TiO₂ micro-flowers composed of nanotubes and their application to dye-sensitized solar cells

Woong-Rae Kim¹*, Hun Park²† and Won-Youl Choi¹,3*

Abstract

TiO₂ micro-flowers were made to bloom on Ti foil by the anodic oxidation of Ti-protruding dots with a cylindrical shape. Arrays of the Ti-protruding dots were prepared by photolithography, which consisted of coating the photoresists, attaching a patterned mask, illuminating with UV light, etching the Ti surface by reactive ion etching (RIE), and stripping the photoresist on the Ti foil. The procedure for the blooming of the TiO₂ micro-flowers was analyzed by field emission scanning electron microscopy (FESEM) as the anodizing time was increased. Photoelectrodes of dye-sensitized solar cells (DSCs) were fabricated using TiO₂ micro-flowers. Bare TiO₂ nanotube arrays were used for reference samples. The short-circuit current (Jsc) and the power conversion efficiency of the DSCs based on the TiO₂ micro-flowers were 4.340 mA/cm² and 1.517%, respectively. These values of DSCs based on TiO₂ micro-flowers were higher than those of bare samples. The TiO₂ micro-flowers had a larger surface area for dye adsorption compared to bare TiO₂ nanotube arrays, resulting in improved Jsc characteristics. The structure of the TiO₂ micro-flowers allowed it to adsorb dyes very effectively, also demonstrating the potential to achieve higher power conversion efficiency levels for DSCs compared to a bare TiO₂ nanotube array structure and the conventional TiO₂ nanoparticle structure.

Keywords: Dye-sensitized solar cells; TiO₂ nanotube; Micro-flowers; Anodizing

Background

Dye-sensitized solar cells (DSCs) have received much attention since Grätzel and O’Regan achieved a remarkable level of efficiency through the use of mesoporous TiO₂ films as a photoanode for DSCs in 1991 [1]. DSCs have several advantages compared to Si or copper indium gallium selenide (CIGS) solar cells as follows: (a) DSCs can be fabricated with non-vacuum processes, as opposed to Si or CIGS solar cells. The use of non-vacuum equipment offers the possibility to reduce costs. (b) Wet etching processes such as saw damage etching and texturing, which are widely used in Si solar cells, are not required during the fabrication of DSCs. The fabrication of DSCs is thus simplified without a wet etching process. (c) Colorful DSCs can be easily fabricated because dyes have various colors according to their light absorption characteristics. Although DSCs have these merits, the relatively low power conversion efficiency has become the main cause which limits the commercialization of DSCs.

Several attempts to enhance the performance levels of dyes [2-12], photoelectrodes [13-30], counter cathodes [31-36], and electrolytes [3,31,37-41] have been attempted in an effort to obtain improved efficiency in DSCs. Among these efforts, increasing the surface area of the photoelectrodes and reducing the degree of charge recombination between the photoelectrodes and electrolytes have been shown to be critical factors when seeking to improve the power conversion efficiency of DSCs. The TiO₂ nanoparticle structure has shown the best performance in DSCs [3]. However, structural disorder, which exists at the contact point of TiO₂ nanocrystalline particles, reportedly prohibits charge transport, resulting in limited photocurrents [27-29].

The effort to find alternative TiO₂ nanostructures has been an important issue to researchers who attempt to increase the power conversion efficiency of DSCs. Various types of nanotechnologies have been applied to alternative TiO₂ nanostructures such as nanorods [13], nanowires [14,15], nanotubes [16,18,19,22,23,25,27-30,42,43], nanohemispheres [21,24], and nanoports [17,20]. These structures...
were used to increase the surface area for dye adsorption and to facilitate charge transport through TiO₂ films. Of these nanostructures, the TiO₂ nanotube structure has the best potential to overcome the limitations of the TiO₂ nanoparticle structure. A previous report showed that the electronic lifetimes of TiO₂ nanotube-based DSCs were longer than those of TiO₂ nanoparticle-based DSCs [30].

Due to the one-dimensional structure of TiO₂ nanotube arrays, charge percolation in TiO₂ nanotube-based films is easier than it is in the TiO₂ nanoparticle structure [27-29].

In this study, TiO₂ micro-flowers composed of nanotubes were fabricated by means of dot patterning, Ti etching, and anodizing methods. The dot patterning and etching of Ti substrates increased the anodizing area to form TiO₂ nanotubes. By controlling the anodizing time, beautiful TiO₂ micro-flowers were successfully made to bloom on Ti substrates and were applied to the photoelectrodes of DSCs. To the best of our knowledge, this is the first study to report the fabrication of TiO₂ micro-flowers and their application to DSCs. The TiO₂ micro-flower structure is strongly expected to enhance the possibility to overcome the limitations of the TiO₂ nanoparticle structure.

**Methods**

To fabricate the protruding dot patterns on a 0.5-mm-thick Ti foil (99%, Alfa Aesar Co., Ward Hill, MA, USA), 5-μm-thick negative photoresists (PR; L-300, Dongjin Co., Hwaseong-Si, South Korea) were coated on a flat layer of Ti foil using a spin coater (Mark-8 Track, TEL Co., Tokyo, Japan). The coated photoresists were softly baked at 120°C for 120 s and hardly baked at 110°C for 5 min. A dot-patterned photomask was used for PR, the patterning process via UV light exposure. UV light having an energy of 14.5 mJ/s was used for illumination for 5 s, and the PR were developed. The PR at areas not exposed to UV light were removed.

The PR-patterned Ti foil was dry-etched at 20°C for 30 min using reactive ion etching (RIE) equipment (ICP380, Oxford Co., Abingdon, Oxfordshire, UK). BCl₃ and Cl₂ were used as the etchant gas in the RIE process with a top power of 800 W and a bottom power of 150 W. The photoresists on the UV-exposed area served to protect the flat Ti surface during the RIE process. Only the Ti surface at the area not exposed to UV was etched out. The remaining photoresist after the RIE process was stripped at 250°C for 20 min using a photoresist stripper (TS-200, PSK Co., Hwaseong-si, South Korea). O₂ and N₂ gases were used to remove the photoresist at a power of 2,500 W.

Before the anodizing process, Ti foil samples patterned with protruding dots were successively sonicated with acetone, ethanol, and deionized (DI) water to remove any residue on their surfaces. TiO₂ micro-flowers, consisting of TiO₂ nanotubes, were fabricated by the anodization of the Ti foil sheets which had been patterned with protruding dots in an ethylene glycol solution containing 0.5 wt% NH₄F. A constant potential of 60 V with a ramping speed of 1 V/s was applied between the anode and the cathode. Pt metal was used as a counter cathode. The anodizing time was controlled for the successful blooming of the TiO₂ micro-flowers. The as-anodized TiO₂ nanotubes were rinsed with DI water and annealed at 500°C for 1 h. The morphologies of the TiO₂ nanotubes and the micro-flowers were studied by field emission scanning electron microscopy (FESEM, Hitachi SU-70, Tokyo, Japan). The as-anodized and annealed TiO₂ nanotubes were analyzed by X-ray diffraction (XRD; Rigaku D/ MAX-RC, Cu Kα radiation, Rigaku Corporation, Tokyo, Japan) to confirm the crystallization characteristics.

Ti substrates based on TiO₂ micro-flowers were used for the photoelectrodes of the DSCs. TiO₂ photoelectrodes were immersed at room temperature for approximately 1 day in an ethanol solution containing 3 × 10⁻⁴ M cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)ruthenium(II) bis-tetrabutylammonium (N719) dye. The dye-adsorbed photoelectrodes were rinsed with an ethanol solution and dried at room temperature. Pt-coated fluorine-doped tin oxide (FTO) glass as a counter electrode was prepared by spin coating a 0.7 mM H₂PtCl₆ solution in 2-propanol at 500 rpm for 10 s followed by an annealing step at 380°C for 30 min. The dye-adsorbed photoelectrodes and the Pt-coated FTO glass samples were spaced using a 60-μm Surlyn® film (DuPont Co., Wilmington, DE, USA). The liquid electrolyte was prepared by dissolving 0.6 M 1-hexyl-2,3-dimethylimidazolium iodide (C6DMIm), 0.05 M iodine, 0.1 M lithium iodide, and 0.5 M 4-tert-butylpyridine in 3-methoxyacetonitrile. The J-V characteristics were measured under an AM 1.5 G condition (model 2400 source measure unit, Keithley Co., Cleveland, OH, USA). A 1,000-W Xenon lamp (91193, Oriel Co., Irvine, CA, USA) was used as a light source.

**Results and discussion**

Figure 1 shows FESEM images of Ti-protruding dots which have a cylindrical shape. The Ti surface at the UV-exposed area was flat because the cross-linked photoresist blocked the etching by reactive ions. However, the surface at the area not exposed to UV was very rough due to the RIE in the vertical direction. The diameter and height of the protruding dots were approximately 4 and 5 μm, respectively.

The microstructures while increasing the anodization time from 1 to 7 min are shown in Figures 2, 3, 4, 5, and 6. Figure 2 shows FESEM images of a Ti surface which was patterned with protruding dots and anodized for 1 min at 60 V in an ethylene glycol solution containing 0.5 wt% NH₄F. Anodized Ti dot arrays are shown in
Figure 1 FESEM images of a Ti surface patterned with protruding dots before the anodizing process. (a) × 2,000 magnification, (b) × 5,000 magnification, (c) × 10,000 magnification, and (d) × 20,000 magnification.

Figure 2 FESEM images of a Ti surface patterned with protruding dots and anodized for 1 min. The Ti surface was anodized at 60 V in an ethylene glycol solution containing 0.5 wt% NH₄F. (a) × 2,000 magnification, (b) × 15,000 magnification, (c) × 15,000 magnification, and (d) × 50,000 magnification.
Figure 3 FESEM images of a Ti surface patterned with protruding dots and anodized for 2 min. The Ti surface was anodized at 60 V in an ethylene glycol solution containing 0.5 wt% NH₄F. (a) × 1,000 magnification, (b) × 5,000 magnification, (c) × 15,000 magnification, and (d) × 50,000 magnification.

Figure 4 FESEM images of a Ti surface patterned with protruding dots and anodized for 4 min. The Ti surface was anodized at 60 V in an ethylene glycol solution containing 0.5 wt% NH₄F. (a) × 1,000 magnification, (b) × 5,000 magnification, (c) × 10,000 magnification, and (d) × 45,000 magnification.
Figure 5 FESEM images of a Ti surface patterned with protruding dots and anodized for 5 min. The Ti surface was anodized at 60 V in an ethylene glycol solution containing 0.5 wt% NH₄F. (a) × 1,000 magnification, (b) × 4,000 magnification, (c) × 10,000 magnification, and (d) × 40,000 magnification.

Figure 6 FESEM images of a Ti surface patterned with protruding dots and anodized for 7 min. The Ti surface was anodized at 60 V in an ethylene glycol solution containing 0.5 wt% NH₄F. (a) × 1,000 magnification, (b) × 4,000 magnification, (c) × 10,000 magnification, and (d) × 50,000 magnification.
Figure 2a, and magnified images of an anodized Ti dot are shown in Figure 2b,c. Several holes were formed on the top and the wall of the protruding dots. TiO$_2$ nanotubes with a thickness of 400 nm were noted on the wall of the protruding dots, as shown in Figure 2d. Fluorine ions in the anodizing solution anisotropically etched the Ti and TiO$_2$ due to the applied voltage between the anode and cathode. The anisotropic etching of Ti and TiO$_2$ led to the creation of the one-dimensional structure of a TiO$_2$ nanotube array. Figure 2d shows that the TiO$_2$ nanotubes grew vertically from the wall of the protruding dots. When the anodization time was increased to 2 min, small cleavages formed between the top areas and side walls of the protruding dots, as shown in Figure 3. Figure 3b,c shows approximately 700-nm-thick TiO$_2$ nanotube arrays.

When the anodization time was increased to 4 min, beautiful TiO$_2$ micro-flowers started to bloom. The arrays of TiO$_2$ micro-flowers are shown in Figure 4a. The thickness of each TiO$_2$ nanotube is linearly correlated with the extent to which the TiO$_2$ micro-flowers bloom. The blooming of the TiO$_2$ micro-flowers is due to the severe cleavages of the TiO$_2$ nanotubes between the top areas and the side walls of the protruding dots. As the anodization time was increased to 5 min, small cleavages formed in the TiO$_2$ nanotubes in the core bundles in TiO$_2$ micro-flowers were slightly bent in random directions, as shown in Figure 5a,b,c,d. This occurred due to the difference in the growing speed of each TiO$_2$ nanotube in the core bundles. The measured thickness of the TiO$_2$ nanotubes in Figure 5d was 2 μm. As the anodization time was increased to 7 min, the center area of the core nanotube bundles in the TiO$_2$ micro-flowers was removed, as shown in Figure 6a,b,c. Figure 6d shows the cleavage areas of the TiO$_2$ micro-flowers. The structure of the TiO$_2$ nanotubes in that area collapsed due to the additional etching by the fluorine ions in the anodizing solution.

Figure 7 shows the schematic mechanism involved in the blooming of the TiO$_2$ micro-flowers. One of the Ti-protruding dots from the photolithography and RIE process shows a cylindrical shape in Figure 7a. Figure 7b shows that the TiO$_2$ nanotubes grew in a vertical direction from the Ti surface due to the anodizing process. As the thicknesses of the TiO$_2$ nanotubes at the cylindrical upper side (area A) and at the cylinder side (area C) increased, the Ti-supporting metal at the cylinder corner (area B) was completely converted into TiO$_2$ nanotubes. The TiO$_2$ nanotubes without Ti-supporting metal in area B finally fell onto the TiO$_2$ nanotubes which had grown in area C, as shown in Figure 7c. Several horizontal cleavages in area B formed due to the collapse of the TiO$_2$ nanotubes in area B. Several vertical cleavages in areas B and C were also observed, resulting from the volume expansion when the Ti was converted into TiO$_2$ nanotubes. Volume expansion in an organic anodizing solution was reported previously [44]. Figure 7d shows that the growing TiO$_2$ nanotubes in area C pushed and pushed TiO$_2$ nanotubes between areas A and B to area C. More horizontal cleavages in area B were created due to the pushing of the TiO$_2$ nanotubes, and these cleavages formed the multi-layered petals in the TiO$_2$ micro-flowers. Figure 7c,d shows the blooming of beautiful TiO$_2$ micro-flowers. This is a first blooming of TiO$_2$ micro-flowers. The thickness of the TiO$_2$ nanotubes
in areas A and C gradually increased with the anodization time. Finally, all Ti metal was converted into TiO₂ nanotubes, leaving no additional Ti metal to support the TiO₂ nanotubes in area A. Figure 7e shows that the TiO₂ nanotubes without Ti-supporting metal in area A were detached from the center of the nanotube bundles. This removal of the TiO₂ nanotubes in area A left an empty core in the TiO₂ micro-flowers. These TiO₂ micro-flowers with empty cores are different from those shown in Figure 7c,d. This result represents a second blooming of the TiO₂ micro-flowers.

Figure 8 shows the results of an XRD analysis of the as-anodized TiO₂ micro-flowers and the annealed TiO₂ micro-flowers. Figure 8a shows only the Ti peaks, revealing that the as-anodized TiO₂ nanotubes in the micro-flowers have an amorphous crystal structure. However, if
the as-anodized TiO2 nanotubes are annealed at 500°C for 1 h, the crystal structure of the TiO2 nanotubes is converted into the anatase phase. Anatase peaks and Ti peaks were found, as shown in Figure 8b. From the XRD results, it can be confirmed that the annealed TiO2 micro-flowers exist in the anatase phase.

As shown in Figure 9, bare TiO2 nanotubes and TiO2 micro-flowers were applied for use in DSC photoelectrodes. DSCs based on bare TiO2 nanotube arrays were used as reference samples to compare the J-V characteristics with DSCs based on TiO2 micro-flowers. Photoelectrodes based on bare TiO2 nanotubes were prepared by an anodizing process of flat Ti foil. On the other hand, photoelectrodes based on TiO2 micro-flowers were fabricated by an anodizing process of Ti foil patterned and shaped such that they approximated cylindrical protruding dots.

Figure 10 shows the J-V characteristics of DSCs based on the bare TiO2 nanotubes and TiO2 micro-flowers when the thicknesses of the TiO2 nanotubes are 1.5 and 2.0 μm, respectively. The Jsc and power conversion efficiency values of DSCs based on TiO2 micro-flowers were higher than those of bare samples. TiO2 micro-flowers facilitated better dye adsorption, resulting in higher Jsc values. The TiO2 micro-flowers had a larger surface area

The conclusion of this report is that DSCs based on TiO2 micro-flowers have the potential to achieve higher efficiency levels compared to DSCs based on normal TiO2 nanotubes and TiO2 nanoparticles.

### Table 1 J-V characteristics of DSCs based on bare TiO2 nanotubes and TiO2 micro-flowers

| Sample | Photoelectrode | Thickness of the TiO2 nanotubes (μm) | Jsc (mA/cm²) | Voc (V) | FF | Efficiency (%) |
|--------|----------------|-------------------------------------|--------------|--------|----|----------------|
| (a)    | Bare           | 1.5                                 | 3.279        | 0.636  | 0.549 | 1.147 ± 0.167  |
| (b)    | Micro-flowers  | 1.5                                 | 3.838        | 0.661  | 0.467 | 1.187 ± 0.041  |
| (c)    | Bare           | 2.0                                 | 4.030        | 0.636  | 0.536 | 1.378 ± 0.092  |
| (d)    | Micro-flowers  | 2.0                                 | 4.340        | 0.644  | 0.542 | 1.517 ± 0.063  |

The thicknesses of TiO2 nanotubes are 1.5 μm and 2.0 μm.
for dye adsorption compared to that of bare TiO₂ nanotubes. The efficiency of the DSCs based on the TiO₂ micro-flowers was found to reach 1.517%. The efficiency levels of the DSCs based on the TiO₂ micro-flowers were relatively low compared to those of conventional DSCs based on TiO₂ nanoparticle structures, as the thickness of the TiO₂ nanotubes in the micro-flowers was very small. To improve the efficiency of DSCs based on TiO₂ micro-flowers, our future work will concentrate on controlling the characteristics of the dot patterns such as the dot diameter, the distance between adjacent dots, and the height of the protruding dots.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
WK and HP conceived the study and drafted the manuscript. WK helped with the organization of the Ti surface. HP helped with the J-V characterization of DSCs. WC supervised the whole work and revised the manuscript. All authors read and approved the final manuscript.

Acknowledgements
This research was financially supported by the Ministry of Education, Science, and Technology (WEST) and by the National Research Foundation of Korea (NRF) through the Human Resources Training Project for Regional Innovation (No. NRF-2012H1B8A2026000).

Author details
1Department of Metal and Materials Engineering, Gangneung-Wonju National University, Gangneung 210-720, South Korea. 2Photovoltaic Research Department, Green Energy Research Institute, Hyundai Heavy Industries Co., Ltd, Yongin 446-912, South Korea. 3Research Institute for Dental Engineering, Gangneung-Wonju National University, Gangneung 210-720, South Korea.

Received: 24 January 2014 Accepted: 12 February 2014 Published: 24 February 2014

References
1. Oregan B, Grätzel M: A low-cost, high-efficiency solar-cell based on dye-sensitized colloidal TiO₂ films. Nature 1991, 353(6346):737–740.
2. Li L-L, Diau EW-G: Porphyrin-sensitized solar cells. Chem Soc Rev 2013, 42(1):291–304.
3. Yella A, Lee H-W, Tsao H-N, Yi C, Chandiran AK, Nazeeruddin MK, Diau EW-G, Yeh C-Y, Zakeeruddin SM, Grätzel M: Effect of a fullerene derivative on the performance of TiO₂-nanotube-based dye-sensitized solar cells. J Nanosc Chem Soc 2013, 13(5):3487–3490.
4. Ko Sh, Lee D, Kang HW, Nam KH, Yeo JY, Hong SJ, Grigoropoulos CP, Sung HJ: Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell. Nano Lett 2011, 11(12):667–671.
5. Yang D-J, Y-S-C, Hong JM, Lee J, Kim I-D: Size-dependent photovoltaic property in hollow hemisphere array based dye-sensitized solar cells. J Electroceram 2010, 24(3):200–204.
6. Park H, Yang DJ, Yoo JS, Mun KS, Kim WR, Choi WY: Surface passivation of highly ordered TiO₂ nanotube arrays and application to dye-sensitized solar cells using the concept of isoelectric point. J Ceram Soc Jpn 2009, 117(365):596–599.
7. Park H, Yang DJ, Kim HG, Choi WY, Choi WY: Fabrication of MgO-coated TiO₂ nanotubes and application to dye-sensitized solar cells. J Electroceram 2009, 23(2–4):146–149.
8. Shao F, Sun J, Gao L, Yang S, Luo J: Forest-like TiO₂ hierarchical structures for efficient dye-sensitized solar cells. J Mater Chem 2012, 22(14):6824–6830.
9. Park H, Kim WR, Yang C, Kim H-G, Choi W-Y: Effect of a fullerene derivative on the performance of TiO₂-nanotube-based dye-sensitized solar cells. J Nanosci Nanotechnol 2012, 12(3):1535–1538.
10. Denko H, Arai S, Furubayashi H: High power efficiency of dye-sensitized solar cells using the concept of isoelectric point. J Ceram Soc Jpn 2009, 117(365):596–599.
11. Ko Sh, Lee D, Kang HW, Nam KH, Yeo JY, Hong SJ, Grigoropoulos CP, Sung HJ: Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell. Nano Lett 2011, 11(12):667–671.
12. Yang D-J, Yang C, Hong JM, Lee J, Kim I-D: Size-dependent photovoltaic property in hollow hemisphere array based dye-sensitized solar cells. J Electroceram 2010, 24(3):200–204.
13. Park H, Yang DJ, Yoo JS, Mun KS, Kim WR, Choi WY: Surface passivation of highly ordered TiO₂ nanotube arrays and application to dye-sensitized solar cells using the concept of isoelectric point. J Ceram Soc Jpn 2009, 117(365):596–599.
14. Park H, Yang DJ, Kim HG, Choi WS, Lee H, Choi WY: Fabrication of MgO-coated TiO₂ nanotubes and application to dye-sensitized solar cells. J Electroceram 2009, 23(2–4):146–149.
15. Yang SC, Yang DJ, Kim J, Hong JM, Kim ID, Lee H: Hollow TiO₂ hemispheres obtained by colloidal templating for application in dye-sensitized solar cells. Adv Mater 2008, 20(15):1505–1506.
16. Yang DJ, Park H, Choi WY: TiO₂–nanotube-based dye-sensitized solar cells fabricated by an efficient anodic oxidation for high surface area. J Phys Chem Solids 2008, 69(5–6):1272–1275.
17. Kang S, Choi S, Kang M, Kim J, Hyeon T, Sung Y: Nanorod-based dye-sensitized solar cells with improved charge collection efficiency. Adv Mater 2008, 20(15):54–58.
18. Zhu K, Vincz T, Neale N, Frank A: Removing structural disorder from oriented TiO₂ nanotube arrays: reducing the dimensionality of transport and recombination in dye-sensitized solar cells. Nano Lett 2007, 7(12):3739–3746.
19. Zhou K, Neale N, Miedaner A, Frank A: Enhanced charge-collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO₂ nanotubes. Adv Mater 2008, 20(15):1505–1506.
20. Mor GK, Shankar K, Paulose M, Varghese OK, Grimes CA: Fabrication of highly-ordered TiO₂ nanotube arrays in dye-sensitized solar cells. Nat Mater 2007, 6(1):169–174.
21. Hauch A, Geong A: Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells. Electrochim Acta 2001, 46(22):3457–3466.
22. Xin X, He M, Han W, Jung J, Lin Z: Low-cost copper zinc tin sulfide counter electrodes for high-efficiency dye-sensitized solar cells. Angew Chem Int Ed 2011, 50(49):11739–11742.
33. Choi H, Kim H, Hwang S, Choi W, Jeon M: Dye-sensitized solar cells using graphene-based carbon nano composite as counter electrode. Sol Energy Mater Sol Cells 2011, 95(1):323–325.

34. Roy-Mayhew JD, Bozym DJ, Pinczuk C, Aksay IA: Functionalized graphene as a catalytic counter electrode in dye-sensitized solar cells. ACS Nano 2010, 4(1):6203–6211.

35. Li G, Wang F, Jiang Q, Gao X, Shen P: Carbon nanotubes with titanium nitride as a low-cost counter-electrode material for dye-sensitized solar cells. Angew Chem Int Ed 2010, 49(21):3653–3656.

36. Han J, Kim H, Kim DY, Jo SM, Jang S-Y: Water-soluble polyelectrolyte-grafted multiwalled carbon nanotube thin films for efficient counter electrode of dye-sensitized solar cells. ACS Nano 2010, 4(10):6203–6211.

37. Yum J-H, Baranoff E, Kessler F, Moehl T, Ahmad S, Bessho T, Marchioro A, Ghadiri F, Moser J-E, Yi C: A cobalt complex redox shuttle for dye-sensitized solar cells with high open-circuit potentials. Nat Commun 2012, 3:631.

38. Bai Y, Cao Y, Zhang J, Wang M, Li R, Wang P, Zakeeruddin SM, Grätzel M: High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts. Nat Mater 2008, 7(8):626–630.

39. Snaith HJ, Schmidt-Mende L: Advances in liquid electrolyte and solid-state dye-sensitized solar cells. Adv Mater 2007, 19(20):3187–3200.

40. Wang P, Zakeeruddin SM, Moser JE, Nazaruddin MK, Sekiguchi T, Grätzel M: A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte. Nat Mater 2003, 2(6):402–407.

41. Nogueira AF, Durrant JR, De Paoli MA: Dye-sensitized nanocrystalline solar cells employing a polymer electrolyte. Adv Mater 2001, 13(11):826–830.

42. Park H, Kim H-G, Choi W-Y: Characterizations of highly ordered TiO2 nanotube arrays obtained by anodic oxidation. J. Trans Electr Electron Mater 2010, 11:112–115.

43. Mor G, Varghese O, Paulose M, Shankar K, Grimes C: A review on highly ordered, vertically oriented TiO2 nanotube arrays: fabrication, material properties, and solar energy applications. Sol Energy Mater Sol Cells 2006, 90(14):2011–2075.

44. Yang D-J, Kim H-G, Cho S-J, Choi W-Y: Thickness-conversion ratio from titanium to TiO2 nanotube fabricated by anodization method. Mater Lett 2008, 62(4):775–779.

doi:10.1186/1556-276X-9-93

Cite this article as: Kim et al.: TiO2 micro-flowers composed of nanotubes and their application to dye-sensitized solar cells. Nanoscale Research Letters 2014 9:93.

Submit your manuscript to a SpringerOpen journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com