COMMUNICATION

A quasi-solid-state dye-sensitized solar cell based on sol–gel derived *in situ* gelation of a siloxane hybrid electrolyte†

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A stable dye-sensitized solar cell (DSSC) was fabricated by a novel *in situ* gelation of the electrolyte. A highly condensed oligosiloxane gel was formed by sol–gel reaction of silane monomers. The oligosiloxane gel DSSC showed reduced charge recombination, and an efficiency of 5.8% with long-term stability.

Dye-sensitized solar cells (DSSCs) have attracted widespread attention as an alternative to conventional silicon-based solar cells due to their high efficiency, simple and cost-effective fabrication process.[1,2] Currently, a solar-to-electricity conversion efficiency of up to 12.3% has been achieved by employing a liquid electrolyte composed of cobalt based redox shuttles.[3,4] However, liquid electrolytes have disadvantages such as the evaporation and leakage of the solvent under practical long-term operation of devices.

In an effort to replace these electrolytes, less volatile gel electrolytes such as polymer gel electrolytes (PGEs),[5,6] room temperature ionic liquids (RTILs),[7–9] and hole transport materials (HTMs)[10] have been extensively studied. Among them, PGE can be simply made by gelation of a liquid electrolyte using polymers such as poly(ethylene glycol),[11] poly(vinylidene fluoride-*co*-hexafluoropropylene),[12] and poly(acrylonitrile-*co*-vinyl acetate).[13] A polymer matrix can effectively trap the liquid solvent, thereby inhibiting evaporation and offering a transfer channel for redox shuttles. On the other hand, polymers have a high molecular weight and require an elevated temperature for casting or injection into the cell, which results in poor interfacial contact between the electrolyte and TiO₂.[13,14] In response to these issues, *in situ* gelation has been studied, as it affords thermal stability and effective penetration of the electrolyte, thereby providing good cell performance. Meanwhile, several gel electrolytes, composed of nano-sized organic and inorganic components, have been fabricated by the sol–gel process.[15–18]

Building on these works, we introduced a novel *in situ* chemical gelation through the sol–gel reaction of silane monomers to form less volatile gel electrolytes for stable DSSCs (Fig. 1a). Moreover, we designed a highly condensed oligosiloxane structure near the TiO₂ surface to retard the recombination of electrons in the TiO₂ particles with redox shuttles. The oligosiloxane gel electrolyte (OGE) was synthesized by a non-hydrolytic sol–gel condensation reaction of 3,4-epoxy cyclohexylethyl trimethoxysilane (ECTS), 3,3,3-trifluoropropyl trimethoxysilane (FTMS), and diphenylsilanediol (DPSD) at 80 °C for 4 h. We aimed to synthesize a highly viscous gel electrolyte with no remaining water. Thus, DPSD containing hydroxyl (–OH) and bulky phenyl groups was selected as the precursor in order to promote a non-hydrolytic condensation reaction and form highly condensed oligosiloxane. We used FTMS for homogeneous mixing of iodide ions with silanes due to the polarity of the fluoro groups. In addition, ECTS was added to balance the polarity and prevent phase
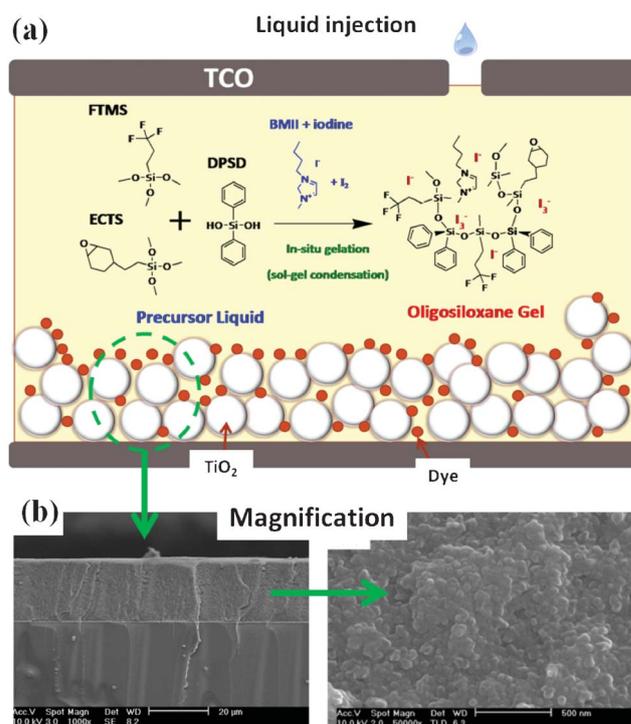

Fig. 1 (a) Scheme for the fabrication of the DSSC using an *in situ* sol–gel reaction of silane monomers in a pre-filled liquid electrolyte. (b) Cross-sectional scanning electron microscopy (SEM) images of the TiO₂ film containing the gelled oligosiloxane electrolyte.

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separation of iodide ions. The fabricated electrolyte was composed of 0.25 M ECTS, 0.75 M FTMS, 1.5 M DPSD, 0.7 M 1-butyl-3-methyl imidazolium iodide (BMII), 0.14 M I_2, 0.1 M lithium iodide (LiI), and 0.25 M 4-*tert*-butylpyridine (tBP) in 3-methoxypropionitrile (MPN). The composition of reference liquid electrolyte was 0.7 M BMII, 0.14 M I_2, 0.1 M LiI, and 0.25 M tBP in MPN. The silane composition (FTMS : ECTS : DPSD = 3 : 1 : 6) was optimized for the homogeneity of the mixed solution and the highest condensation degree of oligosiloxane. We used an increased content of I_2 compared with that of the reported liquid electrolyte. A high I_3^- content is needed for the best ionic conductivity and efficiency in the presence of the highly viscous oligosiloxane.

The DSSCs were fabricated using an electrode coated with a ruthenium dyed 12 μm TiO_2 film with a particle size of 20 nm. The liquid state nano-sized monomers can fully penetrate the TiO_2 pores and achieve intimate contact at room temperature. Through *in situ* gelation inside the cell at elevated temperature, the electrolyte became a highly viscous gel by formation of branched linear oligomers (Fig. S1†), containing I^-/I_3^- redox shuttles (Fig. S2†). Fig. 1b shows the cross-sectional SEM photographs of the TiO_2 particles filled with the OGE. After the pore filling and *in situ* gelation of the precursors, the internal nanoparticles were homogeneously covered with the gelled electrolyte. Also, the photocurrent of the fabricated DSSC using OGE increases with increasing TiO_2 thickness, which is consistent with the infiltration of the electrolyte. (Table S1†). Therefore, nano-sized oligomers were successfully formed inside the TiO_2 pores, promoting good interfacial contact between the TiO_2 and the electrolyte.[19]

Here, the FT-IR spectra were measured to confirm the formation of an oligosiloxane structure inside the gel electrolyte (Fig. 2a). The bands at 1212 and 1263 cm^{-1} are assigned to C–F (fluoro groups). The alkoxy groups (R'–Si(OR)$_3$) of FTMS and ECTS react with the silanol groups (Si–OH) of DPSD to form siloxane (Si–O–Si) bonds. The broad bands at $1020 \sim 1070$ cm^{-1} represent the siloxane network, which appears after the formation of an oligosiloxane gel electrolyte.[20] These results suggest that silane monomers were successfully condensed to siloxane oligomers in the presence of iodide ions.
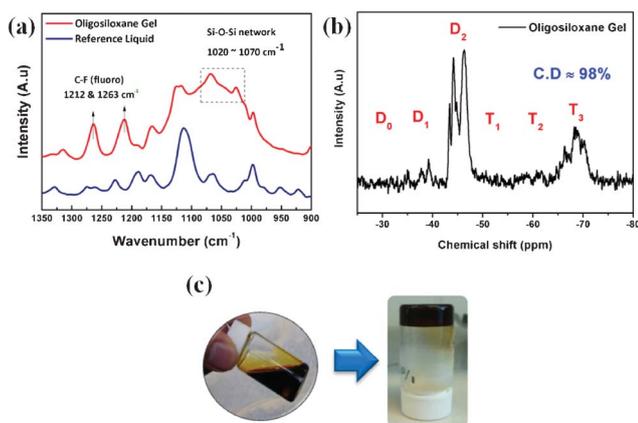
The formation of siloxane bonds and the high degree of condensation (98%) were also investigated using ^{29}Si NMR spectroscopy (Fig. 2b). The chemical shifts of the condensed trialkoxysilanes (R'–Si(OR)$_3$) were from -50 to -70 ppm, while the shifts of condensed diphenylsilandiol were from -29 to -47 ppm. Those are denoted by T^n and D^n, respectively, where n represents the number of siloxane bonds attached to a silicon atom. The OGE was characterized by two major D^2 and T^3 signals, which were assigned to Si species with no remaining methoxy (–OMe) groups, confirming that the condensation reaction of the silane monomers was fully carried out.[21,22]

Fig. 2c shows photographs of two vials containing the precursor liquid electrolyte (left) and the OGE (right). We obtained homogeneous and stable liquid state electrolytes by stirring the silane precursors, iodides, and additives in solvent. Thus, the electrolytes could effectively penetrate the TiO_2 film from the top surface. After the sol–gel reaction, the precursor liquid electrolyte became a viscous gel and showed little flow upon turning the vial upside down.

The photovoltaic parameters and J–V curves of the DSSCs using the liquid electrolytes and OGE are shown in Table 1 and Fig. 3.

The parameters of the DSSC employing the optimized OGE were 10.9 mA cm^{-2} (J_{sc}, short circuit current density), 0.79 V (V_{oc}, open circuit voltage), and 0.68 (FF, fill factor). We confirmed a reliable oligosiloxane gel state at fixed reaction conditions and obtained reproducible viscosity, redox shuttle formation and ionic conductivity, indicating consistent efficiency and parameters for each of the devices (Fig. S2,S3 and Table S2†). An optimized gel DSSC using a TiO_2 layer with a thickness of 12 μm showed the best conversion efficiency of 5.83% (Table S1†).

The limitation of the J_{sc} of the DSSC using the OGE was mainly owing to the retarded ion conduction imposed by the highly condensed Si–O–Si network. On the other hand, the V_{oc} of the oligosiloxane gel DSSC was significantly increased compared with that (0.71 V) of the liquid DSSCs. The increase in the V_{oc} is due to a shift in the conduction band caused by the presence of blocking materials near the TiO_2 surface. In general, the low triiodide mobility of the gel electrolyte causes a build-up near the TiO_2 and increases the probability of electron recombination. However, three dimensional oligosiloxane adsorbed on the TiO_2 surface suppresses the electron transfer from the conduction band of the TiO_2 to I_3^- in the electrolyte. This is because the highly condensed oligosiloxane structure inhibits the access of the redox shuttle to the bare TiO_2 surface and the bulky phenyl functional groups prevent molecular aggregation.[23–25] The fluoro groups also suppress the recombination due to their large electronegativity.[26] These combined effects lead to a reduced electron–hole recombination rate and an increased electron lifetime at the TiO_2/electrolyte interface, and thereby an improved V_{oc}.[24,25]

Fig. 2 (a) FT-IR spectra of the reference liquid (before gelation) and the oligosiloxane gel (after gelation) electrolyte. (b) ^{29}Si NMR spectra and condensation degree of the oilgosiloxane gel electrolyte. (c) Photographs of the precursor liquid electrolyte (left) and the oligosiloxane gel electrolyte (right) in a vial.

Table 1 Photovoltaic parameters of the DSSCs using the reference liquid, precursor liquid and oligosiloxane gel electrolyte measured at 25 °C under simulated air mass 1.5 global sunlight. The thickness and active area of the TiO_2 layers were 12 μm and 0.2 cm^2, respectively

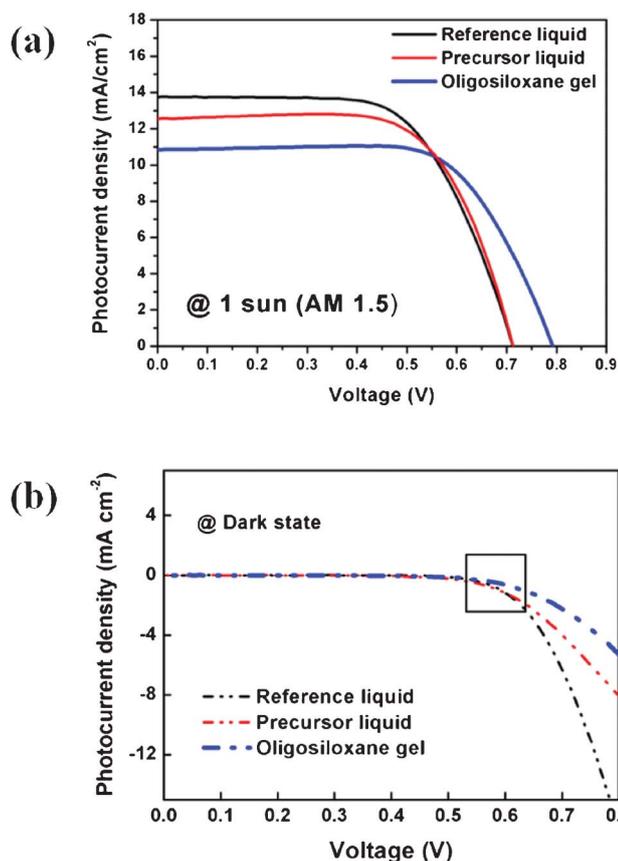| Electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	n (%)
Reference liquid	13.8	0.71	0.63	6.16
Precursor liquid	12.6	0.71	0.67	6.00
Oligosiloxane gel	10.9	0.79	0.68	5.83

Fig. 3 The photocurrent–voltage curve of the DSSCs using the reference liquid, precursor liquid and oligosiloxane gel electrolyte measured under (a) an illumination state and (b) a dark state.

Fig. 4 (a) Open circuit voltage decay measurement of the DSSCs using the reference liquid and the oligosiloxane gel electrolyte. (b) Variation of the normalized conversion efficiency of the DSSCs using the reference liquid and the oligosiloxane gel electrolyte at 50 °C in the dark sate convection oven.

Dark current–voltage analysis also supported the decreased interfacial charge recombination (Fig. 3b). The dark current onset of the oligosiloxane gel DSSC was shifted to a higher voltage compared to that of the liquid DSSC. Also, the dark current density of the DSSC using the oligosiloxane gel electrolyte was decreased, showing that the electron recombination was decreased. It shows a higher FF (0.68) than that of the liquid DSSCs, which is consistent with the low dark current of the oligosiloxane gel DSSC.[27] Therefore, the efficiency of the oligosiloxane gel DSSC (5.83%) was close to the efficiency of the DSSC (6.16%) using reference liquid electrolyte. Due to the enhanced electron liftetime as a result of the retarded electron recombination, the V_{oc} and FF increased and compensated for the drop in the J_{sc}.

Furthermore, we measured the open circuit voltage decay to compare the interfacial recombination rates between the oligosiloxane gel and the reference liquid DSSC. Each V_{oc} was measured under illumination and in a dark state over time. After the light was switched off, we could evaluate the V_{oc} decay rate, which is inversely proportional to the electron lifetime and thus proportional to the electron recombination. The decreased V_{oc} decay rate in the DSSC using OGE suggests a slow rate of electron recombination and a long electron lifetime at the TiO_2/electrolyte interface.[28,29] (Fig. 4a) The fluoro oligosiloxane matrix effectively reduced the electron recombination, playing a role similar to the polymer by acting as a barrier to decrease the interfacial back electron transfer.
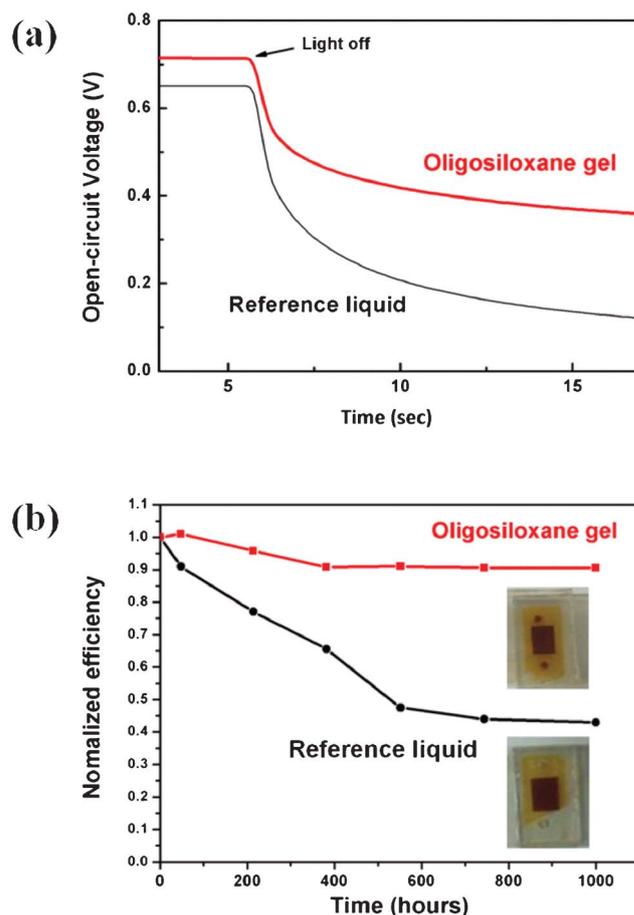
We have investigated the thermal stability of DSSCs (Fig. 4b). The oligosiloxane gel DSSC shows improved long-term stability compared to the reference liquid DSSC. However, the stability did not reach that of reported DSSCs using polymer gel electrolytes at high temperatures and light-soaking conditions. We consider that it is due to the nature of oligomer structure, which has a poorer solvent trapping effect compared to the highly cross-linked polymer structure with a high molecular weight. After 1000 h at 50 °C, the DSSC using the OGE maintained 91% of its initial efficiency, while the efficiency of the liquid DSSC gradually dropped due to a significant decrease in the J_{sc}, indicating solvent leakage at elevated temperatures. This result shows that the chemically bonded oligosiloxane matrix can efficiently trap the solvent, thereby inhibiting evaporation.

Conclusions

We fabricated a stable DSSC employing an oligosiloxane gel electrolyte by introducing a novel *in situ* gelation of a liquid electrolyte. The alkoxysilane monomers are capable of gelling the liquid electrolyte through a sol–gel reaction, resulting in effective infiltration and contact. The existence of a fluoro functional group and the formation of the three dimensional oligosiloxane structure in the gel electrolyte decreased the electron recombination rate at the

electrolyte/TiO$_2$ interface and thereby improved the V_{oc} and FF of the DSSC. Finally, a conversion efficiency of up to 5.83% was achieved with a good long-term stability.

Experimental

3,4-Epoxy cyclohexylethyl trimethoxysilane (ECTS, Aldrich), 3,3,3-trifluoropropyl trimethoxysilane (FTMS,TCI) and diphenylsilane-diol (DPSD, Gelest) were used as the silane precursors. Barium hydroxide monohydrate (BH, Aldrich) was added as a catalyst to promote a reaction. 1-Butyl-3-methyl imidazolium iodide (BMII, C-TRI), iodine (I$_2$, Aldrich), additives and solvent were mixed with the silane precursors in a vial by stirring the solution at room temperature for 6 h. An oligosilxane gel electrolyte was synthesized by a sol–gel condensation reaction of the silane precursors inside the mixed liquid electrolyte at 80 °C for 4 h.

Anatase TiO$_2$ particles were synthesized using a reported sol–gel method[30] and the diameter of the TiO$_2$ particles was adjusted to 20 nm. The synthesized TiO$_2$ particles were converted into a paste using an organic vehicle.[31] The paste was deposited on fluorine doped tin oxide (FTO) coated glass by the doctor blade method. The glass was heat treated at 550 °C for 30 min under an air atmosphere. The 12 μm TiO$_2$-coated FTO glass was immersed in an anhydrous ethanolic solution of 0.3 mM N719 dye (Solaronix SA) at room temperature for 24 h. A counter electrode was fabricated by spin-coating with 5 mM hydrogen hexachloro palatinate(IV) hydrate (H$_2$PtCl$_6$·H$_2$O) in 2-propanol, then annealed at 450 °C for 30 min. The electrode and counter electrode were sealed with a Surlyn (50 μm, Solaronix SA) under a pressure of 200 kPa cm^{-2} at 100 °C. The liquid electrolyte was injected into the space between the electrode and the Pt counter electrode through a pre-drilled hole at room temperature. The oligosiloxane gel DSSC was fabricated using *in situ* gelation by heating the cell inside an oven at 80 °C for 4 h. The hole was sealed with a cover glass heated onto Surlyn.

ATR IR spectra were measured using a Fourier transform infrared (FT-IR) spectrometer (Bruker) in the wavenumber range from 900 to 1350 cm^{-1}. ^{29}Si NMR spectra (Bruker FT 600 MHz) were measured with a sample consisting of 30 vol% of the oligosiloxane gel electrolyte in chloroform-d Chromium(III) acetyla-cetonate (CDCl$_3$). Cross-sectional SEM images of the TiO$_2$ electrodes were obtained using a scanning electron microscope (Phillips, xl30).

The photocurrent-voltage (*J–V*) characteristics of the cells were measured using a Keithley 2400 source meter using an AM 1.5 G solar simulator with a 1000 W xenon lamp (Oriel, 91 193) as a light source. The light intensity was adjusted with a reference solar cell composed of a crystalline Si capped with a KG-5 glass to 1 sun light intensity of 100 mW cm^{-2}. The V_{oc} was measured using a potentiostat/galvanostat (Gamry, Reference 600) and AM 1.5 G solar simulator with a 1000 W xenon lamp (Oriel, 91 : 193). The DSSCs operated under 1 sun light intensity and the V_{oc} was measured as a function of time. After few seconds, the light was turned off and the V_{oc} decay rate was measured as a function of time. To test the thermal stabilities of the cells, the precursor liquid and oligosiloxane gel DSSCs were stored in a dark state at 50 °C for 1000 h.

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