

Supplimentary Information for

Quasi-solid-state dye-sensitized solar cell based on sol-gel derived in-situ gelation of siloxane hybrid electrolyte

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Supplementary figures

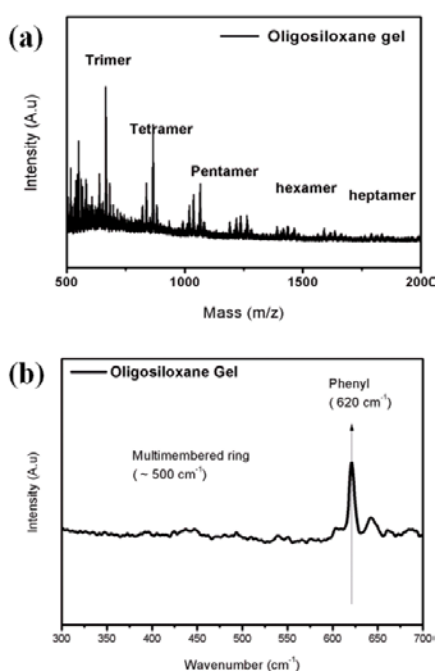


Fig. S1 (a) MALDI-TOF and (b) FT-Raman spectra of the sol-gel fluoro oligosiloxane gel electrolyte

In order to confirm the molecular weight distribution of the fluoro oligosiloxane inside gel electrolyte, MALDI-TOF (Matrix Assited Laser Desorption Ionization – Time of Flight) analysis was carried out (Fig. S1a). The oligosiloxane had a molecular weight in the range of 500~2000, which is assigned to oligomers (trimer ~ heptamer) made by condensation of silane monomers (ECTS, FTMS and DPSD). The pre-penetrated monomers were successfully condensed to oligomers inside nano-sized TiO₂ pores.

FT-Raman (RFS-100, Bruker) spectra were measured to confirm the molecular structure of the gel electrolyte. The band assigned to multi-membered ring structure of the oligosiloxane appeared in the broad range under 500 cm⁻¹, indicating there exists no cyclic structure inside the electrolyte (Fig. S1b). Therefore, the synthesized sol-gel fluoro oligosiloxane gel electrolyte has a branched linear structure.

Table S1. Effect of TiO₂ film thickness on photovoltaic characteristics of DSSC using oligosiloxane gel electrolyte.

TiO ₂ film thickness	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	efficiency (%)
8 μm	10.8	0.76	0.64	5.17
12 μm	10.9	0.79	0.68	5.83
16 μm	12.7	0.69	0.64	5.66
20 μm	13.1	0.63	0.58	4.80

We fabricated oligosiloxane gel DSSCs according to the TiO₂ film thickness. Then, I-V curves and photovoltaic parameters were measured (Table S1). The cell efficiency shows its highest value with 12 μm TiO₂ film. Because, J_{sc} increased according to the film thickness, while V_{oc} decreased.³⁰ Thus, we have to find an optimum film thickness for best cell efficiency. As an amount of dye attached on TiO₂ surface increased, J_{sc} and efficiency increased. However, above a certain thickness (>12 μm), electron diffusion length and recombination site also increased, resulting in a decreased V_{oc}.

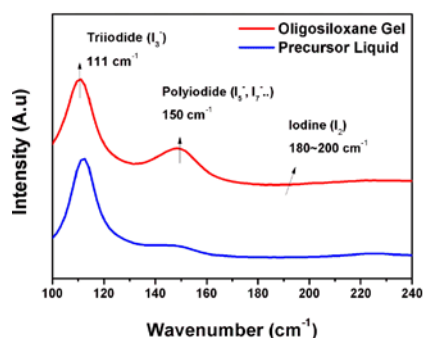


Fig. S2 Dispersive raman spectra of precursor liquid (before gelation) and oligosiloxane gel electrolyte (after gelation).

Dispersive Raman (LabRAM HR UV/Vis/NIR, Horiba Jobin Yvon) spectra of the OGE and liquid electrolyte was measured to confirm the formation of an I⁻/I₃⁻ redox couple (Fig. S2). The spectra were measured in the wavenumber range from 100 to 200 cm⁻¹ using Ar ion CW Laser (514.5 nm, 488 nm). The electrolytes present a band at 111 cm⁻¹, which is assigned to a symmetric stretch of I₃⁻ ions and another band at 150 cm⁻¹, which is assigned to I₅⁻ and polyiodide ions.^{S1,S2} These are attributed to the ease of formation of polyiodide species during the sol-gel condensation, due to the promoted ion dissociation with the polar fluoro group. In the gel state, the presence of highly concentrated polyiodides is important for effective charge transport by a Grothuss electron exchange mechanism. Meanwhile, non-ionized I₂ molecule (band around 180 ~ 200 cm⁻¹)^{S3} was not existed in the electrolyte.

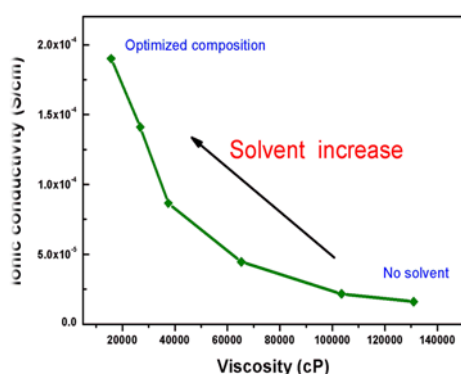


Figure S3. Ionic conductivity versus viscosity of the sol-gel fluoro oligosiloxane gel electrolyte according to the solvent content

Table S2. Viscosity and ionic conductivity of the reference liquid, precursor liquid and oligosiloxane gel electrolyte at fixed sol-gel reaction condition.

Electrolyte	Viscosity (cP)	Conductivity (S/cm)
Reference liquid	2.3	6.5×10^{-3}
Precursor liquid	28.5	4.0×10^{-3}
Oligosiloxane gel	15700	1.9×10^{-4}

Viscosity of the resin was measured by rheometer (RVDV-III+, Brook field) at 25 °C. Ionic conductivity of the resin was measured using conductivity meter (Cond 3210, WTW). The ionic conductivity and viscosity of the gel electrolyte was tunable by varying content of iodide and solvent (Fig. S3). Large amount of solvent promote an ion conduction, however excess solvent caused phase separation of the gel electrolyte. By increasing the iodide content, the conductivity reached its maximum value with 0.7 M of BMII and further increase in content lead a formation of ion pairing which reduces conductivity. The viscosity of the precursor liquid electrolyte (28.5 cP) increased drastically after the sol-gel condensation reaction (Table S2). An increase of viscosity in the gel electrolyte decreased diffusion coefficient of redox species which is related to the ionic conductivity. The ionic conductivity of OGE (1.9×10^{-4} S/cm) with an optimized solvent content was much lower than that of reference electrolyte (6.5×10^{-3} S/cm) due to its high viscosity (15700 cP).

References

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