Grimes, "Extreme changes in the electrical resistance of titania nanotubes with hydrogen exposure," *Advanced Materials*, vol. 15, no. 7-8, pp. 624–662, 2003.

[6] G. K. Mor, M. A. Carvalho, O. K. Varghese, M. V. Pishko, and C. A. Grimes, "A room-temperature TiO_2-nanotube hydrogen sensor able to self-clean photoactively from environmental contamination," *Journal of Materials Research*, vol. 19, no. 2, pp. 628–634, 2004.

[7] O. K. Varghese, G. K. Mor, C. A. Grimes, M. Paulose, and N. Mukherjee, "A titania nanotube-array room-temperature sensor for selective detection of hydrogen at low concentrations," *Journal of Nanoscience and Nanotechnology*, vol. 4, no. 7, pp. 733–737, 2004.

[8] M. Paulose, O. K. Varghese, G. K. Mor, C. A. Grimes, and K. G. Ong, "Unprecedented ultra-high hydrogen gas sensitivity in undoped titania nanotubes," *Nanotechnology*, vol. 17, no. 2, pp. 398–402, 2006.

[9] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films," *Nature*, vol. 353, no. 6346, pp. 737–740, 1991.

[10] U. Bach, D. Lupo, P. Comte et al., "Solid-state dye-sensitized mesoporous TiO_2 solar cells with high photon-to-electron conversion efficiencies," *Nature*, vol. 395, no. 6702, pp. 583–585, 1998.

[11] M. Dürr, A. Schmid, M. Obermaier, S. Rosselli, A. Yasuda, and G. Nelles, "Low-temperature fabrication of dye-sensitized solar cells by transfer of composite porous layers," *Nature Materials*, vol. 4, no. 8, pp. 607–611, 2005.

[12] G. K. Mor, O. K. Varghese, M. Paulose, K. Shankar, and C. A. Grimes, "A review on highly ordered, vertically oriented TiO_2 nanotube arrays: fabrication, material properties, and solar energy applications," *Solar Energy Materials and Solar Cells*, vol. 90, no. 14, pp. 2011–2075, 2006.

[13] A. Heller, "Chemistry and applications of photocatalytic oxidation of thin organic films," *Accounts of Chemical Research*, vol. 28, no. 12, pp. 503–508, 1995.

[14] J. Tang, Y. Wu, E. W. McFarland, and G. D. Stucky, "Synthesis and photocatalytic properties of highly crystalline and ordered mesoporous TiO_2 thin films," *Chemical Communications*, vol. 10, no. 14, pp. 1670–1671, 2004.

[15] H. L. Fei, Y. P. Liu, Y. P. Li et al., "Selective synthesis of borated meso-macroporous and mesoporous spherical TiO_2 with high photocatalytic activity," *Microporous and Mesoporous Materials*, vol. 102, no. 1–3, pp. 318–324, 2007.

[16] K. R. Meier and G. Michael, "Redox targeting of oligonucleotides anchored to nanocrystalline TiO_2 films for DNA detection," *ChemPhysChem*, vol. 3, pp. 371–374, 2002.

[17] E. Topoglidis, A. E. G. Cass, B. O'Regan, and J. R. Durrant, "Immobilisation and bioelectrochemistry of proteins on nanoporous TiO_2 and ZnO films," *Journal of Electroanalytical Chemistry*, vol. 517, no. 1-2, pp. 20–27, 2001.

[18] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.

[19] S. U. M. Khan, M. Al-Shahry, and W. B. Ingler Jr., "Efficient photochemical water splitting by a chemically modified n-TiO_2," *Science*, vol. 297, no. 5590, pp. 2243–2245, 2002.

[20] K. Shankar, J. Bandara, M. Paulose et al., "Highly efficient solar cells using TiO_2 nanotube arrays sensitized with a donor-antenna dye," *Nano Letters*, vol. 8, no. 6, pp. 1654–1659, 2008.

[21] L. Cusack, S. N. Rao, and D. Fitzmaurice, "Heterosupramolecular chemistry: self-assembly of an electron donor (TiO_2 nanocrystallite)-acceptor (viologen) complex," *Chemistry*, vol. 3, no. 2, pp. 202–207, 1997.

[22] J. Cao, J. Z. Sun, H. Y. Li, J. Hong, and M. Wang, "A facile room-temperature chemical reduction method to TiO_2@CdS core/sheath heterostructure nanowires," *Journal of Materials Chemistry*, vol. 14, no. 7, pp. 1203–1206, 2004.

[23] M. Hodos, E. Horváth, H. Haspel, Á. Kukovecz, Z. Kónya, and I. Kiricsi, "Photosensitization of ion-exchangeable titanate nanotubes by CdS nanoparticles," *Chemical Physics Letters*, vol. 399, no. 4–6, pp. 512–515, 2004.

[24] K. S. Brammer, S. Oh, C. J. Cobb, L. M. Bjursten, H. V. D. Heyde, and S. Jin, "Improved bone-forming functionality on diameter-controlled TiO_2 nanotube surface," *Acta Biomaterialia*, vol. 5, no. 8, pp. 3215–3223, 2009.

[25] D. V. Bavykin, V. N. Parmon, A. A. Lapkin, and F. C. Walsh, "The effect of hydrothermal conditions on the mesoporous structure of TiO_2 nanotubes," *Journal of Materials Chemistry*, vol. 14, no. 22, pp. 3370–3377, 2004.

[26] Y. Ding and Z. L. Wang, "Structure analysis of nanowires and nanobelts by transmission electron microscopy," *Journal of Physical Chemistry B*, vol. 108, no. 33, pp. 12280–12291, 2004.

[27] Y. Li, X. Fang, N. Koshizaki et al., "Periodic TiO_2 nanorod arrays with hexagonal nonclose-packed arrangements: excellent field emitters by parameter optimization," *Advanced Functional Materials*, vol. 19, no. 15, pp. 2467–2473, 2009.

[28] Y. Li, T. Sasaki, Y. Shimizu, and N. Koshizaki, "Hexagonal-close-packed, hierarchical amorphous TiO_2 nanocolumn arrays: transferability, enhanced photocatalytic activity, and superamphiphilicity without UV irradiation," *Journal of the American Chemical Society*, vol. 130, no. 44, pp. 14755–14762, 2008.

[29] J. Li, Z. Tang, and Z. Zhang, "H-titanate nanotube: a novel lithium intercalation host with large capacity and high rate capability," *Electrochemistry Communications*, vol. 7, no. 1, pp. 62–67, 2005.

[30] H. P. Langmuir, "Formation of a titanium dioxide nanotube array," *Langmuir*, vol. 12, no. 6, pp. 1411–1413, 1996.

[31] C. R. Xiong and K. J. Balkus Jr., "Fabrication of TiO_2 nanofibers from a mesoporous silica film," *Chemistry of Materials*, vol. 17, no. 20, pp. 5136–5140, 2005.

[32] C. W. Wu, T. Ohsuna, M. Kuwabara, and K. Kuroda, "Formation of highly ordered mesoporous titania films consisting of crystalline nanopillars with inverse mesospace by structural transformation," *Journal of the American Chemical Society*, vol. 128, no. 14, pp. 4544–4545, 2006.

[33] J. H. Jung, H. Kobayashi, K. J. C. Van Bommel, S. Shinkai, and T. Shimizu, "Creation of novel helical ribbon and double-layered nanotube TiO_2 structures using an organogel template," *Chemistry of Materials*, vol. 14, no. 4, pp. 1445–1447, 2002.

[34] S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H. Shirai, and K. Hanabusa, "Preparation of helical transition-metal oxide tubes using organogelators as structure-directing agents," *Journal of the American Chemical Society*, vol. 124, no. 23, pp. 6550–6551, 2002.

[35] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, "Formation of titanium oxide nanotube," *Langmuir*, vol. 14, no. 12, pp. 3160–3163, 1998.

[36] Q. Chen, W. Z. Zhou, G. H. Du, and L. H. Peng, "Trititanate nanotubes made via a single alkali treatment," *Advanced Materials*, vol. 14, no. 17, pp. 1208–1211, 2002.

[37] B. D. Yao, Y. F. Chan, X. Y. Zhang, W. F. Zhang, Z. Y. Yang, and N. Wang, "Formation mechanism of TiO_2 nanotubes," *Applied Physics Letters*, vol. 82, no. 2, pp. 281–283, 2003.

[38] D. Gong, C. A. Grimes, O. K. Varghese et al., "Titanium oxide nanotube arrays prepared by anodic oxidation," *Journal of Materials Research*, vol. 16, no. 12, pp. 3331–3334, 2001.

[39] M. Adachi, Y. Murata, M. Harada, and S. Yoshikawa, "Formation of titania nanotubes with high photo-catalytic activity," *Chemistry Letters*, no. 8, pp. 942–943, 2000.

[40] S. Z. Chu, S. Inoue, K. Wada, D. Li, H. Haneda, and S. Awatsu, "Highly porous $(TiO_2$-SiO_2-$TeO_2)/Al_2O_3/TiO_2$ composite nanostructures on glass with enhanced photocatalysis fabricated by anodization and sol-gel process," *Journal of Physical Chemistry B*, vol. 107, no. 27, pp. 6586–6589, 2003.

[41] V. Georgieva and M. Ristov, "Electrodeposited cuprous oxide on indium tin oxide for solar applications," *Solar Energy Materials and Solar Cells*, vol. 73, no. 1, pp. 67–73, 2002.

[42] G. Korotcenkov, S. H. Han, and B. K. Cho, "Material design for metal oxide chemiresistive gas sensors," *Journal of Sensor Science and Technology*, vol. 22, no. 1, pp. 1–17, 2013.

[43] Z. F. Zheng, J. Teo, X. Chen et al., "Correlation of the catalytic activity for oxidation taking place on various TiO_2 surfaces with surface OH groups and surface oxygen vacancies," *Chemistry*, vol. 16, no. 4, pp. 1202–1211, 2010.

[44] X. G. Wen, S. H. Wang, Y. Ding, Z. L. Wang, and S. Yang, "Controlled growth of large-area, uniform, vertically aligned arrays of α-Fe2O3 nanobelts and nanowires," *Journal of Physical Chemistry B*, vol. 109, no. 1, pp. 215–220, 2005.

[45] G. K. Mor, K. Shankar, O. K. Varghese, and C. A. Grimes, "Photoelectrochemical properties of titania nanotubes," *Journal of Materials Research*, vol. 19, no. 10, pp. 2989–2996, 2004.

[46] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, "Enhanced photocleavage of water using titania nanotube arrays," *Nano Letters*, vol. 5, no. 1, pp. 191–195, 2005.

[47] O. K. Varghese, M. Paulose, K. Shankar, G. K. Mor, and C. A. Grimes, "Water-photolysis properties of micron-length highly-ordered titania nanotube-arrays," *Journal of Nanoscience and Nanotechnology*, vol. 5, no. 7, pp. 1158–1165, 2005.

[48] S. Uchida, R. Chiba, M. Tomiha, N. Masaki, and M. Shirai, "Application of titania nanotubes to a dye-sensitized solar cell," *Electrochemistry*, vol. 70, no. 6, pp. 418–420, 2002.

[49] M. Adachi, Y. Murata, I. Okada, and S. Yoshikawa, "Formation of titania nanotubes and applications for dye-sensitized solar cells," *Journal of the Electrochemical Society*, vol. 150, no. 8, pp. G488–G493, 2003.

[50] G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes, "Use of highly-ordered TiO_2 nanotube arrays in dye-sensitized solar cells," *Nano Letters*, vol. 6, no. 2, pp. 215–218, 2006.

[51] M. Paulose, K. Shankar, O. K. Varghese, G. K. Mor, B. Hardin, and C. A. Grimes, "Backside illuminated dye-sensitized solar cells based on titania nanotube array electrodes," *Nanotechnology*, vol. 17, no. 5, pp. 1446–1485, 2006.

[52] C. R. Martin, "Nanotubule-based molecularfiltration membranes," *Chemistry of Materials*, vol. 8, no. 8, pp. 1739–1746, 1996.

[53] J. C. Hulteen, "A general template-based method for the preparation of nanomaterials," *Journal of Materials Chemistry*, vol. 7, no. 7, pp. 1075–1087, 1997.

[54] F. J. Brieler and M. Froba, "Open problems in strongly correlated electron systems," *Chemistry*, vol. 8, pp. 185–194, 2002.

[55] R. M. Crooks, M. Zhao, L. Sun, V. Chechik, and L. K. Yeung, "Dendrimer-encapsulated metal nanoparticles: synthesis, characterization, and applications to catalysis," *Accounts of Chemical Research*, vol. 34, no. 3, pp. 181–190, 2001.

[56] K. Zhu, T. B. Vinzant, N. R. Neale, and A. J. Frank, "Removing structural disorder from oriented TiO_2 nanotube arrays: reducing the dimensionality of transport and recombination in dye-sensitized solar cells," *Nano Letters*, vol. 7, no. 12, pp. 3739–3746, 2007.

[57] M. C. Miyauchi and T. S. Hiromasa, "Super-hydrophilic and transparent thin films of TiO_2 nanotube arrays by a hydrothermal reaction," *Journal of Materials Chemistry*, vol. 17, no. 20, pp. 2095–2100, 2007.

[58] Q. Y. Cai, M. Paulose, O. K. Varghese, and C. A. Grimes, "The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation," *Journal of Materials Research*, vol. 20, no. 1, pp. 230–236, 2005.

[59] Z. Lockman, S. Sreekantan, S. Ismail, L. Schmidt-Mende, and J. L. MacManus-Driscoll, "Influence of anodisation voltage on the dimension of titania nanotubes," *Journal of Alloys and Compounds*, vol. 503, no. 2, pp. 359–364, 2010.

[60] O. K. Varghese, D. Gong, M. Paulose, C. A. Grimes, and E. C. Dickey, "Crystallization and high-temperature structural stability of titanium oxide nanotube arrays," *Journal of Materials Research*, vol. 18, no. 1, pp. 156–165, 2003.

[61] X. Xu, C. Tang, H. Zeng et al., "Structural transformation, photocatalytic, and field-emission properties of ridged TiO_2 nanotubes," *ACS Applied Materials and Interfaces*, vol. 3, no. 4, pp. 1352–1358, 2011.

[62] X. Xu, X. Fang, T. Zhai et al., "Tube-in-tube TiO_2 nanotubes with porous walls: fabrication, formation mechanism, and photocatalytic properties," *Small*, vol. 7, no. 4, pp. 445–449, 2011.

[63] B. Yu, Y. Q. Xia, F. Zhou, and W. M. Liu, "Microstructured arrays of TiO_2 nanotubes for improved photoelectrocatalysis and mechanical stability," *Advanced Functional Materials*, vol. 19, no. 12, pp. 1930–1938, 2009.

[64] D. Kim, A. Ghicov, S. P. Albu, and P. Schmuki, "Bamboo-type TiO_2 nanotubes: improved conversion efficiency in dye-sensitized solar cells," *Journal of the American Chemical Society*, vol. 130, no. 49, pp. 16454–16455, 2008.

[65] S. P. Albu, D. Kim, and P. Schmuki, "Growth of aligned TiO_2 bamboo-type nanotubes and highly ordered nanolace," *Angewandte Chemie*, vol. 47, no. 10, pp. 1916–1919, 2008.

[66] J. J. Gong, C. J. Lin, M. D. Ye, and Y. K. Lai, "Enhanced photoelectrochemical activities of a nanocomposite film with a bamboo leaf-like structured TiO_2 layer on TiO_2 nanotube

arrays," *Chemical Communications*, vol. 47, no. 9, pp. 2598–2600, 2011.

[67] X. L. Yuan, M. J. Zheng, L. Ma, and W. Z. Shen, "High-speed growth of TiO_2 nanotube arrays with gradient pore diameter and ultrathin tube wall under high-field anodization," *Nanotechnology*, vol. 21, no. 40, Article ID 405302, pp. 1–8, 2010.

[68] K. Lee, D. Kim, P. Roy et al., "Anodic formation of thick anatase TiO_2 mesosponge layers for high-efficiency photocatalysis," *Journal of the American Chemical Society*, vol. 132, no. 5, pp. 1478–1479, 2010.

[69] K. Yasuda and P. Schmuki, "Electrochemical formation of self-organized zirconium titanate nanotube multilayers," *Electrochemistry Communications*, vol. 9, no. 4, pp. 615–619, 2007.

[70] A. Mohammadpour, P. R. Waghmare, S. K. Mitra, and K. Shankar, "Anodic growth of large-diameter multipodal TiO_2 nanotubes," *ACS Nano*, vol. 4, no. 12, pp. 7421–7430, 2010.

[71] C. J. Lin, W. Y. Yu, and S. H. Chien, "Rough conical-shaped TiO_2-nanotube arrays for flexible backilluminated dye-sensitized solar cells," *Applied Physics Letters*, vol. 93, no. 13, Article ID 133107, 2008.

[72] Z. Jin, G. T. Fei, X. Y. Hu, S. H. Xu, and L. De Zhang, "Controllable fabrication of multibranched TiO_2 nanotubes via a two-step anodization method," *Chemistry Letters*, vol. 38, no. 3, pp. 288–289, 2009.

[73] X. Xu, T. Y. Zhai, M. H. Shao, and J. Z. Huang, "Anodic formation of anatase TiO_2 nanotubes with rod-formed walls for photocatalysis and field emitters," *Physical Chemistry Chemical Physics*, vol. 14, no. 47, pp. 16371–16376, 2012.

[74] Q. Zhang, L. S. Ma, X. J. Xu et al., "The influence of oxidation time on the morphologies of TiO_2 nanostructures," *Journal of Nanoscience and Nanotechnology*, vol. 14, no. 4, pp. 3262–3265, 2014.

[75] J. Wang and Z. Lin, "Freestanding TiO_2 nanotube arrays with ultrahigh aspect ratio via electrochemical anodization," *Chemistry of Materials*, vol. 20, no. 4, pp. 1257–1261, 2008.