Journal of the Korean Chemical Society
2018, *Vol. 62, No. 5*
Printed in the Republic of Korea
https://doi.org/10.5012/jkcs.2018.62.5.341

Communications

Quantum Dot-Sensitizers Prepared by SILAR and Cation-Exchange Processes

So-Min Yoo[†], Ji-Young Oh[‡], and Hyo Joong Lee[†,§,*]
[†]*Department of Chemistry, Chonbuk National University, Jeonju 54896, Korea.*
[‡]*Center for University-wide Research Facilities, Chonbuk National University, Jeonju 54896, Korea.*
[§]*Department of Bioactive Material Sciences, Chonbuk National University, Jeonju 54896, Korea.*
[*]*E-mail: solarlee@jbnu.ac.kr*
(Received July 16, 2018; Accepted August 16, 2018)

Key words: Quantum dot, Cation-exchange, Sensitizer, Solar cell, SILAR

Over the last two decades, there have been numerous efforts to prepare well-defined semiconducting nanocrystalline quantum dots (QDs) by the formation of colloidal nanoparticles in solution or by *in-situ* deposition of those over substrates.[1,2] The as-prepared QDs have been utilized in many optoelectronic applications as well as in the investigation of fundamental photophysical properties depending on their different sizes in the realm of quantum confinement.[3,4] Recently, QD sensitizer-based solar cells have attracted much attention due to its intrinsic advantages such as strong light-absorption, easy tuning of band gap, and etc.[5] In particular, QDs could play a crucial role as a photo-sensitizer in the structure of dye-sensitized solar cells (DSSCs) instead of molecular dyes.[6] Besides direct attachment of colloidal QDs,[7,8] those QD sensitizers could be grown *in-situ* on the surface of mesoporous metal oxide films by various chemical bath deposition (CBD) techniques.[9–11] Among the many CBD processes, successive ionic layer adsorption and reaction (SILAR) is considered one of the most effective ways to control the deposition of QDs precisely by alternating dipping of the substrate into each precursor solution.[12–14]

In this communication, we suggest that there is a facile route to converting SILAR-deposited QD sensitizer over mesoporous TiO_2 film into other ones by just using a simple *cation-exchange* process as a post-treatment. As a proof-of-concept experiment, the well-known CdS QD was deposited firstly over TiO_2 film by repeating the SILAR process five times.[15] Then, the as-prepared CdS QD-sensitized TiO_2 electrode was just dipped for 30 seconds into another chemical bath containing a salt of metal cation of target QDs. The typical yellow color of CdS QDs was changed immediately into the different one of the target QDs as shown in the color change of electrodes and their corresponding absorption changes in *Fig*. 1. This very rapid change of color could be explained roughly by different solubility products (K_{sp}) of participating metal cations and sulfide anion. The K_{sp} value of CdS is much larger than those of all the other metal sulfides tested here,[16] which means that Cd^{2+} is subject to be more soluble than other cations when present together with sulfide anion in an aqueous solution. Therefore, Cd^{2+} is diffused out from CdS QD and other cations (Bi^{3+}, Ag^{+}, Cu^{2+}, and Pb^{2+}) are diffused in to make new metal sulfide QD-sensitizers over the mesoporous TiO_2 film. However, more precisely, we have to consider the relative thermodynamic stabilities between the reactant and product phases, and the effect of cation solvation (or ligation) and nanostructures to estimate the driving force for an ion-exchange reaction.[17–19]

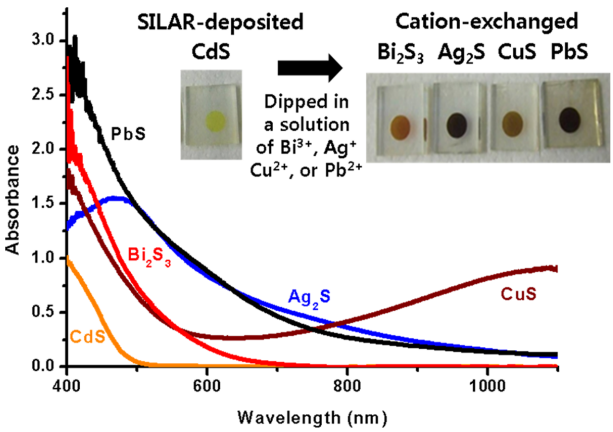

***Figure* 1.** Absorption spectra of SILAR-deposited CdS QD and its converted ones (Bi_2S_3, Ag_2S, CuS, and PbS) by a cation-exchange process over mesoporous TiO_2 film/FTO electrode and a picture of as-obtained electrodes (inset).

This kind of conversion by a cation-exchange reaction was successfully demonstrated before in freely-moving colloidal QDs in solution,[17–20] but not yet in QDs fixed onto the surface of mesoporous metal oxide films. Here, we

have confirmed that the process of cation-exchange is also possible over the electrode-anchored QD by contacting it with a solution with a target cation that shows a lower solubility product with a common anion (S^{2-}). This simple but very effective way of conversion from the preformed SILAR-deposited CdS QD into new one could be useful in preparing QD sensitizers of which preparations were known to be difficult by a direct SILAR process. In the preparation of Sb_2S_3-sensitized solar cells, only time-consuming and inconvenient bulk chemical bath deposition was proven to be effective in preparing Sb_2S_3 over mesoporous metal oxide films.[21,22] The more straightforward and controllable SILAR was rarely applied maybe due to the ineffective adsorption and reaction of Sb^{3+} with (+3) positive charges. To prepare an Sb_2S_3-sensitized TiO_2 electrode, CdS was deposited over the TiO_2 film by a typical SILAR process where cadmium acetate was used to induce more adsorption than in the case of cadmium nitrate.[23] The orange-colored TiO_2/CdS was observed with Cd(acetate)$_2$ (*Fig.* 2) while a yellow one was prepared with Cd(nitrate)$_2$ (*Fig.* 1). This SILAR-deposited orange TiO_2/CdS electrode was dipped into a $SbCl_3$ solution to induce the cation-exchange process between Cd^{2+} and Sb^{3+}. After this dipping, the color of the electrode changed to a little bit deeper one but got to dark brown with the well-known annealing process up to 300 °C under nitrogen atmosphere for the crystallization of Sb_2S_3 (*Fig.* 2).[24] The energy levels of main components were estimated in the inset of *Fig.* 2 from the Tauc plots (*Fig.* S1) and reported data,[25] which indicate a favorable charge transfer after light absorption.

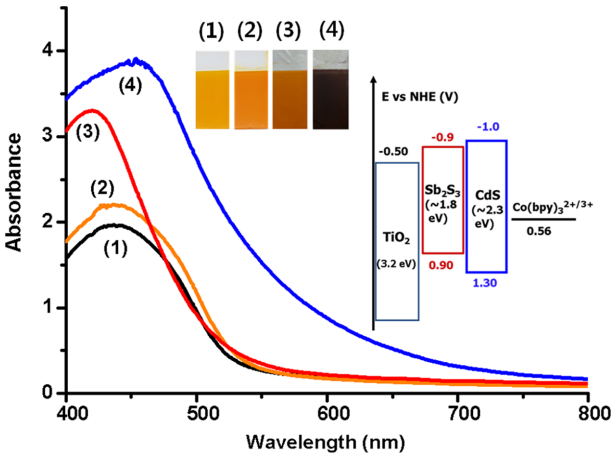

***Figure* 2.** Absorption spectra of (1) SILAR-deposited CdS QD and (3) its converted one to Sb_2S_3 by a cation-exchange reaction over mesoporous TiO_2 film/slide glass while (2) and (4) are annealed ones from (1) and (3), respectively. A corresponding picture of as-obtained substrates and energy levels of main components are shown in the inset.

With this transformed Sb_2S_3 sensitizer, photovoltaic tests were conducted with a cobalt redox couple, $Co(bpy)_3^{2+/3+}$ as a hole mediator in the structure of DSSCs. The overall power conversion efficiency increased from 0.55% (J_{sc}: 3.05 mA/cm^2, V_{oc}: 0.38 V, FF: 0.48) to 0.84% (J_{sc}: 5.22 mA/cm^2, V_{oc}: 0.35 V, FF: 0.46) after conversion from CdS to Sb_2S_3. In the lower intensities than the standard 1 sun, Sb_2S_3-sensitized cell showed about 1.0% efficiency (*Table* S1). This increase could be attributed mainly to the enhanced short-circuit current (J_{sc}) although open-circuit voltage (V_{oc}) and fill factor (FF) decreased slightly in this conversion. As can be seen in the incident photon-to-current conversion efficiency (IPCE) in *Fig.* 3, the Sb_2S_3-sensitizer showed a better conversion efficiency response over a broader region up to ~750 nm, which was limited to ~650 nm in the case of CdS. The direct SILAR-deposited Sb_2S_3-sensitizer only showed about half of the value (0.40%) of this one converted from CdS (see *Table* S1). This lower efficiency could be attributed to a difficulty of controlling the direct adsorption of Sb^{3+} ion over mesoporous metal oxide films, which should be checked more in the research of SILAR-deposited QD sensitized solar cells. Although the overall efficiency of this cation-exchanged Sb_2S_3-sensitized cell is relatively lower compared to the reported CBD-based ones,[26,27] there is still much room left for further optimization and improvements in many parameters of the experimental process. In particular, the relatively low V_{oc} of 0.38 V was one main reason for total low efficiency, and this was confirmed by the measurement of the V_{oc} decay curve as shown in *Fig.* 4. The faster decay of Sb_2S_3 sensitizer than the initial CdS one indicates that TiO_2/Sb_2S_3 is suffering a faster recombination after electron injection

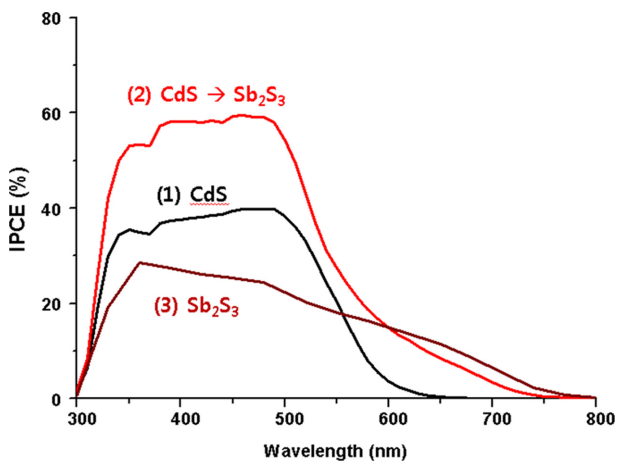

***Figure* 3.** IPCE spectra of solar cells with a QD-sensitizer of (1) SILAR-deposted CdS and (2) its converted one to Sb_2S_3 while (3) was from a direct SILAR-deposited Sb_2S_3.

from Sb_2S_3 to TiO_2, thus leading to a lower V_{oc} due to a shorter electron life-time. If we could passivate the interface of TiO_2/Sb_2S_3, a higher V_{oc} would be possible for better performance.[28,29]

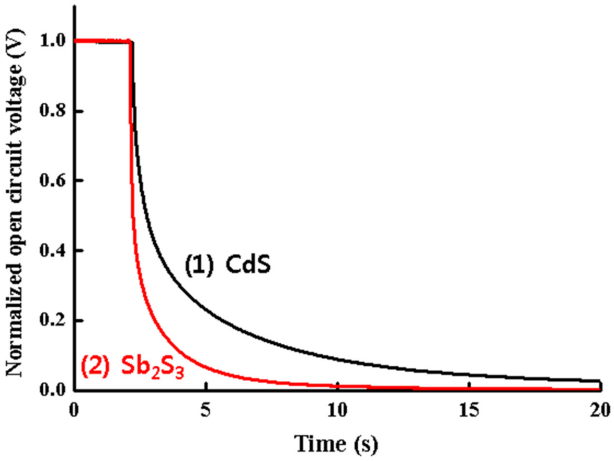

***Figure* 4.** Open-circuit voltage (V_{oc}) decay data from (1) SILAR deposited CdS- and (2) its converted Sb_2S_3-sensitized cells.

In this study, we have successfully demonstrated that it is also possible to prepare new QD sensitizers anchored onto the surface of mesoporous TiO_2 film via effective SILAR deposition firstly and a simple/rapid cation-exchange reaction secondly. As a model system, Sb_2S_3 QD sensitizer was prepared from the preformed CdS QD by SILAR and tested for its photovoltaic performances. This new way of surface-attached QD preparation could find many useful applications in optoelectronic, photonic, and catalytic reactions and devices by constructing tailor-made substrates with metal oxide film/semiconducting QDs.

Acknowledgments. H. J. Lee acknowledges the financial support by the National Research Foundation (no. 2014R1A1A2057772).

Supporting Information. Experimental details and photovoltaic results by different preparation of QD sensitizers.

REFERENCES

1. Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.
2. Kamat, P. V. *J. Phys. Chem. C* **2008**, *112*, 18737.
3. Litvin, A. P.; Martynenko, I. V.; Purcell-Milton, F.; Baranov, A. V.; Fedorov. A. V.; Gun'ko, Y. K. *J. Mater. Chem. A* **2017**, *5*, 13252.
4. Burda, C.; Chen, X. B.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025.
5. Carey, G. H.; Abdelhady, A. L.; Ning, Z.; Thon, S. M.; Baker, O. M.; Sargent, E. H. *Chem. Rev.* **2015**, *115*, 12732.
6. Kamat. P. V. *J. Phys. Chem. Lett.* **2013**, *4*, 908.
7. Jin, H.; Choi, S.; Velu, R.; Kim, S.; Lee, H. J. *Langmuir* **2012**, *28*, 5417.
8. McDaniel, H.; Fuke, N.; Makarov, N. S.; Pietryga, J. M.; Klimov, V. I. *Nat. Commun.* **2013**, *4*, 2887.
9. Niitsoo, O.; Sarkar, S. K.; Pejoux, C.; Rühle, S.; Cahen, D.; Hodes, G. *J. Photochem. Photobiol. A* **2006**, *181*, 306.
10. Lévy-Clément, C.; Tena-Zaera, R.; Ryan, M. A.; Katty, A.; Hodes, G. *Adv. Mater.* **2005**, *17*, 1512.
11. Zhu, G.; Lv, T.; Pan, L.; Sun, Z.; Sun, C. *J. Alloys Compd.* **2011**, *509*, 362.
12. Pathan, H. M.; Lokhande, C. D. *Bull. Mater. Sci.* **2004**, *27*, 85.
13. Lee, H.; Wang, M. K.; Chen, P.; Gamelin, D. R.; Zakeeruddin, S. M.; Gratzel, M.; Nazeeruddin, M. K. *Nano Lett.* **2009**, *9*, 4221.
14. Lee, H. J.; Bang, J.; Park, J.; Kim, S.; Park, S. M. *Chem. Mater.* **2010**, *22*, 5636.
15. Lee, H. J.; Leventis, H. C.; Moon, S.-J.; Chen, P.; Ito, S.; Haque, S. A.; Torres, T.; Nüesch, F.; Geiger, T.; Zakeeruddin, S. M.; Grätzel, M.; Nazeeruddin, Md. K. *Adv. Funct. Mater.* **2009**, *19*, 2735.
16. Dloczik, L.; Könenkamp, R. *Nano Lett.* **2003**, *3*, 651.
17. Beberwyck, B. J.; Surendranath, Y.; Alivisatos, A. P. *J. Phys. Chem. C* **2013**, *117*, 19759.
18. Rivest, J. B.; Jain, P. K. *Chem. Soc. Rev.,* **2013**, *42*, 89.
19. Gupta, S.; Kershaw, S. V.; Rogach, A. L. *Adv. Mater.* **2013**, *25*, 6923.
20. Son, D. H.; Hughes, S. M.; Yin, Y.; Alivisatos, A. P. *Science*, **2004**, *306*, 1009.
21. Moon, S.-J.; Yum, J.-H.; Humphry-Baker, R.; Karlsson, K. M.; Hagberg, D. P.; Marinado, T.; Hagfeldt, A.; Sun, L.; Grätzel, M.; Nazeeruddin, M. K. *J. Phys. Chem. C* **2009**, *113*, 16816.
22. Chang, J. A.; Rhee, J. H.; Im, S. H.; Lee, Y. H.; Kim, H.-J.; Seok, S. I.; Nazeeruddin, Md. K.; Grätzel, M. *Nano Lett.* **2010**, *10*, 2609.
23. Zhou, R.; Zhang, Q.; Tian, J.; Myers, D.; Yin, M.; Cao, G. *J. Phys. Chem. C* **2013**, *117*, 26948.
24. Itzhaik, Y.; Niitsoo, O.; Page, M.; Hodes, G. *J. Phys. Chem. C* **2009**, *113*, 4254.
25. Boix, P. P.; Larramona, G.; Jacob, A.; Delatouche, B.; Mora-Seró, I.; Bisquert, J. *J. Phys. Chem. C* **2012**, *116*, 1579.
26. Lim, C.-S.; Im, S. H.; Rhee, J. H.; Lee, Y. H.; Kim, H.-J.; Maiti, N.; Kang, Y.; Chang, J. A.; Nazeeruddin, Md. K.; Grätzel, M.; Seok, S. I. *J. Mater. Chem.* **2012**, *22*, 1107.
27. Choi, Y. C.; Lee, D. U.; Noh, J. H.; Kim, E. K.; Seok, S. I. *Adv. Funct. Mater.* **2014**, *24*, 3587.
28. Palomares, E.; Clifford, J. N.; Haque, S. A.; Lutz, T.; Durrant, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 475.
29. Kang, H.-W.; Lee, J.-W.; Park, N.-G. *Faraday Discuss.* **2014**, *176*, 287.