

Electronic Supplementary Information

Improvements of photocurrent by using modified SiO₂ in the poly (ether urethane)/poly (ethylene oxide) polymer electrolyte for all-solid-state dye-sensitized solar cells

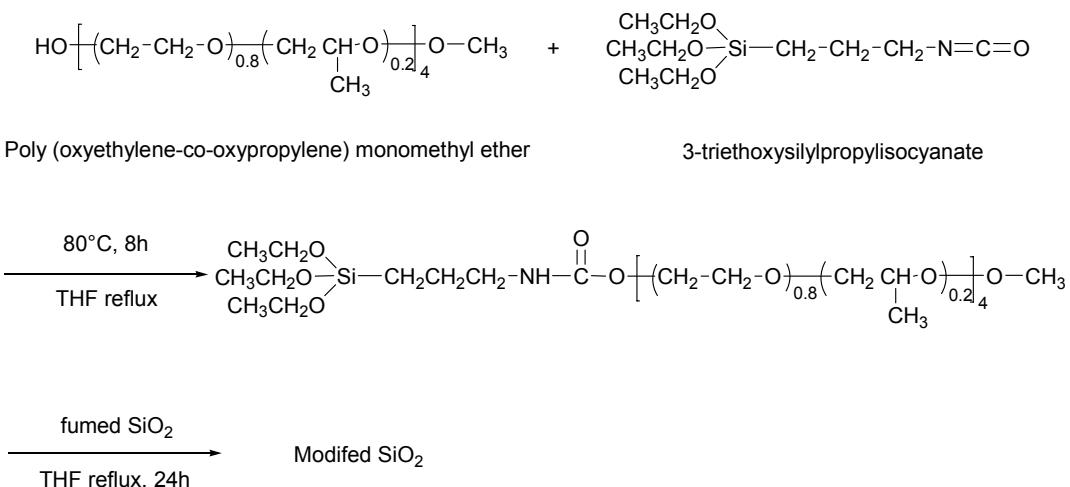
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Preparation of the polar polymer chain modified SiO₂

The detailed fabrication process is presented in Scheme S1. Poly (oxyethylene-co-oxypropylene) monomethyl ether (5g, 0.025mol) was dissolved in 50ml of dry tetrahydrofuran (THF) under N₂ atmosphere. After 6.18g (0.025mol) triethoxysilylpropylisocyanate was added, the mixture was stirred at 80°C for 8h. Then the solvent was removed using rotary evaporation to produce the reaction precursor which is referred to as A. 0.3 g A was then added into a suspension of 0.5g fumed SiO₂ in 50ml dry THF and the resulting mixture was refluxed for 24h. The silica was isolated by removing the excess solvent under vacuum. The obtained modified SiO₂ is referred to as M-SiO₂.



Scheme S1 Preparation process of modified SiO_2

The hydroxyl group on the surface of the nano SiO_2 can react with ethyl oxide group on the structure of precursor A under high temperature. We confirm this reaction through the FT-IR spectra of fumed SiO_2 and M- SiO_2 that presented in Figure S1. In the original SiO_2 nanoparticles, broad stretching band centered at 3417cm^{-1} can be ascribed to the hydroxyl bond (OH) groups. After reacting with A, this stretching band disappeared. The absence band indicated the removal of

surface OH and the replacement of flexible chain on the surface of SiO_2 . Another evidence for the modification of SiO_2 is the concomitant appearance of C=O band at 1722cm^{-1} on the spectrum of M- SiO_2 .

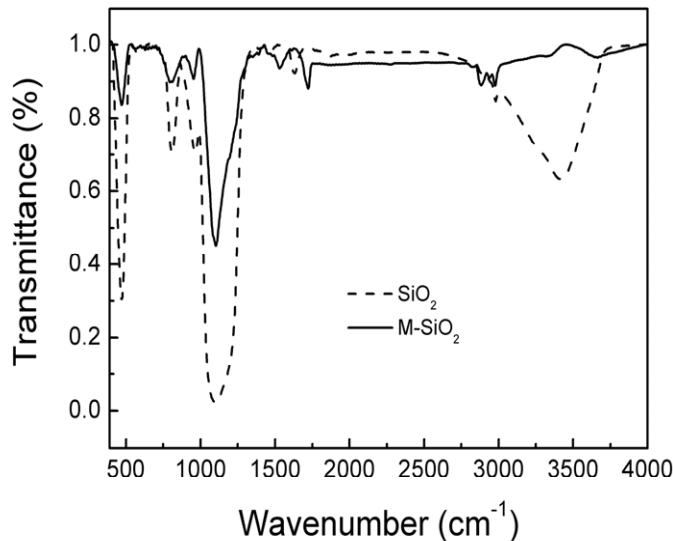


Fig S1 The FTIR spectrums of fumed SiO_2 and M- SiO_2

Preparation of oligomer based PEUR and polymer blend electrolytes

Poly(ether urethane) was synthesized by a two-stage route. In the first stage, PEG 400 was degassed under vacuum at 80°C for 5h. Then the obtained PEG400 (10g, 0.025mol) reacted with an excess 2,4-Diisocyanatotoluene(TDI) (5.24g, 0.03mol) for 2h to form an isocyanate-terminated PEUR prepolymer. In the second stage, the PEUR prepolymer was poured into excess ethanol at room temperature. The mixture was blended uniformly and kept stirring overnight. After removing the excess ethanol by rotary evaporation, the compound was dried under vacuum for 6h at 80°C to get the PEUR compound. The average molecular weight (M_n) of such prepared PEUR was determined to be 7100 and the polydispersity index is 2.57.

For the solid-state-electrolyte preparation, the polymer-blend solution was prepared by mixing 0.264g PEO /PEUR (w:w=5:5) and 4ml acetonitrile under continuous stirring. After 8h, an acetonitrile solution of I^-/I_3^- redox-couple (0.095g LiI, 0.018g I_2) was slowly introduced. Nanocomposite polymer electrolytes were prepared by adding the different amount of SiO_2 and M- SiO_2 into the polymer-blend solution. The solid-state polymer electrolyte membranes were prepared by casting the polymer-blend solutions on teflon planes, which were placed under ventilation for 24h and further dried in a vacuum oven at 40°C for another 24h to completely remove the residue solvent.

Cell assembly

For solar cell fabrication, a polymer electrolyte solution was cast onto a dye sensitized porous TiO_2 electrode and evaporated very slowly for easy penetration of electrolytes through the

nano pores of TiO_2 thin film. The same process was repeated for several times to ensure the good filling into TiO_2 electrodes. Then both the TiO_2 electrode and Pt loaded counter electrode were superposed together and then pressed to get a more compact contact. The cells were placed under ventilation for 24h and further dried in a vacuum oven at 40°C for another 24h to completely remove the residue solvent.

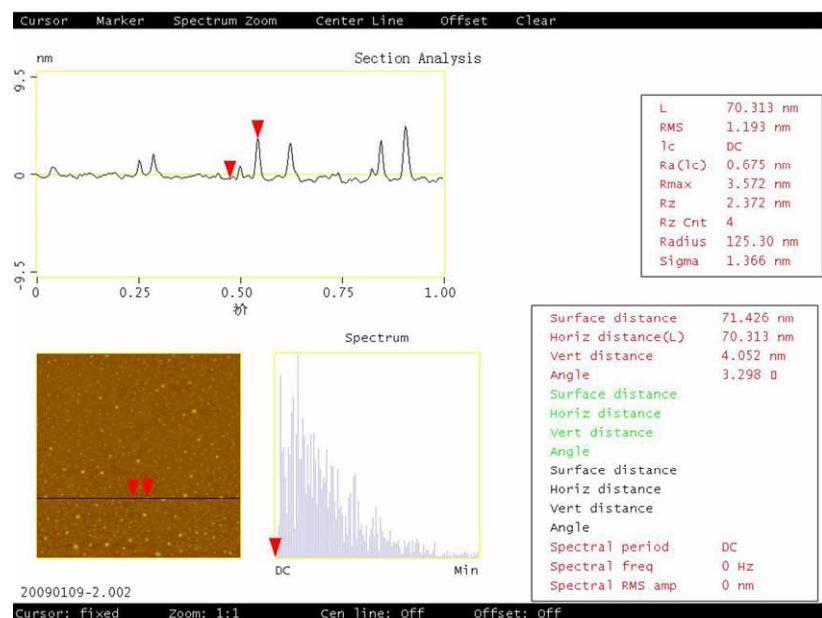


Fig S2 AFM height distribution images of M-SiO₂ based nanocomposite polymer electrolyte.

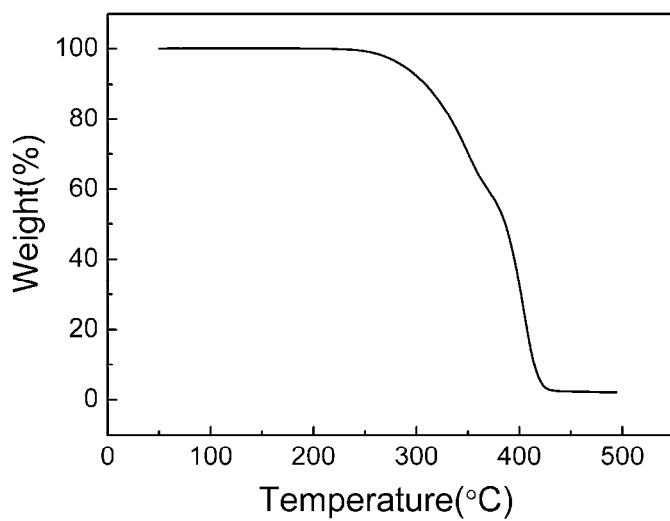


Fig.S3 TGA curves of polymer matrix. The polymer sample was prepared completely according to way our assembling solid-state devices.

TGA analysis of polymer matrix was represented in Fig S3, and the sample was prepared completely according to way our assembling solid-state devices. Nearly no weight loss was

observed below 250°C in the TGA curves, indicating the completely removal of acetonitrile in the preparation process. Also, the cleavage temperature as high as 250°C indicates the thermostability of PEUR/PEO blend compound, which is favourable for the commercial application.