Enhanced Photovoltaic Properties of SiO_2-treated ZnO Nanocrystalline Electrode for Dye-sensitized Solar Cell

Yu-Ju Shin,*[1] Jung-Hun Lee,[1] Ji-Hye Park,[1] and Nam-Gyu Park*[2]
[1]*Department of Chemistry, the Catholic University of Korea, Bucheon, Kyeonggi-Do 420-743, Korea*
[2]*Materials Science and Technology Division, Korean Institute of Science and Technology, Seoul 136-791, Korea*

(Received July 20, 2007; CL-070769; E-mail: yujushin@catholic.ac.kr)

SiO_2-coated ZnO nanocrystalline electrode for dye-sensitized solar cell (DSSC) showed greatly enhanced solar energy conversion efficiency up to 5.2% under AM 1.5 global one sun condition, because of the increased surface stability to acidic dye molecules.

Semiconducting material ZnO with a band gap of 3.3 eV has attracted much attention for the alternative nanocrystalline electrode materials to conventional TiO_2 in DSSC.[1] In addition, various simple fabrication methods for ZnO nanostructures make ZnO attractive for DSSC application.[2,3] Despite similar electronic band structure to TiO_2, however, ZnO-based DSSCs have shown very poor solar energy conversion efficiency (η), below 1% under one sun illumination condition,[4,5] though 5.0% has been achieved using large ZnO particles of 150 nm under weak illumination condition (10 mW/cm^2).[6] Recently, nanostructured ZnO electrodes showed significantly increased efficiencies, 1.5% for nanorod array electrodes,[7] 2.4% for organic dye-sensitized electrode,[8] 3.8–4.1% for 3D network electrodes[9] by improving the surface state or interconnection between particles. Such low photovoltaic features of ZnO are mainly due to the unstable ZnO surface to acidic dye molecules, resulting in the partial dissolution of ZnO by acidic dye to form Zn^{2+}–dye aggregates, which occupy the mesopores of electrode matrix to reduce light-harvesting efficiency and diffusion of electrolyte.[6] The idea of this work lies on the surface modification of ZnO nanoparticles by SiO_2 coating to increase the stability to acid thus to suppress the formation of Zn^{2+}–dye aggregates. We report here the effects of SiO_2 coating on the photovoltaic properties of ZnO electrode in DSSC.

Ethanolic ZnO colloid was prepared by following the method of Spanhel and Anderson with some modification.[10] After preparing transparent ZnO sol from the reaction of zinc acetate and $LiOH{\cdot}H_2O$ at 0 °C, the sol was stored at room temperature for 7 days to get homogeneous nanoparticles, which was finally recovered after washing with ethanol. ZnO content was then controlled to 12 wt % by evaporating ethanol. Surface coating was carried out by adding tetramethylorthosilicate (TMOS) with mole ratios Si/Zn ranged at 0–0.5 and stirring the colloids for 24 h very vigorously. With mild stirring, it was found that Si components tended to aggregate to form a separate SiO_2 phase and surface coating could not be properly carried out. In order to fabricate viscous pastes, 4.8 wt % of hydroxyl-propyl-cellulose (MW: 80,000) was added to SiO_2-coated ZnO colloids and stirred for 24 h. SiO_2-coated ZnO electrodes were prepared by casting the paste on SnO_2:F conducting glass (TEC8, Pilkington) by a doctor blade method. Wet films were heated at 450 °C for 30 min. The film thickness of electrodes was found 3.8–4.5 µm. To get thick films, the coating process was repeated 2–3 times for Si/Zn = 0.20 (SZ20).

To compare the stability of electrode surface to acid, Zn^{2+} extraction from Si-modified ZnO electrodes (area = 1 cm^2) was performed by dipping them in 10 mM aqueous solution of acetic acid (50 mL). The concentration of dissolved Zn^{2+} ion was monitored as a function of dipping time. Sensitization was made by dipping the electrodes into 0.5 mM ethanolic solution of ruthenium dye $Ru[dcbpy(TBA)_2]_2(NCS)_2$ (N719) for 2 h at 60 °C. The amount of adsorbed dye on raw ZnO powder, bare ZnO (BZ) and SiO_2-coated ZnO (SZ20) was measured by UV–vis absorption of the desorbed dye from electrodes with 10 mM NaOH solution.

DSSCs were fabricated by a conventional method using Pt-coated counter electrode,[11] The redox electrolyte solution consisted of 0.6 M 1-hexyl-2,3-dimethylimidazolium iodide (C6DMI), 0.2 M LiI, 0.04 M I_2, and 0.5 M *tert*-butylpyridine (TBP) in 3-methoxypropionitrile/acetonitrile (1:1 v/v). The electrode area was controlled around 0.20 cm^2 and the photovoltaic properties were measured under AM 1.5 global-one sun condition (100 mW/cm^2).

FE-SEM photographs of raw ZnO powder, BZ and SZ electrodes are shown in Figure 1. Heat treatment at 450 °C on raw ZnO with 5 nm (a) increased the particle size up to 20 nm (b), whereas SiO_2-coated ZnO particles did not grow at 450 °C (c). It indicates that SiO_2 components on the surface prevent the thermal interfusion of ZnO particles. When Si/Zn = 0.5, ZnO particles are completely wrapped up by SiO_2 and the excess SiO_2 component appeared to cover the mesopores of electrode, as reflected in (d). XRD results confirmed that SZ is of a single phase for Si/Zn < 0.5, and then SiO_2 component was detected at Si/Zn = 0.5.[12]

Figure 2 shows SiO_2 coating was effective to increase the surface stability of ZnO electrode to acid. For Si/Zn $\geq$ 0.10,

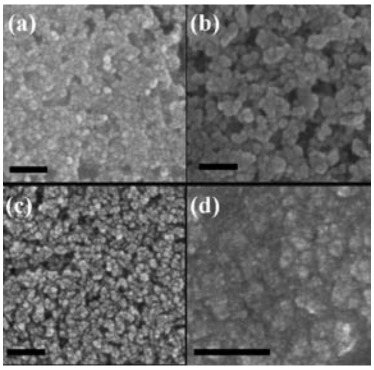

Figure 1. FE-SEM pictures of raw ZnO powder (a), BZ electrode (b), SZ electrode where Si/Zn = 0.2 (c) and 0.5 (d). The scale bar is 100 nm.

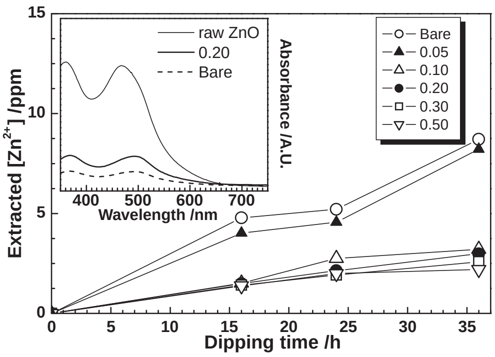

Figure 2. Zn^{2+} extraction from the raw ZnO (powder deposited on the substrate with no sintering), BZ and SZ20 (area = 1 cm^2). Inset shows the amount of adsorbed dye molecules on raw ZnO, BZ, and SZ.

the dissolution of ZnO was considerably suppressed in our experimental condition. This suggests that the surface network (Zn, Si)–O is greatly reinforced compared to the simple Zn–O one owing to the strong interaction between Si^{4+} and O^{2-} ions. The same preference of Si^{4+} with Zn^{2+} for the tetrahedral site seems to make the SiO_2 coating highly effective to increase surface stability. Consequently, Zn^{2+}–dye aggregates should be greatly reduced, and thus the dye molecules are now adequately adsorbed on the electrode surface. The amounts of adsorbed dye of BZ and SZ electrodes were compared by UV–vis absorption method (inset in Figure 2). Compared with raw ZnO powder, SZ electrode showed largely decreased dye adsorption. This strongly implies that Zn^{2+}–dye aggregates are considerably diminished, owing to the increased resistance of electrode surface to acid, though a precise comparison is not possible because of partial sintering of SZ. The moderate increase of adsorption of SZ with respect to BZ can be attributed to the smaller particle size (5 nm) than that of BZ (20 nm).

As Si/Zn increases, photovoltaic performance becomes better till Si/Zn reaches 0.20 and then decreases rapidly. Photovoltaic properties of BZ and SZ20 electrodes are shown in Figure 3 and listed in Table 1. They neatly show that SiO_2 coating remarkably increases the photovoltaic properties of ZnO electrode. Light-harvest efficiency (IPCE) at 520 nm increased from 0.15 (BZ) to 0.47 (SZ20; 4.2 µm) and J_{sc} from 1.02 up to 7.66 mA/cm^2. Considering the slight increase of adsorbed dye of SZ20 from BZ, the observed large enhancement of IPCE in SZ20 suggests that Zn^{2+}–dye aggregates are considerably diminished, leading to the improvement of light-harvesting process in SZ20. SiO_2 coating also seems very effective to reduce the recombination, for J_{sc} increased more largely than expected from the moderate enhancement of IPCE. Considering that the electron diffusion increases and recombination diminishes with the particle size,[13] the high efficiency achieved with very small particles of SiO_2-coated ZnO strongly implies that the surface states of photoanode were greatly diminished. With the thick film (SZ20; 13 µm), the maximum conversion efficiency was found as high as 5.2% (SZ20; 13 µm), which would be, as far as we know, the highest efficiency obtained with ZnO–DSSC under one sun illumination condition.

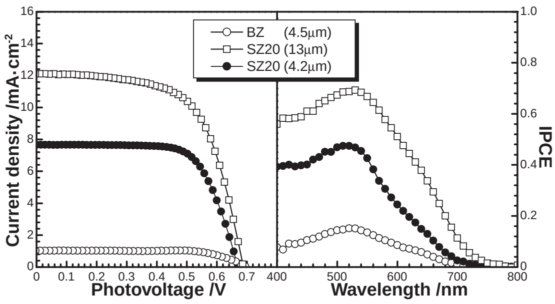

Figure 3. *I*–*V* curves and IPCE spectra of BZ and SZ (Si/Zn = 0.20)–DSSCs.

Table 1. PV properties of SiO_2-coated ZnO electrodes for DSSC

Electrodes (thickness)[a]	J_{sc} /mA cm^{-2}	V_{oc}/V	Fill factor	η/%
BZ (4.0 µm)	1.02	0.694	0.73	0.52
SZ20 (4.2 µm)	7.66	0.670	0.69	3.6
SZ20 (13 µm)	12.10	0.686	0.63	5.2

[a] Surface area of electrodes was controlled around 0.20 cm^2.

In summary, SiO_2 coating was found very effective to improve the surface properties of ZnO both in chemical stability and electronic surface state by reinforcing the surface network and also by decreasing the surface traps.

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References and Notes

1 B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.
2 J. Joo, S. G. Kwon, J. H. Yu, T. Hyeon, *Adv. Mater.* **2005**, *17*, 1873.
3 L. E. Greene, M. Law, D. H. Tan, M. Mantano, J. Goldberger, G. Somorjai, P. Yang, *Nano Lett.* **2005**, *5*, 1231.
4 G. Redmond, D. Fitzmaurize, M. Grätzel, *Chem. Mater.* **1994**, *6*, 686.
5 I. Bedja, P. V. Kamat, X. Hua, A. G. Lappin, S. Hotchandani, *Langmuir* **1997**, *13*, 2398.
6 K. Keis, C. Bauer, G. Boschloo, A. Hagfeldt, K. Westermark, H. Rensmo, H. Siegbahn, *J. Photochem. Photobiol., A* **2002**, *148*, 57.
7 M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. Yang, *Nat. Mater.* **2005**, *4*, 455.
8 W.-J. Lee, H. Okada, A. Wakahara, A. Yoshida, *Ceram. Int.* **2006**, *32*, 495.
9 X. Liu, Y. Luo, H. Li, Y. Fan, Z. Yu, Y. Lin, L. Chen, Q. Meng, *Chem. Commun.* **2007**, 2847; K. Kakiuchi, E. Hosono, S. Fujuhara, *J. Photochem. Photobiol., A* **2006**, *179*, 81.
10 L. Spanhel, M. Anderson, *J. Am. Chem. Soc.* **1991**, *113*, 2826; E. A. Meulenkamp, *J. Phys. Chem. B* **1998**, *102*, 5566.
11 N.-G. Park, M. G. Kang, K. S. Ryu, K. M. Kim, S. H. Chang, *J. Photochem. Photobiol., A* **2004**, *161*, 105.
12 XRD results showed that the particle size is about 4.5–6 nm for Si/Zn ratios of 0.1–0.5, and additional small peaks of SiO_2 component appeared in Si/Zn = 0.5 (Supporting Information). Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
13 S. Nakade, Y. Saito, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Phys. Chem. B* **2003**, *107*, 8607.

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