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TiO_2 Nanotube Utilizing a CNT Template and Its Performance as the Anode of a Dye-sensitized Solar Cell

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A new TiO_2 nanotube (TiO_2-NT) was synthesized utilizing a carbon nanotube template via the precursor of the TiO_2-coated carbon nanotube (TiO_2-CNT). The obtained TiO_2-NT was tubular in shape, several µm in length, 100–150 nm in external diameter, and around 30 nm in inner diameter. The TiO_2-NT was mixed with TiO_2 nanoparticles to fabricate anodes of dye-sensitized solar cells, with the anodes showing an improvement in conversion efficiency from 9.6% of nonadditives to 10.4% of 2 wt % additives.

One-dimensional materials have attracted much attention, since the carbon nanotube (CNT) was discovered by Iijima in 1991.[1] CNT families, i.e., single-walled carbon nanotubes and multiwalled carbon nanotubes have been studied widely and make it possible to control their shape and structure, through the development of synthetic methods, such as the utilization of nanotemplates[2,3] or controlled catalysts.[4,5] CNTs have become the most commonly available and well-controlled nanomaterials for researchers. One-dimensional titanium oxide nanostructures[6–8] also have attracted much attention, although they present some difficulties in realizing controlled structures.

In this study, a new TiO_2 nanotube (TiO_2-NT) material is reported, which is synthesized using the CNT template, and the obtained TiO_2-NT was evaluated as the anode of a dye-sensitized solar cell (DSC).

TiO_2-NTs were obtained by baking the precursors of TiO_2-coated carbon nanotubes (TiO_2-CNTs). CNTs were pretreated in concentrated nitric acid at 90 °C for 6 h and rinsed with water until the filtrate became neutral. The pretreated CNTs (0.4 g) were dispersed in 380 mL of aqueous poly(oxyethylenealkylamine) (4.25 wt %) by applying ultrasonic cavitation. 30 mL of 1 M aqueous ammonium hexafluorotitanate and 60 mL of 1 M aqueous boric acid were added to the CNT-dispersed solution at room temperature and left overnight to precipitate TiO_2 onto CNTs, as shown in the reaction of the "liquid-phase deposition"[9] below.

$$(NH_4)_2TiF_6 + H_3BO_3 + 2H_2O \rightarrow TiO_2 + 2NH_4F + HBF_4 + 3H_2O \quad (1)$$

A black powder of TiO_2-CNTs (1.4 g) was obtained and was baked at 750 °C for 1 h under in the atmosphere to obtain white powder of TiO_2-NTs (0.9 g).

The obtained TiO_2-CNTs and TiO_2-NTs were observed under SEM (Figures 1a and 1b). The SEM image of TiO_2-CNTs (Figure 1a, the precursor of TiO_2-NTs) showed segregated rod shapes coated with several nm grains continuously and homogeneously, comprising around several 10 µm in length and 100–150 nm in external diameter. The SEM image of TiO_2-NTs (Figure 1b, after the heat treatment of TiO_2-CNTs at 750 °C) showed the segregated tubular shapes consisting of several tens of nm grains continuously and homogeneously, comprising several µm in length, 100–150 nm in external diameter, and around 30 nm in inner diameter.

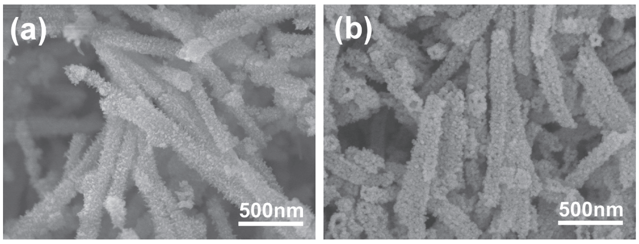

Figure 1. SEM images of the obtained materials of with TiO_2-CNTs (a) and TiO_2-NTs (b), respectively.

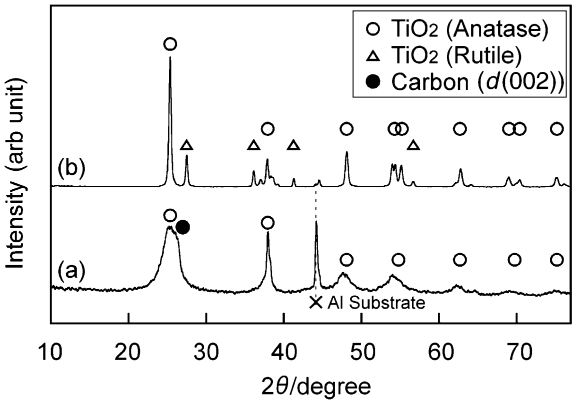

Figure 2. X-ray diffraction patterns of the obtained materials of TiO_2-CNTs (a) and TiO_2-NTs (b).

X-ray diffraction patterns for TiO_2-CNTs and TiO_2-NTs are shown in Figures 2a and 2b, respectively. Every peak of TiO_2-CNTs was attributed to anatase TiO_2 and $d(002)$ of carbon. After the heat treatment of TiO_2-CNTs at 750 °C in air, the carbon peak disappeared, and small amounts of rutile TiO_2 appeared with all peaks of TiO_2 sharpened.

TiO_2-NTs were mixed with TiO_2 nanoparticles at a concentration of 1–3 wt %, and the mixture was dispersed in anhydrous terpineol with ethyl cellulose to prepare screen-printing pastes, following the procedure by Ito et al.[10] The paste

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Table 1. Photovoltaic parameters of DSCs

Amount of TiO_2-NT/wt%	η /%	J_{sc} /mA cm^{-2}	V_{oc} /V	*FF*
0	9.5	18.7	0.76	0.67
1	10.1	19.8	0.75	0.69
2	10.4	19.4	0.75	0.72
3	9.8	19.4	0.76	0.69

was printed on fluorine-doped tin oxide glass substrate to form a film of $5 \times 5\,mm^2$ in area and 15 µm in thickness, on which a further 9 µm thickness of 400 nm-sized TiO_2 was formed as a light-scattering layer on the DSC anode, and *cis*-bis(thiocyanato-*N*)bis(4,4′-tetrabutylammonium hydrogen dicarboxylato-2,2′-bipyridine-$\kappa^2 N$)ruthenium(II) (N-719) was loaded. The anodes mixed with Ti-NT at the concentration of 1–3 wt% displayed no morphology change, compared to the nonmixed material in SEM observation. The obtained anode was assembled with a Pt cathode and an electrolyte of 0.06 M I_2, 0.1 M LiI, 0.5 M 1-ethyl-3-methylimidazolium iodide (EMImI), and 0.5 M *tert*-butylpyridine (TBP) in CH_3CN. The performance of the DSC for the TiO_2-NT-incorporated anodes was evaluated as the parameter of the conversion efficiency (η), short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (*FF*) under irradiation of AM 1.5.

The obtained parameters for the TiO_2-NT incorporated anodes of the DSC are listed in Table 1. It shows that the incorporation of TiO_2-NT from 1 to 3 wt% improved the conversion efficiency. The maximum value of 10.4% was obtained for the 2 wt% incorporated anode, that is, a 1.9% improvement compared with the standard TiO_2 nanoparticle anode. The anode also showed improvements in J_{sc} and *FF*, suggesting smooth electron movement in a thick TiO_2 anode (15 µm).

A new TiO_2-NT utilizing a CNT template was revealed to carry excellent properties for DSC anodes. This encouraging result was thought to be due to the synthetic method using a size-controlled CNT template, which made TiO_2-NT as one-dimensional anatase material of several µm in length, 100–150 nm in external diameter, and around 30 nm in inner diameter. The good effects on the DSC's performance were thought to be attributed to the following.

1) The one-dimensionally aligned anatase crystals might enhance electron mobility in the conduction band of the thick TiO_2 anode layer, as reducing electron leakage in the anode improving the short-circuit photocurrent density and *FF*.

2) The tubular structure might enhance the ion movement, accompanied by electron transfer to neutralize the charges through the thick TiO_2 anode layer, by passing ions through the one-dimensional central space in the tubular structure, to improve the short-circuit photocurrent density and *FF*.

3) The comparatively long shape of the TiO_2 might provide a good light harvesting by scattering the incident light into the TiO_2 anode, thereby improving the short-circuit photocurrent density.

Further investigation is necessary to predict which of the above three factors are the main effect at this moment, and this would be reported by investigating the relations between the photovoltaic parameters and the shapes or structures of one-dimensional TiO_2-NTs in the near future.

References

1 S. Iijima, *Nature* **1991**, *354*, 56.
2 T. Kyotani, L.-f. Tsai, A. Tomita, *Chem. Mater.* **1996**, *8*, 2109.
3 H. Nishino, R. Nishida, T. Matsui, N. Kawase, I. Mochida, *Carbon* **2003**, *41*, 2819.
4 K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, *Science* **2004**, *306*, 1362.
5 G. Lolli, L. Zhang, L. Balzano, N. Sakulchaicharoen, Y. Tan, D. E. Resasco, *J. Phys. Chem. B* **2006**, *110*, 2108.
6 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* **1998**, *14*, 3160.
7 H. Dai, A. G. Rinzler, P. Nikolaev, A. Thess, D. T. Colbert, R. E. Smalley, *Chem. Phys. Lett.* **1996**, *260*, 471.
8 Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* **2003**, *15*, 353.
9 S. Deki, Y. Aoi, O. Hiroi, A. Kajinami, *Chem. Lett.* **1996**, 433.
10 S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin, M. Grätzel, *Thin Solid Films* **2008**, *516*, 4613.