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Communication

Quasi-solid state electrolytes with silica nanomaterial for high efficiency dye-sensitized solar cells

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ABSTRACT : Silica nanoparticles were synthesized with various silane coupling agents to make specific pathway of electrons and anti-recombination system when solidifying liquid electrolytes. In this study, we used an appropriate method of synthesis for activated silica nanoparticles and silane coupling agents with 3-(triethoxysilyl)propionitrile, Trimethoxy[3-(methylamino)propyl]silane, Triethoxyoctylsilane, and octadecyltrimethoxy silane. Dye-sensitized solar cells using solidified electrolytes with silica nanoparticles exhibit comparatively excellent efficiency, ranging from 2.3 to 7.0% under similar conditions.

For the fast two decades, dye-sensitized solar cells (DSSCs) have been intensively studied because of their advantages such as low production cost, high conversion efficiency, environmental friendliness, and easy fabrication procedure.[1-6] A typical DSSC is comprised of TiO_2 working electrode with dye molecules on transparent conductive oxide (TCO) glass, platinum coated counter electrode, and a liquid electrolytes with redox couple (I_3^-/I^-) between the electrodes.[7,8] However, some of problems caused by these liquid electrolytes such as leakage, volatilization limit, long-term performance and practical use of these DSSCs. To solve these problems, many attempts have been made to replace the liquid electrolytes with gel or quasi-solid type.[9-12] At this point of view, we adopted an activated silica nanoparticles with various silane groups to solidifying a liquid electrolytes and to enhance the stability of the solar cells by creating a pathway for ion transportation and prevent electron recombination at the interfaces.

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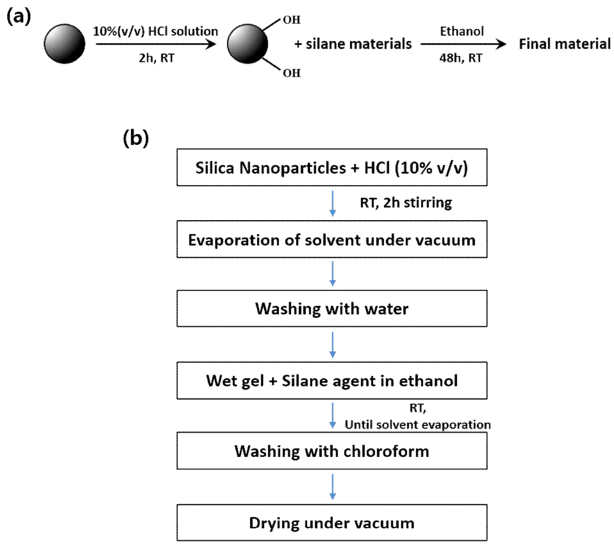


Figure 1. Scheme of synthetic route for silica nanomaterials (a) and process.

Figure 1 represents the synthetic route and molecular scheme of silica nanoparticles. Using acidic solution (10% v/v HCl), 12nm primary sized silica nanoparticles (Aerosil 200, Evonic) were activated by stirring 2h at room temperature. The activated silica was dried under vacuum and cleaned with DI water until the pH of wet-gel shows 4~5. 40ml of ethanol was used as solvent for wet-gel with 42mmol of silane coupling agents by dropwise addition. The solution becomes a visible gel after stirring and was dried under vacuum. Unreacted alkoxysilane molecules were removed by chloroform. At the surface of silica which was achieved with hydroxy1 groups (-OH) under vacuum dry, various silane coupling agents were grafted by O-Si-O covalent bond in condition of specific chain.[12] Before the gelation of electrolyte, an liquid electrolyte solution was prepared which is containing a mixture of 0.6 M 1-hexyl-2,3-dimethyl-imidazolium iodide, 0.1 M Guanidine thiocyanate, 0.03 M iodine, and 0.5 M 4-tert-butylpyridine in acetonitrile. By adding synthesized silica nanoparticles into liquid electrolytes, the solution becomes a visible quasi-solid state and finally the solidified electrolyte. Used silane coupling agents with their chemical structures are listed in table 1. and the picture of electrolytes is shown in figure 2.

Table 1. Silane reagent with their chemical structure.

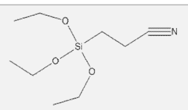
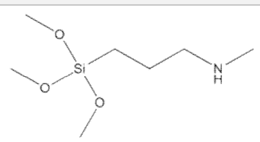
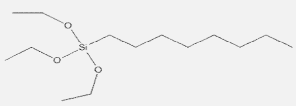
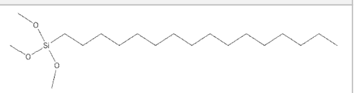
No.	Silane reagent	Chemical structure
1	Reference	Liquid electrolyte
2	None-reagent (Silica only)	Quasi-solid state electrolyte
3	3-(triethoxysilyl)propionitrile (Si_EL 1)	
4	Trimethoxy[3-(methylamino)propyl]silane (Si_EL 2)	
5	Triethoxyoctylsilane (Si_EL 3)	
6	octadecyltrimethoxysilane (Si_EL 4)	

Figure 2. Liquid electrolyte and silica-added gel type electrolytes.

To prepare electrodes, nanocrystalline TiO_2 was coated onto the cleaned FTO glasses using a doctor blade and annealed at 500℃ for 1.5h; then the substrate was immersed in dye solution for 24h. To prepare counter electrodes, H_2PtCl_6solution in ethanol were coated onto a cleaned FTO glass with a dropwise coating and followed by annealing at 450℃. To introduce a liquid electrolytes into the system, a Surlyn film (DuPont) was placed in between the two electrodes to form a sandwich structure and liquid electrolyte were injected through a hole using a vacuum pump. The synthesized quasi-solid state electrolytes (Si_EL) were placed in the middle of the photoanode and both electrodes pressed together with clips. The fabricated DSSCs were kept at room temperature and characterized after 24h. The cells with Si_ELs show an efficiency of 7.7%, 5.3%, 7.0%, 6.7%, 2.3%, and 4.9% respectively as shown in Figure 3 and their parameters are listed in Table 2.

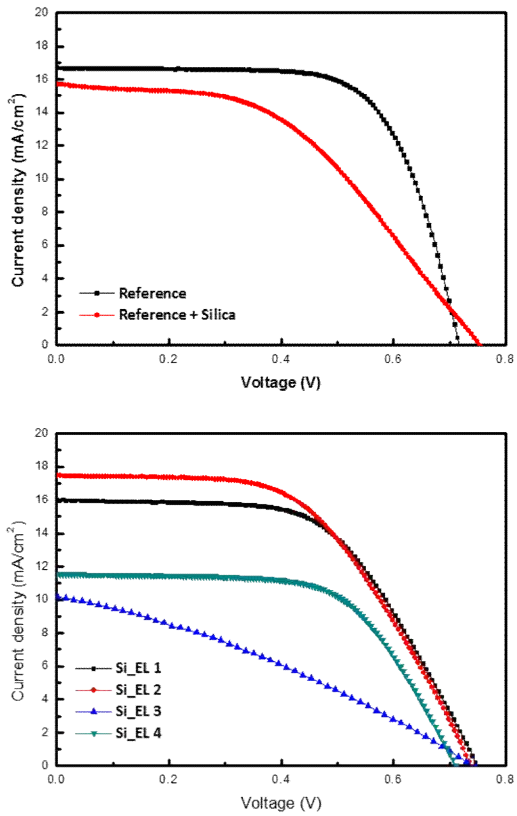


Figure 3. Photocurrent-voltage curves of the liquid electrolyte and silica electrolytes.

Table 2. Photovoltaic performance of the liquid electrolyte and silica electrolytes.

Electrolytes	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Eff (%)
Reference	0.71	16.7	64.6	7.7
(Silica only)	0.75	15.6	45.7	5.3
Si_EL 1	0.75	15.9	58.7	7.0
Si_EL 2	0.73	17.5	52.8	6.7
Si_EL 3	0.74	10.0	30.7	2.3
Si_EL 4	0.71	11.5	59.6	4.9

Figure 3. and Table 2. show the corresponding current-voltage characteristics for liquid and various Si_EL under AM 1.5 irradiation. At 1 sun illumination, the open circuit voltage (V_{oc}) of 0.71V and short circuit current (J_{sc}) of 16.7mA/cm2 were measured for the cell with a liquid electrolyte. As reported in Table 2, the gelled electrolyte by modified silica surprisingly shows that the photovoltaic of V_{oc} properties is improved. Despite a high V_{oc} value, the low J_{sc} and FF are obstacles to get high efficiency. To overcome these double edges, increasing J_{sc} with similar FF is necessary for the quasi-solid state electrolytes cells. As shown in figure 3, even though the gelled electrolytes without a reagent could get higher V_{oc}, internal series resistance was increased by silica nanoparticles and the FF was dramatically decreased with 45.7%. At the modified silica, Si_EL 1 and Si_EL 2 have shown the comparatively high efficiency of 7.0% and 6.7% with the quasi-solid state electrolytes. Although further investigation is required, the functional groups of silane reagents on silica may increase electron transfer through the functional groups. In addition, extra reagents of 3-(triethoxysilyl)propionitrile and Trimethoxy[3-(methylamino)propyl]silane could be transfered to the vacancy of TiO_2 surfaces where is not covered with dye molecules. These functional groups increased the electron density of TiO_2 surface and the electron recombination could be prevented from TiO_2 to electrolyte. In case of the Si_EL 2, by blocking the recombination, quasi-solid state electrolyte can reducing the electron leakage and J_{sc} can be increased with efficiency of 6.7%. However, the performance of DSSCs with the Si_EL4 and Si_EL5 electrolytes showed efficiency of 2.3% and 4.9%. The solidified electrolytes may increase the stability of the cells by prevent the leakage, however, they could not improve other photovoltaic properties. Be so much the worse it reduces the speed of electrons diffusion, the gelled electrolyte usually shows the low J_{sc} and FF than that of the liquid electrolyte. At this study, we have successfully synthesized the quasi-solid state electrolytes with various silane agents with proper chain length with similar viscosity.

In conclusion, we have successfully fabricated dye-sensitized solar cells with various quasi-solid state electrolytes. The simple method of solidifying electrolytes with different silane reagent-assisted silica nanoparticles were tested and well performed cells yield 7.0 and 6.7% efficiency at AM 1.5 condition with increased V_{oc} and J_{sc}. The aspect of FF requires further investigation but these result is very encouraging. Besides, the quasi-solid state electrolyte improved the cell stability with I^-/I_3^- redox couple and they will enable the fabrication of flexible, compact, laminated all solid-state devices free of leakage.

KEYWORDS: Dye-sensitized solar cells, electrolyte, silica nanoparticles, quasi-solid state.

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REFERENCES AND NOTES

1. B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737-740.
2. Y. Jo, J. Y. Cheon, J. Yu, H. Y. Jeong, C. H. Han, Y. Jun and S. H. Joo, *Chem. Commun*, 2012, **48**, 8057-8059.
3. M. Gratzel, Nature, 2001, **414**, 338-344.
4. M. Law, L. E. Greene, J. C. Johnson, R. Saykally and P. Yang, *Nat. Mater,* 2005, **4**, 455-459.
5. J. Lim, M. Lee, S. K. Balasingam, J. Kim, D. Kim and Y. Jun, *RSC Adv,* 2013, **3**, 4801.
6. C.-l. Jung, J. Lim, J.-H. Park, K.-H. Kim, C.-H. Han and Y. Jun, *RSC Adv*, 2013, **3**, 20488.
7. H.-S. Lee, S.-H. Bae, Y. Jo, K.-J. Kim, Y. Jun and

C.-H. Han, *Electrochim. Acta,* 2010, **55**, 7159-7165.

8. S. Jeon, Y. Jo, K. J. Kim, Y. Jun and C. H. Han, ACS *applied materials & interfaces,* 2011, **3**, 512-516.
9. W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida, *Chem. Commun*. 2002, 374-375.
10. R. Kawano and M. Watanabe, *Chem. Commun*. 2003, 330-331.
11. P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi and M. Gratzel, *Nat. Mater,* 2003, **2**, 402-407.
12. S. Cerneaux, S. M. Zakeeruddin, J. M. Pringle, Y. B. Cheng, M. Grätzel and L. Spiccia, *Adv. Funct. Mater.* 2007, **17**, 3200-3206.