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

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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 4.3% with the standard organic sensitizer (coded Y123) and cobalt bipyridine redox mediator.

1. 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]. Although many studies have been done on TiO_2 photoanodes [3], ZnO has been explored as a promising alternative material for DSCs since the inception of research on TiO_2-based DSCs; 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 [4,5]. However, the best photovoltaic performance for DSC based on hierarchical aggregates ZnO up to now was achieved by Memarian et al. [6] who obtained power conversion efficiency of 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 [7], nanosheet [8] and nanoforest [9] 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 [10].

In this study, we propose 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 nanoparticle Al_2O_3 template is developed by employing Atomic Layer Deposition (ALD) as a surface saturative and self-limiting technique.

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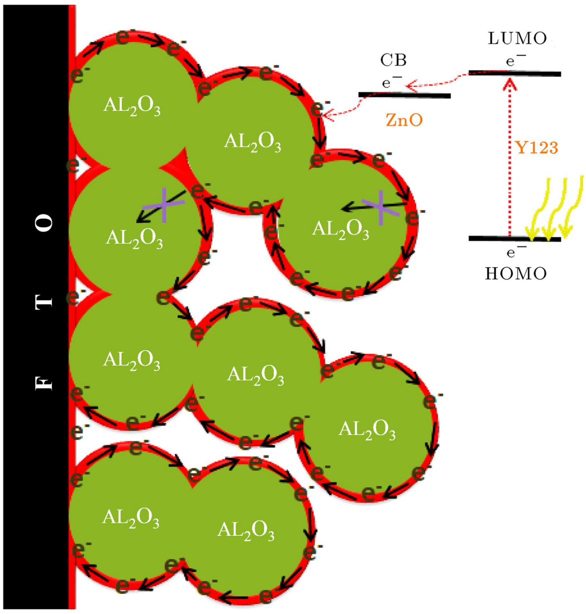

Figure 1. Schematic of photoanode based on ALD ZnO on alumina template.

2. Materials and method

All chemicals in this work, unless noted otherwise, were used as received. The alumina paste 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 Figure 1. The alumina scaffold has a porosity of 75%, mean particle size of 23 nm and pore diameter of 48 nm.

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 (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 thickness of the ALD ZnO layer was evaluated using spectroscopic ellipsometry by depositing a similar number of cycles with identical growth conditions on Si wafers having native oxide. 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 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).

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

Thickness of ZnO over-layer (nm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	PCE (%)
2	2.51	891	69.8	1.6
3	6.19	924	70.3	4.0
5	7.75	914	55.6	3.9
6	8.18	904	58.2	4.3
10	8.06	885	51.1	3.6

3. 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 evolution of the photovoltaic parameters in different thickness of zinc oxide thickness and the corresponding data are shown in Figure 2 and Table 1, respectively. The device with the smallest ZnO overlayer thickness shows the lowest short-circuit density (J_{sc}) of 2.51 mA/cm^2. A small increase to 3 nm, enhanced the J_{sc} significantly near to 6.20 mA/cm^2; when the thickness is 5-6 nm, J_{sc} reaches the highest, i.e. 8.18 mA/cm^2. 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 compared to devices with thicker layer. The lower photovoltaic performance in 8-10 nm of ZnO overlayer can be attributed to the difficulty of shuttling of Co^{3+}/Co^{2+} in narrow pores due to the reduction of pore size from 45 nm to around 25 nm.

As shown in Figure 3, the Incident-Photon-to-electron Conversion Efficiency (IPCE) is measured for the devices with 3 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.

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 with 3 nm overlayer exhibits the highest, V_{oc}, i.e. 924 mV; this increase diminishes ceaselessly by further increase in the thickness. This subtractive trend in V_{oc} can be rationalized by

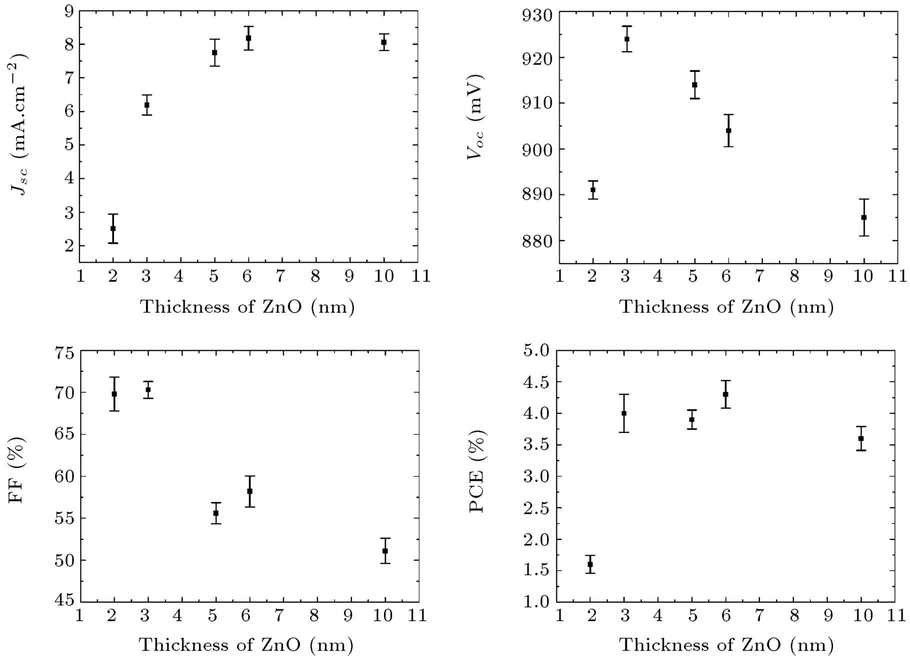

Figure 2. Evolution of the photovoltaic parameters versus thickness of zinc oxide on alumina template measured under AM 1.5 G solar irradiance (100 mW/cm^2 photon flux). The error bars represent the standard deviation from the mean value of photovoltaic parameters for five solar cells per each condition.

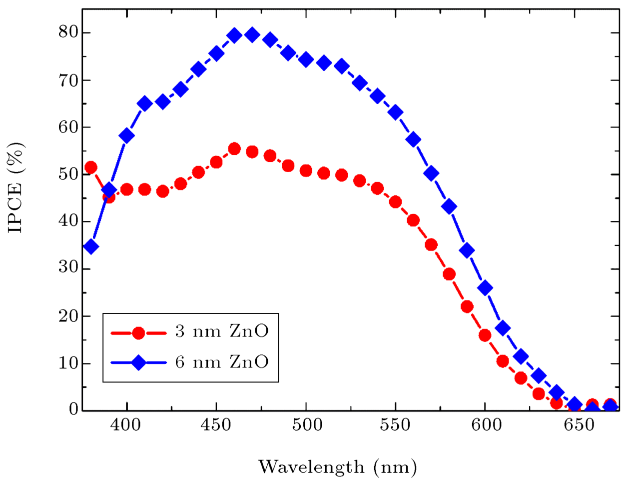

Figure 3. The incident-photon-to-electron conversion efficiency of DSC with photoanodes containing various overlayers of ZnO on insulating mesoporous template.

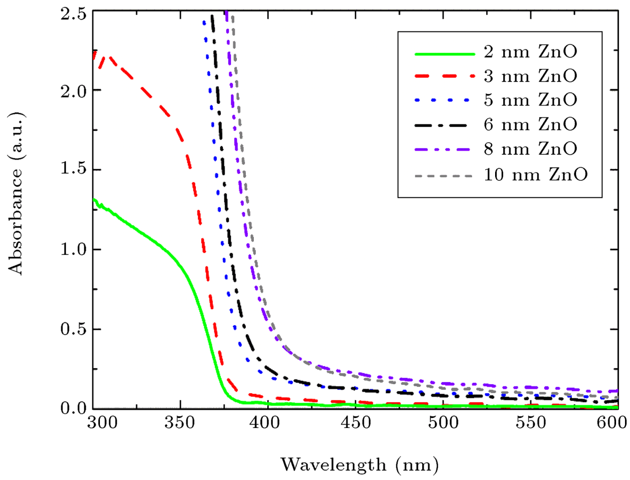

Figure 4. UV-vis absorbance versus wavelength for solar cells with different thicknesses of zinc oxide on alumina template.

quantum confinement effect in zinc oxide due to size reduction [11]. Figure 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 and 3 nm layers can be explained by the dark current-voltage plot (Figure 5). The dark current onset begins at around 300 mV when the thickness of the layer is 2 nm, while it shifts to $\sim$ 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 semiconductor layer or insulating layers

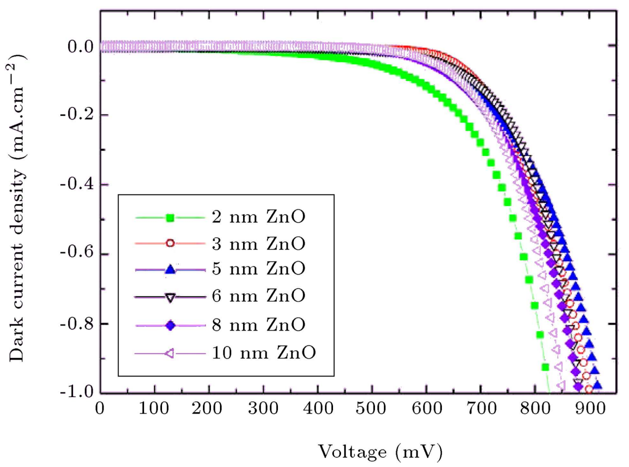

Figure 5. The current-voltage characteristics measured under dark, for solar cells with different thicknesses of zinc oxide on alumina template.

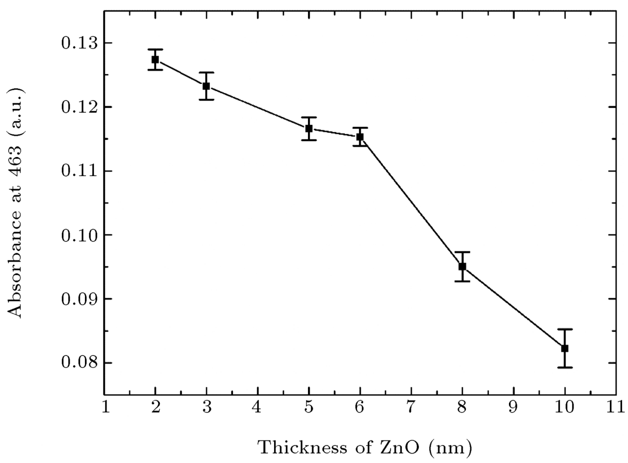

Figure 6. Evolution of the absorbance of the Y123 dye (desorbed in the basic solution of DMF) is plotted as a function of ZnO overlayer thickness on the alumina template. Mean values and standard deviation (STDEV) of dye absorbance of five films per each condition are shown in the figure.

like Ga_2O_3 need to be used [12]. 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 the applied potential (0-0.9 V) is not also 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 maximum absorbance, at 463 nm, is plotted in Figure 6 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.

4. 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 confirm 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.

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Biographies

Mojtaba Abdi-Jalebi is currently a PhD student in Cavendish laboratory, University of Cambridge. He received his BSc and MSc in Materials Science and Engineering from Sharif University of Technology, Tehran and École Polytechnique Fédérale de Lausanne (EPFL), Switzerland, respectively. He joined the world's leading Dye-Sensitized Solar Cell (DSC) laboratory, laboratory of interfaces and photonics (LPI), led by Prof. Graetzel, as a researcher between 2012 and 2014. In addition, he worked as a senior scientist in the R&D Department at Solaronix SA, a specialist company on DSCs, for about a year. His research area focuses on synthesis of novel functional materials for mesoscopic solar cells and various spectroscopy techniques to investigate the mechanism of sensitized solar cells.

Aravind Kumar Chandiran received his B. Tech. in Rubber and Plastics Technology from Anna University in India and his MSc in Materials for Energy Storage and Conversion from University of Paul Sabatier, France, in 2007 and 2009, respectively. He received his PhD from Swiss Federal Institute of Technology (EPFL), Switzerland, in 2013. He is currently a post-doctoral fellow in Berkeley in University of California. His research focuses on dye-sensitized solar cells since 2009, and his current research is devoted to water splitting area.

Mohammad Khaja Nazeeruddin received MSc and PhD degrees in inorganic chemistry from Osmania University, Hyderabad, India. He joined, as a Lecturer, Deccan College of Engineering and Technology, Osmania University, in 1986, and subsequently, moved to Central Salt and Marine Chemicals Research Institute, Bhavnagar, as a Research Associate. He was awarded by the Government of India's fellowship, in 1987, for study abroad. After one year postdoctoral, under supervision of Prof. Graetzel at Swiss Federal Institute of Technology, Lausanne (EPFL), he joined the same institute as a Senior Scientist. His current research focuses on dye-sensitized solar cells, hydrogen production, light-emitting diodes and chemical sensors. Dr Nazeeruddin has published more than 420 peer-reviewed papers, ten book chapters, and is the inventor of 40 patents. The high impact of his work has been recognized with his invitations to speak at over 80 international conferences, including the MRS Fall (USA, 2006) and Spring 2011 Meetings, and GORDON conference (2014). He has also been nominated to the OLLA International Scientific Advisory Board, and has appeared in the ISI listing of most cited chemists, having more than 33500 citations with an h-index of 93. He teaches "Functional Materials" course at EPFL, and Korea University, and directs and manages several industrial, national, and European Union projects on hydrogen energy, photovoltaics (DSC), and organic light emitting diodes. Dr Nazeeruddin was awarded EPFL Excellence prize in 1998 and 2006, and received awards from Brazilian FAPESP Fellowship in 1999, Japanese Government Science & Technology Agency Fellowship, in 1998, and Government of India National Fellowship in 1987-1988. Recently, he has been appointed as World Class University (WCU) Professor by the Korea University, Jochiwon, Korea, and Adjunct Professor by the King Abdulaziz University, Jeddah, Saudi Arabia.

Michael Grätzel, Professor at the Ecole Polytechnique de Lausanne, directs, there, the Laboratory of Photonics and Interfaces. He pioneered the use of mesoscopic materials in energy conversion systems, in particular photovoltaic cells, lithium ion batteries and photo-electrochemical devices for the splitting water into hydrogen and oxygen by sunlight. He discovered a new type of solar cell based on dye sensitized nanocrystalline oxide films, whose mass production has started since October 2009. He is the author of over 1000 publications, two books and inventor of more than 50 patents. His work has been cited over 134'000 times (h-index 167), making him one of the 10 most highly cited chemists in the world.

He has received prestigious awards, including the Balzan Prize, the Galvani Medal, the Faraday Medal, the Harvey Prize, the Gerischer Award, the Dutch Havinga Award and Medal, the International Prize of the Japanese Society of Coordination Chemistry, the ENI-Italgas Energy-Prize and the year 2000 European Grand Prix of Innovation. His most recent awards include the 2012 Albert Einstein World Award of Science, 2011 Gutenberg Research Award, 2011 Paul Karrer Gold Medal and the 2010 Millenium Technology Grand Prize. He was selected, by the Scientific American, as one of the 50 top researchers in the world. He received a doctor's degree in Natural Science from the Technical University Berlin, and honorary doctor[s degrees from 11 distinguished universities of the world. He has been the Mary Upton Visiting Professor at Cornell University and a Distinguished Visiting Professor at the National University of Singapore. He was an Invited Professor at the University of Berkeley, the Ecole National de Chachan (Paris) and Delft University of Technology. In 2009 he was named Distinguished Honorary Professor by the Chinese Academy of Science (Changchun) and the Huazhong University of Science and Technology. He is a member of the Swiss Chemical Society as well as of the European Academy of Science, and a Fellow of the Royal Society of Chemistry. He was also elected honorary member of the Société Vaudoise des Sciences Naturelles and the Bulgarian Academy of Science.