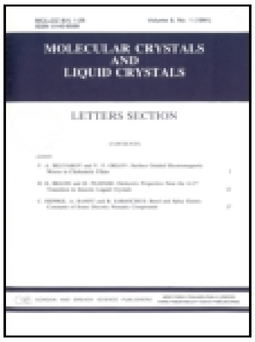

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Enhanced Chemical Stability of ZnO Electrode for Dye-Sensitized Solar Cells with Ru Dyes Containing Limited Acidic Anchor Group

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Two new Ruthenium-based dyes with carbazole groups (Ru-DiCz) or triphenyl amine groups (Ru-DiTPA) as donor moieties of a ligand were studied for ZnO-based dye-sensitized solar cells. Strong electron-rich donor moieties in both dyes induced a high molar extinction coefficient, thereby enhancing the overall power conversion efficiency through high J_{SC} value. With limited acidic carboxyl anchor groups on the new Ru-dyes, the solar cells showed superior stability without aggregation of ZnO nanoparticles for a long-term immersion compared with a reference N3 sensitizer.

Keywords Dye Sensitized Solar Cell; Ruthenium complex; Chemical stability; ZnO electrode

1. Introduction

Zinc oxide (ZnO)-based dye-sensitized solar cells (DSSCs) has been a class of promising energy conversion devices due to excellent properties of ZnO for DSSCs in terms of wide band gap, high electron mobility, long electron life time, good photostability, and wide range of feasible synthetic methods based on low-cost solution-processing [1–3]. However, commercially available dyes, such as N3 or N719, have not been successful for direct use in the ZnO-based-DSSCs, because of low chemical stability of the oxide in an acidic dye solution [4]. In such an acidic condition, ZnO dissolves and forms Zn^{2+}/dye aggregates instead of well-defined binding between ZnO and dyes [5, 6]. On this perspective, we report the enhanced stability of ZnO-nanoparticles-based DSSCs observed in various processing conditions (i.e. dye adsorption time) through a design of new dye molecules with donor

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moiety of ligand instead of an acidic carboxyl group. Direct comparison between DSSCs based on the new dyes and a commonly used N3 dye as a reference showed the superior stability of ZnO films without aggregation of nanoparticles during a long-term immersion.

2. Experimental

New Ru-dyes, cis-[Ru(H_2dcbpy)(L)($NCS)_2$], where H_2dcbpy = 4,4'-dicarboxylic acid-2,2'-bipyridine and L = 4,4'-bis-(4-(N-carbazolyl)-phenyl-2-vinyl)-2,2'-bipyridine (Ru-DiCz), or L = 4,4'-bis-(4-di-p-hexyloxyphenyl amino)-styryl-2,2'-bipyridine (Ru-DiTPA) (Fig. 1(a)) were synthesized through multi-step routes using a modification of the previously reported methods [7, 8]. ZnO-based-DSSCs were fabricated by using a method commonly used for TiO_2-based DSSCs [9]. The ZnO electrodes were prepared by using a doctor blade method with ZnO paste on a pre-cleaned FTO glass substrate. Each Ru-dye was adsorbed onto the ZnO electrode surface by immersing the electrode into a solution of $CH_3CN/^tBuOH$ containing the sensitizer at room temperature for various times ranging from 15 min to 24 h. The redox electrolyte solution was Iodolyte PMI 50 obtained from Solaronix.

3. Results and Discussion

We have designed and synthesized the Ru-sensitizers having an optimizing acidity, containing an electron donor moiety such as carbazole or triarylamine, and a conjugated linker for a high extinction coefficient in the visible region of solar spectrum [7].

The absorption spectra of the Ru-DiCz and Ru-DiTPA along with the N3 reference sensitizer are shown in Figure 1(b). The molar extinction coefficients (ε) of the metal-to-ligand charge transfer transition (MLCT) absorption bands for Ru-DiCz and Ru-DiTPA are 2.14×10^4 $M^{-1}cm^{-1}$ and 2.36×10^4 $M^{-1}cm^{-1}$ at near 540 nm, respectively, which are significantly higher than the corresponding coefficient of N3 (1.43×10^4 $M^{-1}cm^{-1}$). The increased π-conjugation length of ancillary ligands in Ru-DiCz and Ru-DiTPA, relative to N3, are likely responsible for the increased molar extinction coefficients in the visible region. Compared with the N3 dye, the Ru-DiCz dye exhibited a slightly red-shifted MLCT absorption band at of 539 nm.

Figure 2 shows the SEM images of ZnO nanoparticle films before and after immersion in the dye solutions for 24h. After absorbing the N3 dye onto the ZnO film for 24 h, the surface of ZnO film was damaged (Fig 2(b)), whereas the ZnO films in Ru-DiCz and Ru-TPA were physically stable and undamaged (Fig 2(c,d)) upon immersion into the dye

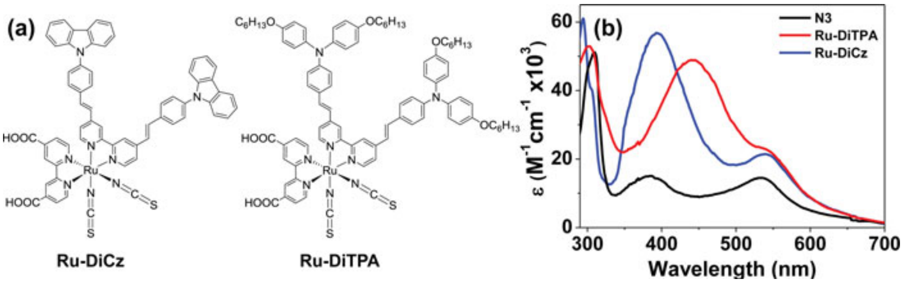

Figure 1. (a) Chemical structure of the Ru-dyes, (b) Molar extinction coefficient (ε) of Ru-dyes in DMF/CH_3CN (1:3) with a concentration of 1.0×10^{-5} M.

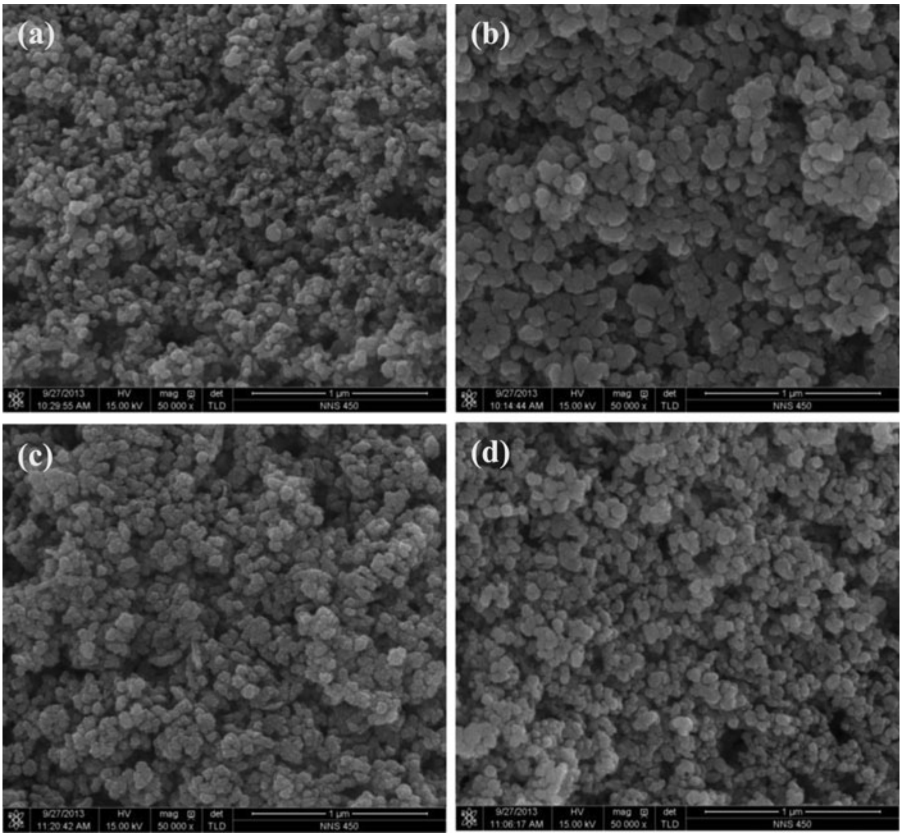

Figure 2. SEM image of ZnO film (a) before and after immersion in a solution of the (b) N3, (c) Ru-DiCz, and (d) Ru-DiTPA dye for 24 h, scale bar: 1 μm.

solutions. It is believed that Zn^{2+} ions were released from the surface of ZnO due to formation of Zn^{2+}/dye complex [4, 10]. The morphological change of ZnO film caused by an acidic group of the dye would have reduced the dye loading and resulted in degradation of ZnO nanostructures.

The loading amount on ZnO electrode of the dyes, Ru-DiTPA, Ru-DiCz, and N3, and the photovoltaic performance of the corresponding ZnO-based DSSCs as a function of the immersion time were shown in Figure 3. The dye-loading amounts of the new Ru-dyes were monotonically increased with increasing immersion time. A higher value of Ru-DiCz loading on the nanostructured ZnO surface than Ru-DiTPA might have come from the relatively smaller molecular footprint of Ru-DiCz, due to the absence of bulky hexyloxy groups. In the case of N3, the dye loading amount was increased until 60 min, and then decreased with longer immersion. Short-circuit current density (J_{SC}) are known to be influenced on the amount of dyes adsorbed onto ZnO films [11]. Indeed, we have observed that J_{SC} of the DSSCs showed similar tendency with the loading amounts of the dyes. The maximum J_{SC} of the reference N3-sensitized DSSCs was 11.55 mA/cm^2 when immersed for 60 min, and since then J_{SC} decreased to 4.00 mA/cm^2 when immersed for 24 h. As mentioned above, excessive immersion in an N3 dye solution could have induced the morphological degradation of ZnO nanoparticles and formed the Zn^{2+}/dye complex via

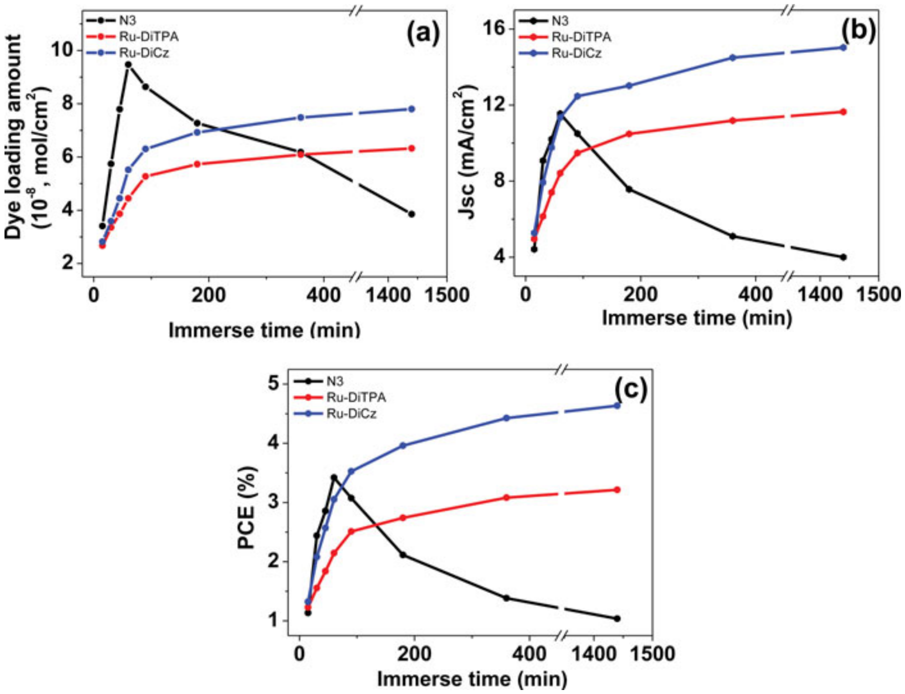

Figure 3. (a) Amount of adsorbed Ru-dyes on ZnO films. (b) Short-circuit current and (c) power conversion efficiency of DSSCs with the various immersion time.

dissolution of Zn^{2+} ions by acidic carboxylate groups of the dye molecule. This complex would have interrupted the injection of electrons from the excited dye to ZnO. The power conversion efficiencies (PCE) of the DSSCs based on our new dyes and N3 followed the same trends as J_{SC} (Fig. 3(c)). Ru-DiCz- and Ru-DiTPA-based DSSCs have monotonically increasing efficiency as increasing the dye loading time. With larger J_{SC}, the DSSCs based on Ru-DiCz and Ru-DiTPA after loading the dye for 24 hours showed a higher efficiency than a N3 device fabricated under same conditions.

4. Conclusions

We have studied a rationally designed and synthesized Ru-dyes with conjugated ligands containing carbazole (Ru-DiCz) and triarylamine (Ru-DiTPA) units as electron-donating moieties for the application in ZnO-based DSSCs. Combination of strong electron-donating moieties and absence of excessive carboxylic acid groups has increased the molar extinction coefficient of dyes and stability of ZnO films during dye adsorption processing for a prolonged time. The high density of the dyes adsorbed onto the ZnO nanoparticle surface has enhanced the overall power conversion efficiency with a high J_{SC} value. We believe that this study provides a new perspective in designing molecular architecture of dyes for ZnO-based DSSCs.

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References

[1] Klingshirn, C. (2007). *ChemPhysChem*, *8*, 782.

[2] Look, D. C., Reynolds, D. C., Sizelove, J. R., Jones, R. L., Litton, C. W., Cantwell, G., & Harsch, W. C. (1998). *Solid State Commun.*, *105*, 399.

[3] Ibrahem, M. A., Wei, H.-Y., Tsai, M.-H., Ho, K.-C., Shyue, J.-J., & Chu, C. W. (2013). *Sol. Energy Mater. Sol. Cells*, *108*, 156.

[4] Anta, J. A., Guillén, E., & Tena-Zaera, R. (2012). *J. Phys. Chem. C*, *116*, 11413.

[5] Katoh, R., Furube, A., Tamaki, Y., Yoshihara, T., Murai, M., Hara, K., Murata, S., Arakawa, H., & Tachiya, M. (2004). *J. Photochem. Photobiol. A*, *166*, 69.

[6] Keis, K., Lindgren, J., Lindquist, S.-E., & Hagfeldt, A. (2000). *Langmuir*, *16*, 4688.

[7] Ganesh, T., Nguyen, H.-M., Mane, R. S., Kim, N., Shinde, D. V., Bhande, S. S., Naushad, M., Hui, K. N., & Han, S. H. (2014). *Dalton Trans.*, *43*, 11305.

[8] Wang, P., Zakeeruddin, S. M., Moser, J. E., Nazeeruddin, M. K., Sekiguchi, T., & Gratzel, M. (2003). *Nat. Mater.*, *2*, 402.

[9] Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L., & Pettersson, H. (2010). *Chem. Rev.*, *110*, 6595.

[10] Nguyen, H.-M., Mane, R. S., Ganesh, T., Han, S.-H., & Kim, N. (2009). *J. Phys. Chem. C*, *113*, 9206.

[11] Chou, T. P., Zhang, Q., & Cao, G. (2007). *J. Phys. Chem. C*, *111*, 18804.