

Dye-Sensitized Photovoltaic Wires Using Highly Ordered TiO₂ Nanotube Arrays

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ABSTRACT Dye-sensitized photovoltaic wires (DSPVWs) are developed using anodized Ti wires that contain ordered arrays of TiO₂ nanotubes. The prototype DSPVW consists of N719 dye-adsorbed TiO₂ nanotube arrays around a Ti wire as a working electrode, a platinum wire as a counter electrode, and an organic electrolyte encased in a capillary glass tube. The effect of length of nanotube arrays on the photovoltaic performance of DSPVWs is studied systematically. A solar-to-electric conversion efficiency of 2.78% is achieved with 55 μm long nanotubes under 98.3 mW/cm² AM 1.5 simulated full light. The prototype device is capable of achieving a long distance transport of photocurrent and harvesting all light from any direction in surroundings to generate electricity.

KEYWORDS: photovoltaic wires · dye-sensitized · nanotube arrays

Dye-sensitized solar cells (DSCs) are attracting extensive interest in scientific and industrial fields because of their low cost and high efficiency.^{1,2} A dye-molecule-chemisorbed mesoporous TiO₂ photoactive layer applied to a conductive glass is the key component of the DSCs. Under illumination, the excited dye molecules inject photogenerated electrons into the conduction band of TiO₂, with holes transferring to the counter electrode *via* redox relays. At present, planar DSCs have achieved a conversion efficiency up to 11% in combination with a volatile triiodide/iodide electrolyte and a platinized counter electrode.^{3–5}

DSCs in a wire format, which is named as dye-sensitized photovoltaic wires (DSPVWs),⁶ have opened up a promising possibility to produce cost-effective and scalable solar energy harvesting by being integrated with current textile technology. A similar idea has been demonstrated in recent developments in fiber-based organic photovoltaic devices.^{7,8} Some attempts to make DSPVWs by depositing TiO₂ nanoparticles concentrically around metal wires have been reported recently.^{6,9} However, the conversion efficiency of DSPVWs has not been reported. Therefore, fabrication

of high-efficiency DSPVWs still remains a challenge.

Development of a more efficient TiO₂ photoactive layer consisting of one-dimensional ordered nanostructures has the potential to improve the conversion efficiency of DSPVWs. Highly ordered TiO₂ nanotube arrays formed by electrochemical anodization are particularly attractive because they can provide an intuitive one-dimensional electric channel and a large internal surface area.^{10–13} Previous studies have shown that the use of TiO₂ nanotube arrays in conventional planar DSCs can effectively improve the charge collection efficiency.^{10–12} Our recent work¹⁴ and other groups' studies^{15,16} indicate that electrochemical anodization has the versatility to grow TiO₂ nanotube arrays on any Ti substrate independent of its geometry. Very recently, DNA-like structured DSCs using TiO₂ nanotube arrays on Ti wires have been reported by Wang *et al.*¹⁷ In this work, we demonstrate that a prototype DSPVW with a conversion efficiency of 2.78% can be developed using highly ordered TiO₂ nanotube arrays radially grown around a Ti wire.

RESULTS AND DISCUSSION

Figure 1 shows the typical top view and cross-sectional FESEM images of the TiO₂ nanotube arrays grown around a Ti wire prepared by 12 h anodization. As shown in Figure 1a, the diameter of the anodized Ti wire is determined to be 0.31 mm, which is larger than that of Ti wire prior to the anodization (0.25 mm). Considering the density of Ti metal and anatase TiO₂ to be 4.5 and 3.8 g/cm³, respectively, the molar volumes of Ti metal and anatase TiO₂ are calculated as 10.7 and 21.1 cm³/mol, respectively. Although significant amounts of Ti atoms are

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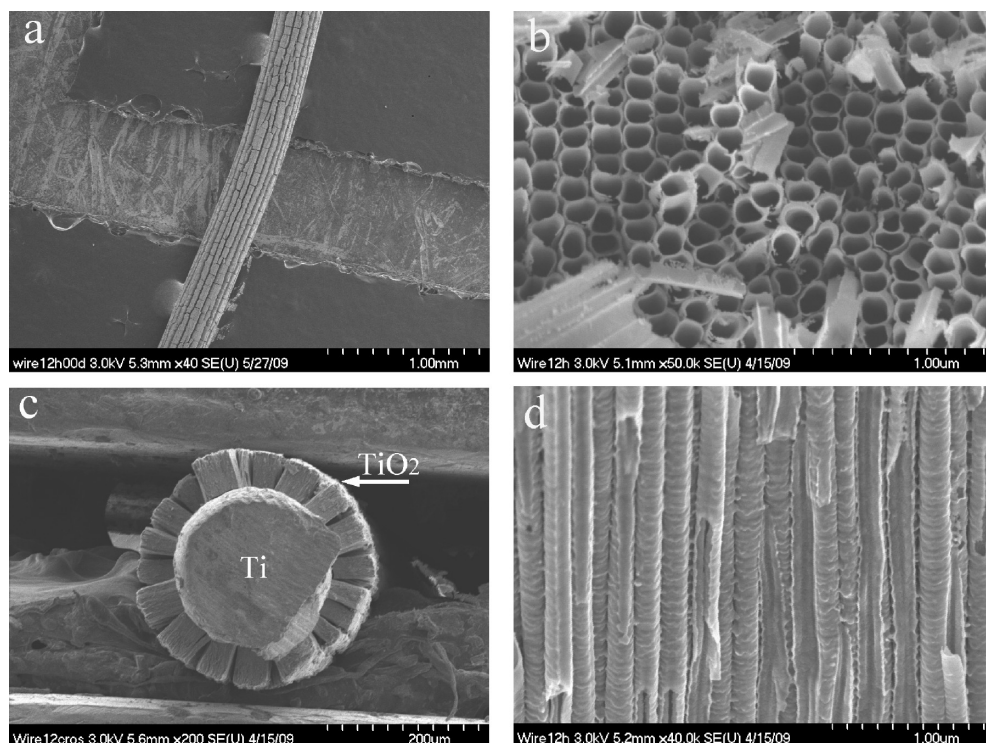


Figure 1. Top view (a,b) and cross-sectional (c,d) FESEM images of TiO_2 nanotube arrays grown around a Ti wire fabricated by anodization at 60 V for 12 h.

dissolved during the anodization, it is reasonable to infer that the increased diameter of the Ti wire after anodization results from the oxidation from Ti to TiO_2 . Figure 1b,c shows that well-defined TiO_2 nanotube arrays with a length of 55 μm , an internal diameter of about 140 nm, and a wall thickness of about 10 nm are grown in a radially outward direction on the circumference of Ti wire. Figure 1d depicts that TiO_2 nanotube arrays are vertical to the Ti wire substrate, which provide unidirectional channels for the charge transport. The crystallization of TiO_2 nanotube arrays is determined to be anatase phase according to our previous work.¹⁴

Similar to the anodization of Ti foils and Ti meshes,^{14,18} the length of TiO_2 nanotube arrays around Ti wires can be controlled simply by altering the anodization duration. As shown in Figure 2, the length of

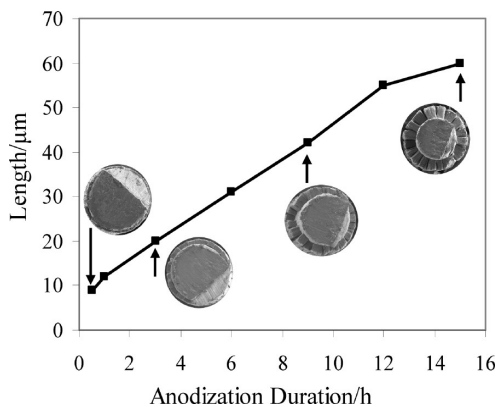


Figure 2. Effect of the anodization duration on the length of TiO_2 nanotube arrays grown around Ti wires.

nanotube arrays increases from 9 to 60 μm by increasing the anodization duration from 0.5 to 15 h. Although there are some cracks on the surface of TiO_2 nanotube arrays because of the bundling of nanotubes, the array layer has a flat bottom plane, which well adheres to the Ti substrate. Furthermore, a dense TiO_2 barrier layer forms at the interfaces of Ti metal and TiO_2 nanotube arrays when the sample is anodized and further annealed.¹⁰ Therefore, the concentrically grown TiO_2 nanotube arrays are able to efficiently block the back electron transfer from the substrate to the electrolyte, which is considered to be quite vital to suppress the generation of dark current in the DSCs.¹⁹

Scheme 1 shows a digital photograph of a prototype DSPVW and its schematic cross section. The TiO_2 nanotube arrays have enough mechanical stability for the assembly of DSPVWs (Supporting Information, Figure S1). J - V curves of the prototype DSPVWs with different nanotube lengths are shown in Figure 3a. For a clear comparison, the variations of short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (FF), and solar-to-electric conversion efficiency (η) with the lengths of nanotube arrays are shown in Figure 3b,c. Although the anodization increases the diameter of Ti wires slightly, the actual η is calculated on the basis of Ti wire's diameter (0.25 mm) prior to the anodization. As shown in Figure 3a,b, by increasing the lengths of nanotube arrays from 9 to 55 μm , we improve the J_{sc} from 2.61 to 10.9 mA/cm^2 systematically, which is accompanied with a slight reduction in V_{oc} from 0.612 to 0.522 V and a reduction in FF from 0.621



Scheme 1. Digital Photograph of a Prototype DSPVW and Its Schematic Cross Section

to 0.48. Because of the offset of the large improvement in J_{sc} to the small reduction in V_{oc} and FF, the η of DSPVWs exhibits a continuous increase from 1.01 to 2.78% with the increase in the nanotube lengths from 9 to 55 μm (Figure 4c). The trend of FF is attributed to the increased series resistance¹⁰ of DSPVWs caused by the increased lengths of nanotube arrays. The slight decrease in V_{oc} by the increased nanotube lengths, on one side, is related to the augmentation in the surface area of the working electrode, which provides additional charge recombination sites. On the other hand, due to the filtering of incident light by the outer dye molecules (which locate far from the Ti substrate), the inner dyes (which locate close to the Ti substrate) generate fewer electrons compared to the outer dyes. The accumulation of these photogenerated electrons on the conduction bands of TiO_2 nanotube arrays lowers their quasi-Fermi level, resulting in a low V_{oc} .²

We investigated the amount of dye loading in DSPVWs to clarify the reasons for the large J_{sc} improvement as it relates to an increase in the nanotube lengths. As shown in Figure 3c, by the amount of adsorbed dye that increases linearly from 2.9 to 13.3 nmol/cm with the lengths from 9 to 55 μm , we may assume this contributes to the J_{sc} improvement. It is also noted that by further extending the length of nanotube arrays to 60 μm , we can still increase the dye adsorption to 15.6 nmol/cm. However, this increment in dye adsorption cannot continue to improve the J_{sc} of DSPVWs. This may be related to the limited optical penetration depth or the electron diffusion length when the DSPVWs are illuminated from the side of TiO_2 nanotube arrays. The prototype DSPVW with a nanotube length of 60 μm generates a slightly lower J_{sc} of 10.8 mA/cm^2 , a concomitantly reduced V_{oc} of 0.504 V, and a reduced FF of 0.459, resulting in a lower η of 2.54%.

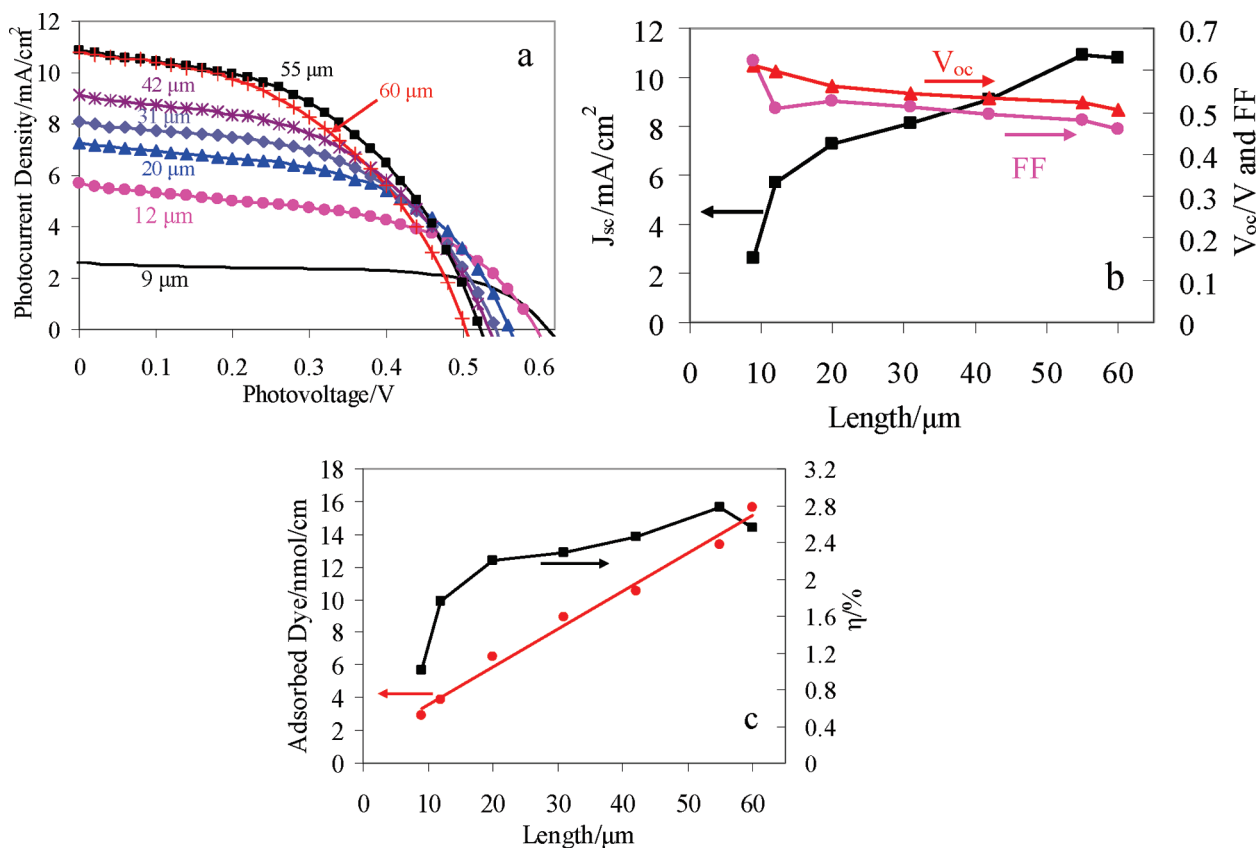


Figure 3. (a) J - V curves of prototype DSPVWs using TiO_2 nanotube arrays with lengths of 9 μm (no symbol), 12 μm (circle), 20 μm (triangle), 31 μm (diamond), 42 μm (star), 55 μm (square) and 60 μm (cross). (b) Effects of the lengths of nanotube arrays on J_{sc} (square), V_{oc} (triangle), and FF (circle). (c) Effects of the lengths of nanotube arrays on η (square) and amount of adsorbed N719 dye (circle).

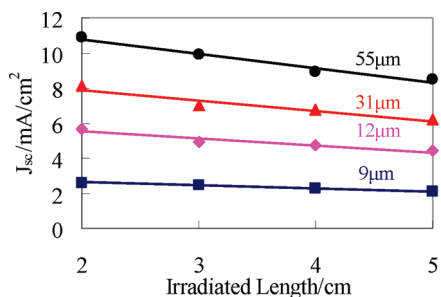


Figure 4. Effect of the irradiated lengths on the J_{sc} of prototype DSPVWs using TiO₂ nanotube arrays with lengths of 9 (square), 12 (diamond), 31 (triangle), and 55 μm (circle).

One special characteristic for DSPVWs is that they require a long distance transport of photocurrent⁸ because of the wire-shaped configuration. Therefore, a substrate with high conductivity is necessary to reduce the loss of photocurrent during the transport. In our prototype DSPVWs, the underlying Ti wires provide an extremely effective transporter for the photogenerated electrons. In order to support this speculation, we measured the J_{sc} of DSPVWs under different irradiated lengths (*i.e.*, the irradiated surface area). As shown in Figure 4, the J_{sc} of DSPVWs with nanotube lengths of 9, 12, 31, and 55 μm decreases as the irradiated length increases, which implies that an internal series resistance exists in the prototype DSPVWs. However, the reduction slope of J_{sc} depends closely on the length of nanotube arrays. The prototype DSPVW with 9 μm long TiO₂ nanotube arrays shows a rather small J_{sc} reduction slope of 0.176 mA/cm³, demonstrating a small series resistance. Increasing the nanotube lengths to 12, 31, and 55 μm increases the J_{sc} reduction slope to 0.401, 0.598, and 0.825 mA/cm³, respectively, which indicates that the internal series resistance increases significantly. Therefore, it is the TiO₂ nanotube arrays, not the Ti wires, that induce the series resistance. These results support our claim that Ti wires in the prototype DSPVWs ensure an effective transport of photogenerated electrons to the outer circuit. This is critical for long and scalable DSPVWs.

Because of the wire shape (*i.e.*, circular cross section) of the working electrode, DSPVWs can harvest all the light from any direction in the surroundings. To confirm this character by experiments, we measured two typical J – V curves of a prototype DSPVW using 55 μm

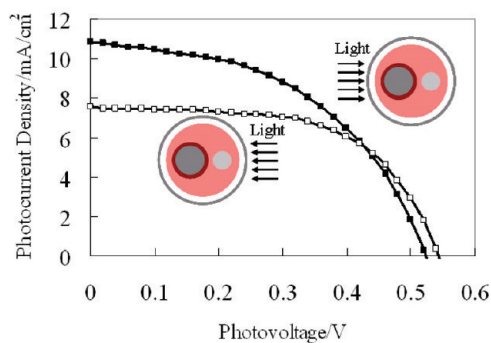


Figure 5. J – V curves of a prototype DSPVW using 55 μm long TiO₂ nanotube arrays under illumination from the working electrode (solid symbols, ■) and from the platinum counter electrode (hollow symbols, □). Insets show the incident direction of light irradiation.

long nanotube arrays under illumination from the working electrode (front-illumination) and platinum counter electrode (rear-illumination). As shown in Figure 5, although the working electrode is shadowed partially by the counter electrode, the J_{sc} under rear-illumination can still reach 7.56 mA/cm², which is about 69% of the J_{sc} (10.9 mA/cm²) under front-illumination. Normally, a lower J_{sc} will result in a higher FF. As expected, Figure 5 shows that the rear-illumination indeed induces a higher FF of 0.59 than the front-illumination (FF = 0.48). Because of the large improvement of FF, the rear-illumination generates an η of 2.46%, which is about 88.5% of the η induced by front-illumination. These results confirm that our present prototype DSPVWs are capable of harvesting all light from any direction in the surroundings to generate electricity, which makes them suitable for the application in some places where a high albedo radiation is available. For example, in outer space, a high earth's albedo for sunlight is available.²⁰

In summary, novel DSPVWs have been developed by using highly ordered TiO₂ nanotube arrays radially grown around Ti wires. The length of nanotube arrays affects the η of DSPVWs demonstrably. Our results indicate that 55 μm long TiO₂ nanotube arrays achieve an η of 2.78% under 98.3 mW/cm² AM 1.5 simulated full light. In addition, prototype DSPVWs are capable of harvesting the light from any direction. Therefore, they may have some applications in places with high albedo radiation.

METHODS

Highly ordered TiO₂ nanotube arrays around Ti wires (Φ = 0.25 mm, 99.7%, Aldrich) were prepared by electrochemical anodization^{21,22} in a two-electrode electrochemical cell with a platinum wire as a counter electrode. The electrolyte consisted of 0.25 wt % ammonium fluoride (Fisher Scientific) and 2 vol % Milli-Q water in ethylene glycol (Aldrich). Ti wires were anodized at 60 V (E3649A, Agilent) for 1–15 h to vary the lengths of nanotube arrays. The anatase crystallization of TiO₂ was achieved by annealing the as-anodized samples at 500 °C under ambient air for 3 h.¹⁴ When cooled to about 80 °C, TiO₂ nanotube arrays were

stained by immersing them into 0.5 mM *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bistetrabutyl ammonium (N719, Solaronix) in 1:1 (v/v) acetonitrile/*tert*-butanol (Aldrich) for 24 h at room temperature, followed by an acetonitrile rinse to remove the physically adsorbed dye molecules.

To assemble a prototype device of DSPVW, we inserted N719-sensitized TiO₂ nanotube arrays around a Ti wire in a capillary glass tube (Aldrich, internal Φ = 0.5 mm, outer Φ = 3.0 mm) along with a platinum wire counter electrode (Aldrich, Φ = 0.127 mm). On the basis of the diameters of the Ti wire, plati-

num wire, and the internal diameter of capillary glass tube, the approximate distance between the working electrode and counter electrode is determined to be about 0.12 mm. The electrolyte consisting of 1.0 M 1-methyl-3-propylimidazolium iodide (Fluka), 0.15 M iodine (Aldrich), 0.1 M guanidine thiocyanate (Aldrich), and 0.5 M 1-methyl benzimidazole (Aldrich) in 3-methoxypropionitrile (Aldrich)²³ was introduced into the glass tube by capillary action. Photocurrent density–photovoltage (J – V) curves under AM 1.5 simulated full sunlight with an intensity of 98.3 mW/cm² (measured by a thermopile transducer, Newport model 70268) provided by a solar simulator (model SP91160–3381, Newport) were recorded by a computer-controlled potentiostat (SI 1286, Schlumberger). The irradiated length of the prototype DSPVWs from the side of working electrode was 2 cm, which was fixed by a photomask. The irradiated area of DSPVWs was taken as its length multiplied by the diameter of the Ti wire, which is the projected area.⁸

The morphologies of TiO₂ nanotube arrays were observed on a Hitachi S-4700 field emission scanning electron microscope (FESEM). The amount of adsorbed dye on the working electrode was measured by desorbing N719 dye in 4 mL of 0.01 M KOH (Fisher Scientific) in 1:1 (v/v) ethanol/water solution for 2 h.²⁴

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Supporting Information Available: SEM images of the tops of 55 μ m long TiO₂ nanotube arrays on a Ti wire under different bending angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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