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Nanoporous tin oxide photoelectrode prepared by electrochemical anodization in aqueous ammonia to improve performance of dye sensitized solar cell

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In this work, a nanoporous thin film consisting of sieve-like tin oxide (SnO₂) sheets was prepared by anodization of tin foil in aqueous ammonia and applied as a photoelectrode for dye-sensitized solar cell (DSSC). Compared to the conventional SnO₂ nanoparticle-based photoelectrode, the anodized nanoporous SnO₂ electrode offers higher short circuit current (6.85 vs. 3.64 mA/cm²) and open circuit voltage (0.56 vs. 0.51 V) due to better charge transportation and better suppression of charge recombination. Consequently, the power conversion efficiency of the DSSC equipped with the anodized SnO₂ electrode is enhanced by 63%. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4798316>]

I. INTRODUCTION

Dye-sensitized solar cell (DSSC) has been intensively researched over the last few decades due to its low fabrication cost and potential high power conversion efficiency.^{1–3} Currently, most DSSCs use TiO₂ nanoparticle based photoanodes which could achieve relatively high power conversion efficiency. Recently, n-type tin oxide (SnO₂) has attracted great interest as the photoelectrode material in DSSC owes its favorable properties over TiO₂ such as wider bandgap (3.5 vs. 3.0 eV) and higher electron mobility (>100 vs. ~1 cm² V⁻¹ s⁻¹).⁴ Wider bandgap reduces the internal recombination between injected electrons with holes in the valence band, and reduces light adsorption (particularly in UV region) which, in turn, increases the light adsorption by loaded dye molecules and long-term stability of the electrode. And higher electron mobility enhances transport of injected electrons and suppresses their internal recombination. In most DSSCs, the photoelectrode uses fluorine doped tin oxide (FTO) as the supporting substrate because of its high transparency, excellent conductivity, and tolerance to high temperature. SnO₂ can compatibly interface with FTO to ensure good adhesion and small interfacial resistance.

However, current SnO₂ nanoparticle-based DSSCs exhibit lower open circuit voltage (V_{oc}, typically between 0.3–0.4 V) due to poor interconnectivity between particles that results in high recombination losses and low fill factor (FF),^{5–9} as compared to the conventional TiO₂-based DSSCs (0.7–0.8 V). Such small V_{oc} is attributed to the lower conduction band edge E_c of SnO₂ (by ~0.3 eV) than that of anatase TiO₂.¹⁰ SnO₂ also has a low charge recombination resistance which ensures fast backflow of photoelectrons to the electrolyte and a negative shift

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of the electron quasi-Fermi level (E_{F-n}), leading to further reduction of V_{oc} .¹¹ To overcome these issues, this study develops a photoelectrode based on sieve-like SnO_2 nanoporous sheets formed through anodization of tin foil in aqueous ammonia solution. Similar to the recent application of orderly one-dimensional SnO_2 nanostructures such as nanowires and nanotubes,^{12,13} the well-interconnected SnO_2 sieve walls were found to achieve better charge transportation to suppress charge recombination events. As a result, DSSC with anodized sieve-like SnO_2 sheet (ASnO_2) based photoelectrode achieves higher V_{oc} (0.61 V) than that based on SnO_2 nanoparticles (0.51 V) with TiCl_4 treatment. The closely packed pore arrangement of the metal oxide sheets also provides higher charge injection rate, which in turn leads to better photocurrent and enhanced device performance.

II. EXPERIMENTAL PROCEDURES

A. Synthesis of anodized SnO_2

High purity of tin foils (0.126 mm thick, 99.9% purity, Sigma-Aldrich) with dimensions of $2\text{ cm} \times 1\text{ cm}$ were cleaned in ethanol and deionized (DI) water under sonication before it was being used as the working electrode in anodization. Platinum foil with the same dimensions was used as the counter electrode. At room temperature, a constant voltage (60 V) was applied to the electrodes in an electrolyte of 0.5 M NH_4OH (Sigma-Aldrich) for 45 min of anodization. As prepared ASnO_2 on tin foil was immersed into DI water and put under sonication for 10 min to detach nanoporous tin oxide from tin substrate. This was repeated for several times to obtain significant amount of nanoporous tin oxide. Nanoporous tin oxide suspended in DI water was then tip-sonicated for 30 times with 2 s sonication and 2 s pause. The solution was filtered using membrane filter with pore size of $0.22\text{ }\mu\text{m}$ and then dried at $70\text{ }^\circ\text{C}$.

B. Synthesis of SnO_2 nanoparticle

Over 1.2 g of anhydrous SnCl_2 (Sigma-Aldrich, 99.9%) was added into 60 ml of distilled water with stirring, and formation of white precipitate was observed. Subsequently, 1 ml of 40% HCl was added to dissolve the precipitate. The solution was then refluxed at $90\text{ }^\circ\text{C}$ for 5 h under continuous stirring. During the reaction, the solution gradually turned opaque. After synthesis, SnO_2 nanoparticles were collected by centrifugation and rinsed with DI water and ethanol, followed by drying at $70\text{ }^\circ\text{C}$ in air.

C. Electrode preparation and DSSC fabrication.

ASnO_2 or SnO_2 nanoparticle powder was made into paste, following the standard procedure for making TiO_2 paste for DSSCs.¹⁴ The photoelectrode was made by blading the paste on the conductive substrate (FTO glass), with an active area of 0.12 cm^2 . The electrode was annealed at $450\text{ }^\circ\text{C}$ for 1 h to obtain higher crystallinity, followed by immersion into TiCl_4 solution (20 mM) for 30 min at $70\text{ }^\circ\text{C}$. It was subsequently sintered at $450\text{ }^\circ\text{C}$ for 30 min in air. Finally, the photoelectrode was soaked in a mixture solution of equal amount of tert-butanol and acetonitrile containing 0.5 mM N719 dye for 16 h at room temperature and then washed with ethanol. Platinum sputtered FTO was used as the counter electrode. 50 mM tri-iodide in acetonitrile (AN-50, Solaronix) was used as the low viscosity electrolyte.

D. Characterizations

The crystallinity of the nanostructures were investigated using Siemens D5008 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) at 40 kV and 40 mA, scanning from $2\theta = 20^\circ$ to 70° with a scan rate of 2° per minute. The morphology was observed using field emission scanning electron microscopy (FESEM, JEOL JSM-6700). UV-vis absorbance spectra were measured by Shimadzu 3600 UV-vis spectrophotometers. Infrared analysis of the samples was performed on Perkin Elmer Spectrum GX Fourier transform infrared (FTIR) spectrometer. The deposited films were scraped off as powders from the substrate and mixed with potassium

bromide powders as the reference for FTIR analysis. The amount of adsorbed dye was determined by desorbing the dye into 20 mM NaOH solution with equal amount of deionized water and ethanol and subsequent measurement of the absorption peak intensity of N719 at 500 nm. The current-voltage tests of DSSCs were performed under one sun condition using a solar light simulator (Abet Technologies S2000 with 550 W xenon lamp and an AM 1.5 filter, 100 mW/cm²). Electrochemical impedance spectroscopy (EIS) was performed under illumination of solar light simulator and the cell was biased at the V_{OC} induced by the illumination with the frequency range of 0.1 Hz to 0.1 MHz. Spectra of the monochromatic incident photon-to-current conversion efficiencies (IPCEs) for the solar cells were measured with IPCE measurement kit from Newport and it was calibrated using a silicon reference photodiode. Brunauer–Emmett–Teller (BET) specific surface areas of the samples were determined by measuring nitrogen adsorption-desorption isotherms using a Quantachrome NOVA-3000 system.

III. RESULTS AND DISCUSSION

A. Material characterization

Fig. 1(a) shows the scanning electron microscopy (SEM) image (top view) of the $ASnO_2$ sheets formed after anodization of a tin foil at 60 V. Unlike TiO_2 nanotube array obtained from anodization of titanium foil,¹⁵ $ASnO_2$ has a sieve-like nanoporous structure with an average pore size ~ 40 nm, which is in good agreement with the previously reported works.^{16–19} Fig. 1(b) depicts the cross-section of $ASnO_2$, in which multiple sheets of sieve-like $ASnO_2$ are formed during the anodization process due to internal cracking of the anodized oxide caused by gases generated from hydrolysis of water.¹⁷ The thickness of each $ASnO_2$ sheet is ~ 150 nm. $ASnO_2$ sheets were harvested from the tin substrate by sonication and made into paste in order to be coated on the photoelectrode as a thin-film. As revealed by SEM (Fig. 1(c)), the $ASnO_2$ sheets on photoelectrode form aggregates while retaining its nanoporous structure to pose a large surface area. SnO_2 nanoparticles (~ 100 nm in diameter) (Fig. 1(d)) were also synthesized as the comparison material for photoelectrodes.

As shown in Fig. 2(a), X-ray diffraction (XRD) spectrum of $ASnO_2$ exhibits prominent diffraction angles at 26.5° , 34° , and 52° , corresponding well to the tetragonal SnO_2 (JCPDS,

FIG. 1. SEM images of (a) $ASnO_2$ sheet (top view), (b) $ASnO_2$ sheets (cross-section), (c) $ASnO_2$ coated on photoelectrode, (d) SnO_2 nanoparticles.

FIG. 2. (a) XRD spectrum, (b) infrared spectrum, (c) UV-vis absorbance spectra, and (d) optical bandgap calculation of ASnO_2 annealed at 450°C .

41-1445). The presence of such sharp peaks signifies that the ASnO_2 sheets exhibit high crystallinity with the grain size of 4.8 nm, as estimated by Scherer's formula: $D = K\lambda/(\beta\cos\theta)$, where D is the grain size, K is Scherer constant (usually taken as 0.94), and β is the full-width-at-half-maximum (FWHM) for the peak centered at 0.463 radians.²⁰ In the spectrum of FTIR spectroscopy shown in Fig. 2(b), the vibration absorption peak of the Sn-O bond in SnO_2 is detected at 593 cm^{-1} ,²¹ while that of Sn-OH bond is absent at 530 cm^{-1} . This confirms that ASnO_2 consists only of the stannic oxide and not a mixture of both oxide and hydroxide. The stretching adsorption peak of O-H is located at 3390 cm^{-1} while the peak at 1640 cm^{-1} could be attributed to the adsorption of moisture on the metal oxide. ASnO_2 was also found to have a strong light adsorption at 394 nm, which indicates an optical bandgap of 3.15 eV (Fig. 3(c)). This bandgap is slightly lower than that of reported 3.6 eV.²²

FIG. 3. Photocurrent density-voltage curves measured under simulated sunlight power of 100 mW cm^{-2} (a) and dark currents (b) of the DSSCs equipped with ASnO_2 or SnO_2 nanoparticles based photoelectrode.

TABLE I. Photovoltaic parameters (mean $\pm$ standard deviation from 5 samples) for DSSCs with ASnO_2 photoelectrodes (film thickness = 5, 8, 10, or 13 μm) or SnO_2 nanoparticle photoelectrode (film thickness = 8 μm).

Film	Specific surface area (m^2/g)	Dye loading ($\times 10^{-7} \text{ mol}/\text{cm}^2$)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
8 μm SnO_2 nanoparticles	166.7	0.45 ± 0.05	0.51 ± 0.00	3.64 ± 0.05	55.0 ± 2.4	1.02 ± 0.02
5 μm ASnO_2	72.5	0.10 ± 0.02	0.61 ± 0.01	4.44 ± 0.11	47.5 ± 1.7	1.29 ± 0.03
8 μm ASnO_2	-	0.36 ± 0.04	0.56 ± 0.02	6.85 ± 0.25	43.2 ± 1.8	1.66 ± 0.04
10 μm ASnO_2	-	0.63 ± 0.05	0.53 ± 0.00	7.60 ± 0.07	40.0 ± 1.6	1.71 ± 0.02
13 μm ASnO_2	-	1.04 ± 0.14	0.48 ± 0.01	7.30 ± 0.05	33.4 ± 1.1	1.14 ± 0.01

B. DSSC performance

Fig. 3(a) shows the characteristic current density-voltage (J-V) curves of DSSCs based on TiCl_4 -treated ASnO_2 photoelectrodes with different film thickness. Their corresponding photovoltaic parameters are summarized in Table I. The commonly used DSSCs based on TiCl_4 -treated SnO_2 -nanoparticle-coated photoelectrodes were also prepared as a comparison (control). As shown in Table I, with identical film thickness (8 μm), the ASnO_2 photoelectrode significantly outperforms the SnO_2 nanoparticle electrode in terms of short-circuit photocurrent density (J_{sc} : 6.85 vs. 3.64 mA/cm^2) and open circuit voltage (V_{oc} : 0.56 vs. 0.51 V). While the thickness of ASnO_2 film increasing from 5 μm to 10 μm , the dye loading increases from 0.10 to $0.63 \times 10^{-7} \text{ mol}/\text{cm}^2$ and the photocurrent is improved from 4.44 to 7.60 mA/cm^2 . Although both V_{oc} and FF decrease with thicker oxide film, the large enhancement in photocurrent leads to significant improvement in the overall power conversion efficiency (PCE) (from 1.29% with 5 μm film to 1.71% with 10 μm film).

Interestingly, although the 8 μm thick ASnO_2 photoelectrode has lower dye loading (due to smaller specific surface area) as compared to the SnO_2 nanoparticle based photoelectrode of the same film thickness (Table I), its performance is superior. The PCE improves with increasing film thickness from 5–10 μm because of increased dye loading (thus short-circuit current). But further increase of film thickness to 13 μm leads to drastic reduction of PCE mainly due to large decrease of open-circuit voltage and fill factor. To better understand the enhancement mechanism for ASnO_2 based DSSC, the dark currents were measured (Fig. 3(b)). Since the dark current of a DSSC represents the backflow of electrons from the photoelectrode to the redox electrolyte,^{23,24} the higher onset potential of ASnO_2 electrode suggests that it has a lower charge recombination rate as compared to SnO_2 nanoparticle electrode. It is also noted from Fig. 3(b) that the recombination rate undesirably increases with the increasing thickness of ASnO_2 film, as evidenced by the decreasing onset potential. This explains the drop of V_{oc} and FF with a thicker film. The better performance of ASnO_2 over SnO_2 nanoparticle is also attributable to the enhanced IPCE at 550 nm (absorption peak of N719 dye), as demonstrated in Fig. 4. Similar to PCE, the optimal IPCE obtained with 8 or 10 μm ASnO_2 film decreases when the film thickness is thinned (to 5 μm) or thickened (to 13 μm).

To further investigate the effects of increasing ASnO_2 thickness on charge recombination, open-circuit voltage-decay (OCVD) technique was employed in which the decrease in V_{oc} is continuously monitored while turning off the light shone on the device (Fig. 5(a)). The electron lifetime is given by $\tau_n = -(kT/e)(dV_{\text{oc}}/dt)^{-1}$, where kT is the thermal energy, e is the positive elementary charge, and dV_{oc}/dt is the decaying rate of V_{oc} .²⁵ As shown in Fig. 5(b), a thicker ASnO_2 photoelectrode has a shorter electron life time, which implies a higher charge recombination rate.²⁶ The dependence of τ_n on V_{oc} is linear, indicating the absence of surface traps which could cause recombination of electrons with the redox electrolyte through tunneling.²⁷

EIS measurements were also employed to provide further understanding of charge transport and transfer properties of the ASnO_2 based DSSC.^{28–32} Fig. 6(a) shows the Nyquist plots of DSSCs with SnO_2 nanoparticle electrode and ASnO_2 electrode with different film thickness,

FIG. 4. IPCE spectra of DSSCs based on ASnO₂ and SnO₂ nanoparticle electrodes.

measured under 100 mWcm^{-2} light illumination. In each plot, the smaller (preceding) semi-circle at the high-frequency region represents the redox reaction of I^-/I_3^- at the Pt(counter electrode)/electrolyte interface (enlarged view shown in Fig. 6(b))^{30,33} while the larger semicircle at the low-frequency region is ascribed to the combined effect of charge transfer and/or recombination across the oxide/dye/redox electrolyte interface.^{28,34–36} The equivalent circuit of the DSSC device is depicted in Fig. 6(b) (inset), where R_s is the series resistance; R_1 and R_{pt} represent the interfacial charge transfer resistances at the photoelectrode and counter electrode, respectively. The fitted values of R_s , R_1 , and R_{pt} are summarized in Table II. As shown, R_1 ($162.6 \, \Omega$) of the ASnO₂ photoelectrode ($8 \, \mu\text{m}$ thick film) is much smaller than that of the SnO₂ nanoparticle based electrode of the same film thickness ($366.9 \, \Omega$). Such reduction in the interfacial charge transfer resistance implies a faster electron injection rate; therefore, an improved photocurrent. This is likely attributed to the interconnected sieve-like structure of ASnO₂ which provides a large porous and conductive surface for rapid transfer of electrons from photo-excited dye molecules. When the thickness of the ASnO₂ film is increased to $10 \, \mu\text{m}$, R_1 is further reduced to $87.1 \, \Omega$ which in turn contributes to the even better device performance. However, further increase of ASnO₂ film thickness to $13 \, \mu\text{m}$ causes dramatic increase of R_1 (to $202.8 \, \Omega$), therefore, largely compromised conversion efficiency. High interfacial charge transfer resistance of a thick film is likely resulted from high charge recombination (Figs. 3(b) and 5) and hindered filtration of electrolytes.

FIG. 5. OCVD curves (a) and electron lifetime as a function of V_{oc} (b) for DSSCs using ASnO₂ photoelectrodes with different film thicknesses.

FIG. 6. Nyquist plots (a) and their zoom-in views in high-frequency region (b) of the ASnO₂ and SnO₂ nanoparticles based DSSCs.

TABLE II. The series resistance (R_s) and interfacial charge transfer resistance (R_1 at photoelectrode and R_{pt} at counter electrode).

	R_s/Ω	R_1/Ω	R_{pt}/Ω
8 μm SnO ₂ nanoparticles	35.26	366.9	5.20
5 μm ASnO ₂	31.16	201.9	1.85
8 μm ASnO ₂	33.05	162.6	2.02
10 μm ASnO ₂	37.64	87.1	5.58
13 μm ASnO ₂	43.45	202.8	12.9

IV. CONCLUSION

In summary, nanoporous sieve-like SnO₂ sheets were synthesized by anodization in aqueous ammonia solution (ASnO₂). DSSCs equipped with ASnO₂ based photoelectrode were found to outperform DSSCs using SnO₂ nanoparticle based photoelectrode of the same film thickness (8 μm), in terms of open circuit voltage (0.56 vs. 0.51 V), short circuit current (6.85 vs. 3.64 mA/cm²), and power conversion efficiency (1.66% vs. 1.02%). The enhancement is attributed to suppressed charge recombination and reduced charge transfer resistance. We demonstrate that the highest conversion efficiency of 1.71% is achieved with 10 μm film of ASnO₂ as the result of optimal balance between dye loading (thus charge injection), charge recombination, and electrolyte penetration. In this study, N719 dye commonly used for TiO₂ based DSSCs is employed. The performance of our ASnO₂ based DSSC may be further improved by using other dyes that can interact better with SnO₂ (e.g., indoline dyes³⁷). This study corroborates the potentials of SnO₂ in the solar cell applications and suggests that the performance of SnO₂ based DSSCs could be improved by engineering the interconnectivity of SnO₂ structure.

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¹G. H. Guai, M. Y. Lei, C. M. Ng, and C. M. Li, *Adv. Energy Mater.* **2**, 334 (2012).

²G. H. Guai, Y. Li, C. M. Ng, C. M. Li, and M. B. Chan-Park, *ChemPhysChem* **13**, 2566 (2012).

³B. O'Regan and M. Gratzel, *Nature* **353**, 737 (1991).

⁴M. S. Arnold, P. Avouris, Z. W. Pan, and Z. L. Wang, *J. Phys. Chem. B* **107**, 659 (2003).

⁵S. Chappel and A. Zaban, *Sol. Energy Mater. Sol. Cells* **71**, 141 (2002).

⁶Y. Fukai, Y. Kondo, S. Mori, and E. Suzuki, *Electrochem. Commun.* **9**, 1439 (2007).

⁷N. Nang Dinh, M.-C. Bernard, A. Hugot-Le Goff, T. Stergiopoulos, and P. Falaras, *C. R. Chim.* **9**, 676 (2006).

⁸K. Sayama, H. Sugihara, and H. Arakawa, *Chem. Mater.* **10**, 3825 (1998).

- ⁹K. Zhu, N. R. Neale, A. Miedaner, and A. J. Frank, *Nano Lett.* **7**, 69 (2007).
- ¹⁰A. N. M. Green, E. Palomares, S. A. Haque, J. M. Kroon, and J. R. Durrant, *J. Phys. Chem. B* **109**, 12525 (2005).
- ¹¹A. J. Nozik and R. Memming, *J. Phys. Chem.* **100**, 13061 (1996).
- ¹²C. Gao, X. Li, B. Lu, L. Chen, Y. Wang, F. Teng, J. Wang, Z. Zhang, X. Pan, and E. Xie, *Nanoscale* **4**, 3475 (2012).
- ¹³S. Gubbala, H. B. Russell, H. Shah, B. Deb, J. Jasinski, H. Rypkema, and M. K. Sunkara, *Energy Environ. Sci.* **2**, 1302 (2009).
- ¹⁴S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy, and M. Grätzel, *Prog. Photovoltaics* **15**, 603 (2007).
- ¹⁵Y.-L. Xie, Z.-X. Li, H. Xu, K.-F. Xie, Z.-G. Xu, and H.-L. Zhang, *Electrochem. Commun.* **17**, 34 (2012).
- ¹⁶S. Feng, Y. Tang, and T. Xiao, *J. Phys. Chem. C* **113**, 4809 (2009).
- ¹⁷J.-W. Lee, S.-J. Park, W.-S. Choi, and H.-C. Shin, *Electrochim. Acta* **56**, 5919 (2011).
- ¹⁸H. C. Shin, J. Dong, and M. Liu, *Adv. Mater.* **16**, 237 (2004).
- ¹⁹M. Wang, Y. Liu, D. Xue, D. Zhang, and H. Yang, *Electrochim. Acta* **56**, 8797 (2011).
- ²⁰L. V. Azároff, *Elements of X-ray Crystallography* (McGraw-Hill, New York, 1968), p. 552.
- ²¹D. L. Perry, *Handbook of Inorganic Compounds* (CRC Press, New York, 1995), p. 4170.
- ²²G. E. Patil, D. D. Kajale, V. B. Gaikwad, and G. H. Jain, *Int. Nano Lett.* **2**, 17 (2012).
- ²³B. C. O'Regan, I. López-Duarte, M. V. Martínez-Díaz, A. Forneli, J. Albero, A. Morandeira, E. Palomares, T. Torres, and J. R. Durrant, *J. Am. Chem. Soc.* **130**, 2906 (2008).
- ²⁴K. E. Splan, A. M. Massari, and J. T. Hupp, *J. Phys. Chem. B* **108**, 4111 (2004).
- ²⁵P. S. Archana, R. Jose, C. Vijila, and S. Ramakrishna, *J. Phys. Chem. C* **113**, 21538 (2009).
- ²⁶J. Bisquert, F. Fabregat-Santiago, I. Mora-Seroó, G. García-Belmonte, and S. Giménez, *J. Phys. Chem. C* **113**, 17278 (2009).
- ²⁷J. Bisquert, A. Zaban, M. Greenshtein, and I. Mora-Seró, *J. Am. Chem. Soc.* **126**, 13550 (2004).
- ²⁸M. C. Bernard, H. Cachet, P. Falaras, A. H.-L. Goff, M. Kalbac, I. Lukes, N. T. Oanh, T. Stergiopoulos, and I. Arabatzis, *J. Electrochem. Soc.* **150**, E155 (2003).
- ²⁹J. Bisquert, *J. Phys. Chem. B* **106**, 325 (2002).
- ³⁰C.-P. Hsu, K.-M. Lee, J. T.-W. Huang, C.-Y. Lin, C.-H. Lee, L.-P. Wang, S.-Y. Tsai, and K.-C. Ho, *Electrochim. Acta* **53**, 7514 (2008).
- ³¹C. Longo, J. Freitas, and M.-A. De Paoli, *J. Photochem. Photobiol., A* **159**, 33 (2003).
- ³²Q. Wang, S. Ito, M. Grätzel, F. Fabregat-Santiago, I. Mora-Seró, J. Bisquert, T. Bessho, and H. Imai, *J. Phys. Chem. B* **110**, 25210 (2006).
- ³³S. Lee, J. H. Noh, H. S. Han, D. K. Yim, D. H. Kim, J.-K. Lee, J. Y. Kim, H. S. Jung, and K. S. Hong, *J. Phys. Chem. C* **113**, 6878 (2009).
- ³⁴N. Fuke, A. Fukui, R. Komiya, A. Islam, Y. Chiba, M. Yanagida, R. Yamanaka, and L. Han, *Chem. Mater.* **20**, 4974 (2008).
- ³⁵N. Papageorgiou, W. F. Maier, and M. Grätzel, *J. Electrochem. Soc.* **144**, 876 (1997).
- ³⁶Q. Wang, J.-E. Moser, and M. Grätzel, *J. Phys. Chem. B* **109**, 14945 (2005).
- ³⁷B. K. Onwona-Agyeman, S. Kaneko, A. Kumara, M. Okuya, K. Murakami, and A. Konno, *Jpn. J. Appl. Phys., Part 2* **44**, L731 (2005).