Proceedings of the 5th International Conference on Nanostructures (ICNS5)
6-9 March 2014, Kish Island, Iran

Low temperature dye-sensitized solar cells based on conformal thin zinc oxide overlayer on mesoporous insulating template by atomic layer deposition

Mojtaba Abdi-Jalebi[a], Aravind Kumar Chandiran[b], Mohammad. K. Nazeeruddin[b*], and Michael Grätzel[b*]

[a] Department of Materials Science and Engineering, Swiss Federal Institute of Technology (EPFL), Lausanne, CH1015, Switzerland
[b] Institute of Chemical Sciences and Engineering, Swiss Federal Institute of Technology (EPFL), Lausanne, CH1015, Switzerland
* mdkhaja.nazeeruddin@epfl.ch, michael.graetzel@epfl.ch

Abstract: Low temperature processing of dye-sensitized solar cells (DSCs) is essential to enable commercialization with low cost plastic substrates and diminish the overall manufacturing cost.We report a low temperature processing route for photoanodes where thin ZnO nanoshell is deposited by atomic layer deposition at 150°C, on a mesoporous insulating template. We found that a 6 nm ZnO overlayer on a 3 µm mesoporous nanoparticle Al_2O_3 template shows a power conversion efficiency of 4.2 % with the standard organic sensitizer (coded Y123) and cobalt bipyridine redox mediator.

Keywords: Dye-sensitized solar cell, zinc oxide, atomic layer deposition, mesoporous template

Introduction

Dye sensitized solar cells (DSC) based on wide bandgap mesoscopic oxide semiconductor film and organic dye or metallo-organic complex dye is one of the most promising molecular photovoltaics as a flexible and cost-effective alternative to the p-n junction solar cells [1, 2]. ZnO has been explored as a promising alternative photoanode material for DSSCs since the inception of research on TiO_2-based DSSCs; this trend is to be attributed to the facts that TiO_2 and ZnO have similar electron affinities and almost the same band gap energies, i.e., ~3.2 eV and ~3.3 eV, respectively, and ZnO has much higher electron diffusivity than that of TiO_2 [3]. However, the best efficiency for DSC based on hierarchical aggregates ZnO up to now was achieved by Memarianet.al [4] who obtained 7.5% which is around half of the record efficiency for TiO_2.

In the context of nanoarchitecture, ZnO in several morphologies such as single crystal nanowires [5], nanosheet [6] and nanoforest [7] has been successfully implemented as photoanodes for DSC. Although the transport rate of electrons enhanced significantly in these structures, the lower available surface area for the effective dye loading in 1D structures and experimental complications of 3D structures, wherein the small nanowire branches were grown from the stem, are the main restrictions of these approaches [8].

In this study, we proposed a new method for the production of ZnO photoanodes, which is simple, reproducible, and scalable for large area fabrication. In this method, a conformal layer of zinc oxide photoanode (thickness between 3 and 10 nm) on screen printed mesoporous np-Al_2O_3 template is developed by employing atomic layer deposition (ALD) as a surface saturative and self-limiting technique.

Materials and method

All chemicals in this work, unless noted otherwise, were used as received. The alumina paste with a porosity of 75%, mean particle size of 23 nm and pore diameter of 48 nm was screen printed onto a pre-cleaned TCO glass (NSG 10, Nippon sheet glass, Japan) followed by a multi-step sintering process and ZnO was deposited on the aforementioned sintered film by ALD technique as shown in Fig.1.

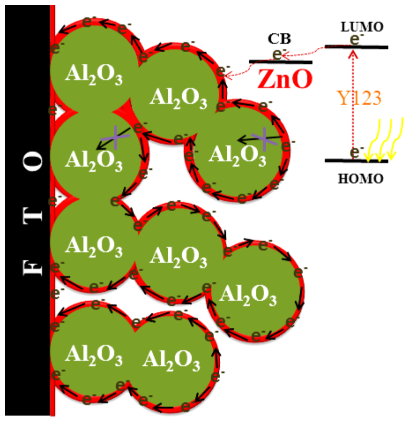

Fig.1: Schematic of photoanode based on ALD ZnO on Alumina template.

The ALD ZnO overlayer of different thickness (2, 3, 5, 6, 8, 10 nm) on a mesoporous alumina template were treated in O_2 plasma plasma (model: PDC- 379 32G, Harrick Plasma, USA) for 5 min before dipping them in a 0.1 mM Y123 solution in 1:1 (v:v) acetonitrile/t-butanol mixture for 5 h. The dye loaded photoanodes were immersed in acetonirile for 30 minutes prior to the device assembly. The counter electrode was made by depositing ethanolic solution of carbon (stacked graphene platelet nanofiber (acid washed) ABCR, Germany) on the FTO glass (TEC7, Solaronix, Switzerland). The two electrodes were

assembled in to a sandwich type cell and sealed with a spacer of 25 µm thick Surlyn (Dupont, USA). The electrolyte containing a mixture of Co^{3+}, 100 mM $LiClO_4$, and 200 mM tert-butyl pyridine in acetonitrile solvent was injected through a hole sand blasted at the backside of the counter electrodes.
For the photovoltaic measurements, a 450W xenon lamp (Oriel, USA) equipped with a Schott K113 Tempax filter (Präzisions Glas & Optik GmbH, Germany) was used as solar simulator and cells were equipped with a UV cut-off filter and masked with a thin metal mask to make an active area of 0.159 cm^2. The incident photon-to-current conversion efficiency measurements were recorded using a 300 W xenon light source (ILC Technology, USA).

Results and Discussion

The photovoltaic characteristics of photoanodes with different thickness of ZnO overlayer on the mesoporous insulating template are evaluated in the dark and under AM 1.5G solar illumination (100 mW/cm^2 photon flux). The J-V curves and the corresponding data are shown in Fig.2 and Table 1 respectively. The device with the smallest ZnO over-layer thickness shows the lowest short-circuit density (J_{sc}) of 2.5 mA/cm^2. A small increase to 3 nm, enhanced the J_{sc} significantly near to 6 mA/cm^2 obtaining to the highest of 8 mA/cm^2 for 5-6 nm overlayer. A slight drop of J_{sc} can be seen by further increase in ZnO layer thickness to 10 nm. The 3-6 nm ZnO overlayer shows the highest power conversion efficiency (PCE) around 4% due to higher internal surface area compare to devices with thicker layer. The lower photovoltaic performance in 8-10 nm of ZnO overlayer can be attributes to the difficulty of shuttling of Co^{3+}/ Co^{2+} in narrow pores due to reduction of pore size from 45 nm to around 25 nm.

Table 1: The photovoltaic characteristics of the dye-sensitized solar cells are given for different thickness of the zinc oxide deposited on the 3µm alumina mesoporous template.

Thickness of ZnO over-layer (nm)	J_{SC} (mA/cm^2)	V_{OC} (mV)	FF (%)	PCE (%)
2	2.5	890.6	67.4	1.5
3	6.1	923.9	69.5	3.9
5	7.7	913.7	54.3	3.8
6	8.1	903.9	56.9	4.2
10	8.0	885.0	49.8	3.5

As shown in Fig.3, the incident-photon-to-electron conversion efficiency (IPCE) is measured for the devices with 3 nm and 6 nm overlayer. The integrated current under IPCE spectrum of the mentioned DSCs matches closely with the photocurrent density acquired by J-V measurements.

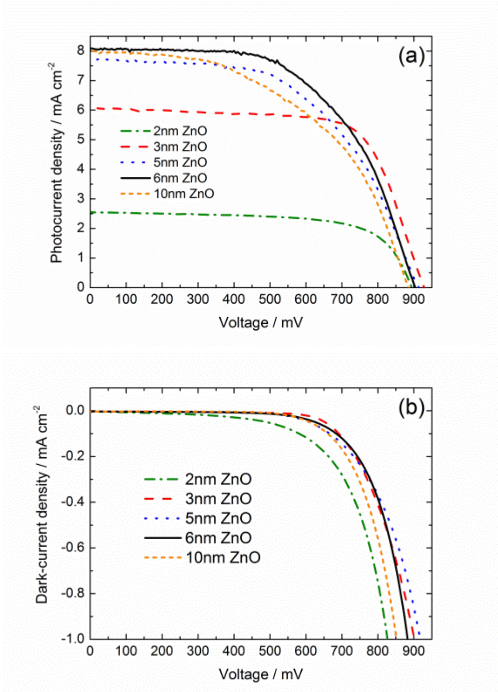

Fig.2: The current-voltage characteristics measured under a) AM 1.5 G solar irradiance (100 mW/cm 2 photon flux); b) dark, for solar cells with different thicknesses of zinc oxide on alumina template.

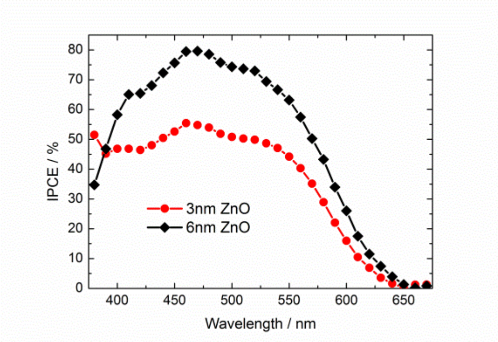

Fig.3: The incident-photon-to-electron conversion efficiency of DSC with photoanodes containing various overlayers of ZnO on insulating mesoporous template.

Reversely to J_{sc}, a continuous drop in the open-circuit potential (V_{oc}) is observed by increasing the thickness. The DSC with 2 nm ZnO overlayer shows V_{oc} of 891 mV and 3 nm layer exhibits the highest V_{oc} of 924 mV and it diminished ceaselessly by further increase in the thickness. This subtractive trend in V_{oc} can be rationalized by quantum confinement effect in zinc oxide due to size reduction [9]. Fig.4 analyses the optical absorption of photoanodes. The absorbance onset for the 8-10 nm ZnO overlayer starts from around 420 nm while it shifts slightly to 400 nm when the layer thickness is 5-6 nm and reaches huge change to 350 nm in 2-3 nm overlayer. This blue shift in UV-visible onset by decreasing the overlayer thickness confirms the changing in the bandgap of ZnO. Therefore, V_{oc} as the energy gap between the Fermi level of ZnO and the energy level of redox mediator increases by diminishing the overlayer thickness from 10 nm to 3 nm. The different V_{oc} for 2 nm

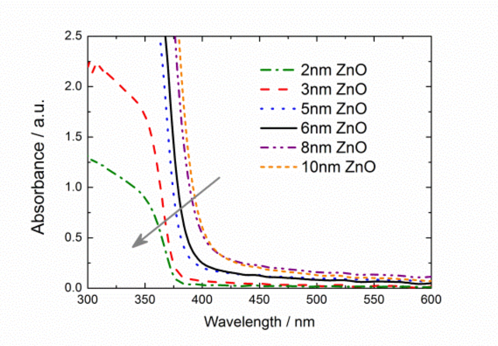

Fig.4: UV-vis absorbance versus wavelength for solar cells with different thicknesses of zinc oxide on alumina template.

and 3 nm layer can be explained by the dark current-voltage plot (Figure 1b). The dark current onset begins at around 300 mV when the thickness of the layer is 2 nm while it shifts to ~650 mV in other cells with overlayer thickness beyond 2 nm. On forward biasing, the recombination of the photogenerated electrons at the interfaces between FTO or ZnO and electrolyte is the source of dark current. It is shown that the recombination of electrons at the interface of oxide semiconductor is considerably lower than FTO with cobalt redox shuttle and so very thick under layer of semiconductor or insulating layers like Ga_2O_3 need to be used [10]. In this work, the recombination at the FTO-electrolyte interface for 2 nm ALD layer of ZnO on the alumina template due to weak coverage of the conducting substrate dominates and leads to lower V_{oc}. It is notable that the effect of recombination from the Al_2O_3-electrolyte interface is excluded due to whole coverage of alumina by zinc oxide and also the applied potential (0-0.9 V) is not sufficient to extract electrons from the template to recombine with the holes of redox mediator at their interface.

In order to investigate the trend of the photocurrent in the devices, dye uptake measurement is carried out. The amount of dye loading on the photoanodes is evaluated by absorption spectroscopy and the change in the absorbance maximum at 463 nm is plotted in Fig. 5 as the function of ZnO overlayer thickness. The continuous drop in the photoanode absorbance from 2 nm to 10 nm thickness of ZnO overlayer can be explained by the reduction in the internal available surface area at higher thickness due to ALD of ZnO overlayer on mesoporous template.

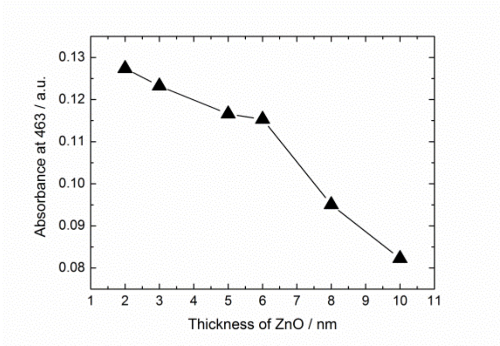

Fig.5: Evolution of the absorbance of the Y123 dye (desorbed in the basic solution of DMF) is plotted as a function of ZnO overlayer thickness on the alumina template.

Conclusions

In summary, we present a new low-temperature ZnO based DSC by utilizing a templated photoanode on the mesoporous insulating oxide with high surface area like nanoparticles. In this study, we confirms that there is a blue shift in the adsorption of ZnO overlayers in smaller thickness due to quantum confinement effect and generates high open-circuit voltage in thinner layer. In addition, thinner overlayer with larger internal surface area shows higher amount of dye loading on the surface of mesoporous template. In terms of economics, this study not only shows a simple structure and low temperature route for DSC manufacturing, but also represents a significant reduction in material usage by using only 3-6 nm ALD zinc oxide.

References

[1] Oregan, B.; Gratzel, M., Nature **1991**, 353, 737.

[2] Zhang, Q.; Dandeneau, C. S.; Zhou, X.; Cao, G., *Adv. Mater*. **2009**, 21, 1–22.

[3] P. S. Archana, R. Jose, C. Vijila and S. Ramakrishna, J. *Phys. Chem. C*, **2009**, 113, 21538..

[4] N. Memarian, I. Concina, A. Braga, S. M. Rozati, A. Vomiero, G. Sberveglieri, *Angew. Chem., Int. Ed.* **2011**, 50, 12321−12325.

[5] Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. D. *Nat. Mater.* **2005**, *4*, 455.

[6] Chia-Yu Lin, Yi-Hsuan Lai, Hsin-Wei Chen, Jian-Ging Chen, Chung-Wei Kung, R. Vittala and Kuo-Chuan Ho, *Energy Environ. Sci.*, **2011**, 4, 3448.

[7] S. Ko, D. Lee, H. W. Kang, K. H. Nam, J. Y. Yeo, S. J. Hong, C. P. Grigoropoulos, H. J. Sung, *Nano Lett.* **2011**, 11, 666–671.

[8] George, S. M. *Chemical Reviews* **2009**, *110*, 111–131.

[9] Detlef W. Bahnemann, Claudius Kormann, and Michael R. Hoffmann, *J. Phys. Chem.* **1987,** *91,* 3789-3798.

[10] A. K. Chandiran , N. Tetreault , R. Humphry-Baker , F. Kessler , E. Baranoff , C. Yi , M. K. Nazeeruddin , M. Grätzel , *Nano Lett.* **2012** , *12* , 3941 .