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Verification of necessity of one-dimensional titania nanoscale materials for dye-sensitized solar cells

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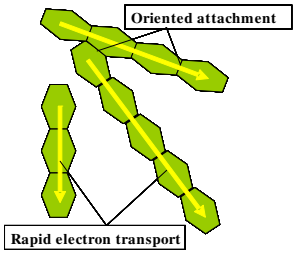
HIGHLIGHTS

- Three one-dimensional titania nanoscale materials synthesized in our laboratory show high conversion efficiency around 9%.
- Necessity of highly crystallized 1-dimensional titania nanoscale materials was elucidated by theoretical consideration.
- The consideration was verified by systematic experiments based on the measurements of (I–V) relation and EIS analysis.

GRAPHICAL ABSTRACT



Necessity of highly crystalline 1-dimensional titania nanoscale materials was elucidated by theoretical consideration and verified by experiments.

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ABSTRACT

Necessity of highly crystallized 1-dimensional titania nanoscale materials (1DTNM) was elucidated by theoretical consideration based on both the electron transfer processes shown by Nyquist plots obtained in electrochemical impedance spectroscopy (EIS) and current–voltage (I–V) measurements. The consideration was verified by systematic experiments, in which titania nanowires (TNWs) with network structure were chosen as a highly crystallized 1DTNM. The cells with electrodes made of various TNW content from 0% to 100% of TNWs mixed with P-25 were fabricated. Based on the measurements of I–V relationship and EIS measurements of these cells, the following three points were clearly demonstrated as verification of the consideration; 1) resistance of electron transport in the titania electrode to the conducting glass electrode is small, 2) the ratio of the resistance for the recombination reactions against that for the transport rate to the conducting glass electrode is large, i.e., efficiency of electron collection is high, and 3) electron density in the titania electrode is high. These points are essentially important to realize high efficiency in DSSCs.

1. Introduction

Light from the sun is the ideal source of energy. Fortunately, the supply of energy is gigantic, i.e., 3×10^{24} J year^{-1} or about 10^4 times more than what mankind consumes currently. The energy demand is expected to touch 30 TW by 2050 [1,2]. Dye-sensitized solar cells (DSSCs) have attracted much attention as they offer a possibility of extremely inexpensive and efficient solar energy conversion. In 1991, O'Regan and Grätzel [3] published a remarkable report, and the Grätzel group attained 10% efficiency in 1993 [4]. The system already reached conversion efficiency 12.3% [5], which exceeds the level to supply electricity at the rate of home use, i.e., 10%. Nevertheless, the

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energy conversion efficiency of the cells for commercial devices has not yet reached the level, which provides lower cost than that of conventional methods of electricity generation using fossil fuel. Therefore, attainment of higher efficient cells is one of the most important challenges for the dye-sensitized solar cells.

Titanium dioxide is the most promising material for the electrode of DSSCs. Many investigators have improved the anodic electrode over 10 years [6–14]. Since 1991, various improvements to the TiO_2 electrode in the DSSCs have been made in terms of light absorption, light scattering, charge transport, suppression of charge recombination, and improvement of the interfacial energetics. In order to prevent contact between the redox mediator in the electrolyte and the fluorine doped tin oxide (FTO), a TiO_2 blocking layer (around 50 nm thick) prepared by chemical bath deposition, spray pyrolysis, or sputtering is used [6]. A light scattering layer on the top of the mesoporous film, consisting of an around 3 μm porous layer containing around 400 nm sized TiO_2 particles [7,8]. Voids of similar size in a mesoporous film can also give effective scattering [9]. The $TiCl_4$ treatment leads to the deposition of an ultrapure TiO_2 shell (around 1 nm) on the mesoporous TiO_2 [10], resulting in increased dye adsorption due to increased roughness [6,11,12]. For flexible polymer cells, a compression technique was developed [13,14].

One-dimensional titania nanoscale materials (1DTNM) have been investigated for attainment of highly efficient solar cells [15–25]. One of the earliest papers describing the utility of one-dimensional TiO_2 nanoscale materials in DSSCs was ours describing application of single crystalline TiO_2 nanotubes for DSSCs [2,15]. This early research has spurred further activity of one-dimensional nanostructured in DSSCs. Ohsaki et al. [16] improved the Kasuga's method of synthesis of titania nanotubes (TNTs) [17,18] by high temperature sintering (higher than 700° C) and fabricated anatase TNTs, attaining 7.1% conversion efficiency. Higher efficiency 8.9% was obtained for the same system by Hsaio et al. [19] Kim et al. [20] used electrophoretic deposition of TNTs and attained 6.7% efficiency. Wei et al. [21] fabricated large surface area 117 m^2/g using TNTs and got 7.5% conversion efficiency. By replacing nanoparticulate films with one-dimensional materials, charges are allowed to move only in one-dimension instead of randomly in three-dimension. The directed movement improves cell currents and reduces losses by increasing the residence lifetime of charge carriers, typically measured with intensity modulated photovoltage spectroscopy (IMVS) for titania nanotube arrays [22]. Many one-dimensional architectures were developed, such as titania nanotube arrays by anodic oxidation [22–28], carbon nanotube–TiO_2 composite nanostructures [29–33], and electrospun anisotropic TiO_2 [32–35]. High conversion efficiencies 9.1% [28], 10.6% [32], and 9.52% [34] were obtained for the above investigations of titania nanotube arrays, carbon nanotube–TiO_2 composite, and electrospun method, respectively.

It is important to make clear the reason for necessity of 1DTNM for attainment of higher efficient DSSCs through theoretical consideration and its verification based on the experimental evidences. In this article first we present that DSSCs with electrodes composed of three kinds of highly crystalline 1DTNM synthesized in our laboratory, i.e., single crystal-like network structure of titania nanowires (TNWs) [36], titania nanorods (TNRs) [37] and newly synthesized titania nanochains (TNCs, Fig. 1), showed high light-to-electricity conversion efficiency around 9%. Next, necessity of highly crystalline 1DTNM for fabricating highly efficient DSSCs is deduced based on the theoretical consideration of electron transport processes derived from Nyquist plots obtained by electrochemical impedance spectroscopy (EIS) and *I–V* measurement. We verify then the consideration by an intentional experiment, measuring the electron transport properties by EIS on the cells with

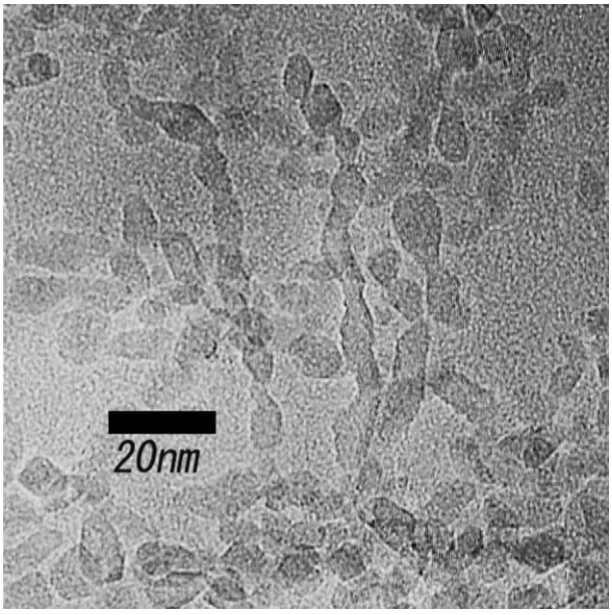

Fig. 1. TEM image of titania nanochains.

electrodes made of single crystal-like TNWs, a representative of highly crystalline 1DTNM, and P-25 with various TNW contents.

2. Experimental

2.1. Formation of single crystal-like network structure of titania nanowires (TNWs), titania nanorods (TNRs) and titania nanochain (TNCs)

Formation procedures of single crystal-like network structure of TNWs and TNRs have been reported in our previous reports [36,37]. Formation procedure of TNCs is almost the same as that of formation procedure of TNRs, except usage of HCl instead of ethylenediamine to adjust pH values to 1.3–5.

2.2. Preparation of titania thin films and solar cells

We have synthesized titania nanoparticles (TNPs) with diameter of 3–5 nm [38,39] in addition to 1DTNM described above. The TNPs and P-25 were used for stabilizing structurally the 1DTNM electrode films. Fluorine doped tin oxide (FTO) was used as an electric conducting oxide. In the case of TNWs, a gel solution of TNWs mixed with P-25 was made by mixing the gel solution of P-25 with reaction products of TNWs in a gel state after centrifugation. Here, the aqueous gel solution of P-25 with polyethylene glycol (PEG) was made after the procedure reported by Grätzel's group [4]. Solar cells were fabricated as follows. First, the gel solution of TNPs with 3–5 nm in diameter was coated 3 times by doctor blade on FTO. The gel solution of TNWs mixed with P-25 was coated by doctor blade method by 8–10 times. In the case of cells made of TNRs, the reaction product after centrifugation was mixed with gel solutions of TNPs. The mixed gel solution was coated by 7–10 times on FTO. In the case of TNCs, the procedure was the same as the case of TNRs.

After each coating, the sample was calcined at 773 K for 10 min. The last calcination was made for 30 min at 773 K. And then dye was introduced to the titania thin films by soaking the film 1–3 days in 3×10^{-4} M solution of a ruthenium dye in a mixed solvent of tert-butanol and acetonitrile. Cis-di(thiocyanate) bis(2,2′-bipyridyl-4,4′-di-carboxylate)-ruthenium(II) bis-tetra-butyl-ammonium (N719) (Solaronix SA) produced by Grätzel's group [4] was used as the dye.