Electronic Supplementary Information

Amphiphilic-Like SiO_2 Nanoparticles@Nafion Proton Exchange Membrane with Excellent Fuel Cell Performance

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Experimental Details

Synthesis of fluoroalkyl modified SiO_2. In a typical synthesis, 300 µL ammonia was added into 5 mL ethanol followed by addition of 1 mL tetraethyl orthosilicate (TEOS). TEOS was allowed to hydrolyzed and condensed for a certain period (e. g., 24 h). 100 uL fluoroalkyl silane, 1H, 1H, 2H, 2H, -perfluorooctyl triethoxysilane, was then injected into the mixture, which was further allowed to react for the surface functionalization. The obtained SiO_2-fluoroalkyl (hereafter denoted as SiO_2-F) nanoparticles were collected by centrifugation at 8000 rpm 5 min, and washed by several times, and dried at 70 ºC for overnight.

Preparation of SiO_2-F@Nafion nanocomposite membrane. Sulfonic perfluoro polymer resin solution (Nafion-117®, 5 wt%, Aldrich, 5 g) was placed in a ventilation hood at 50 ºC to remove the solvent (iso-propanol, n-propanol and water). The solid SPFP of 0.25 g obtained was re-dissolved in N, N-dimethylacetamide (DMAc) (99%, Aldrich, 5ml) solvent to formulate a 5 wt% solution. A 5 wt% of fluoroalkyl modified SiO_2 nanoparticles was introduced into the solution and mixed uniformly with the aid of ultrasonication. The resulting solution (ca. 5ml) was cast in a Petri dish (d = 6 cm). The dish was then placed in an oven at 60 ºC for 3h to allow the formation of a solid membrane, and then the temperature was increased to 120 ºC for another 3 h to undertake curing of the composite membrane in the air. The pure SPFP membrane was also prepared using the same procedure. The thicknesses of all the membrane samples were 60 ± 1 µm.

Material characterization. The morphology and microstructure of the synthesized SiO_2 nanoparticles were characterized by field emission electron microscopy (FESEM, Zeiss) and transmission electron microscopy (TEM, JEOL 2010). Fourier transform infrared (FTIR) spectra were collected via Cary 660 FTIR spectrometer by 64 scans with anominal resolution of 1 cm^{-1}. XPS analysis was conducted using a Kratos Axis Ultra X-ray photoelectron spectroscopy (Kratos Analytical) with a momochromated Al K_α source (1486.5 eV) under the chamber pressure of 10^{-9} torr, where the elemental scans were based on 20 meV pass energy. The dynamic mechanical analysis (DMA) was performed on a TA Instruments (DMA 2980) using a heating rate of 3 ºC·min^{-1} and a vibration frequency of 1 Hz.

Evaluation of electrochemical properties. To evaluate the performance of the membranes in fuel cell, a single cell was operated at 1 bar for both H_2 and O_2 without humidification. Before the membrane-electrolyte assembly (MEA) was prepared, the membrane was placed in de-ionized water at 80 °C for 30 min and washed by de-ionized water for one time in order to remove sulfuric acid remains in the membrane. The MEA was prepared by sandwiching the membrane, saturated with 1M sulfuric acid solution, between an anode and a cathode sheet. The MEA was then cold pressed by screwing it in two flat steel plates to assure sufficient contact. The anode and cathode sheet were a carbon paper (SGL, Germany) with carbon-supported 20 wt% Pt catalyst layer supplied by E-TEK, Natick, MA. The catalyst loadings at the anode

and cathode were 2 $mg \cdot cm^{-2}$, thus Pt loadings at the anode and cathode were 0.4 $mg \cdot cm^{-2}$. The effective electrode area was 2 cm^2. The H_2 and O_2 flow rates were regulated at 50 $cm^3 \cdot min^{-1}$. The electrode polarization curve was obtained by setting a series of cell current and recording the corresponding cell voltages.

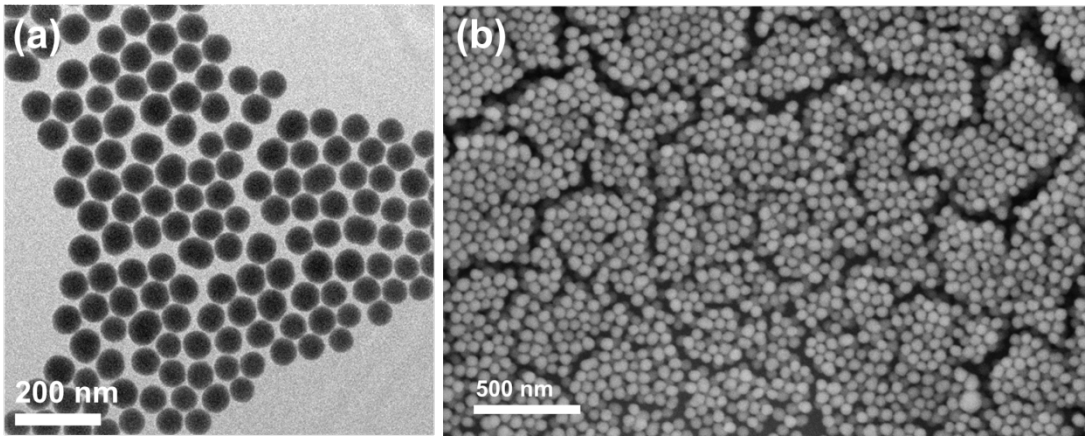

Figure S1. (a) TEM and (b) SEM images of the unmodified SiO_2 nanoparticles.

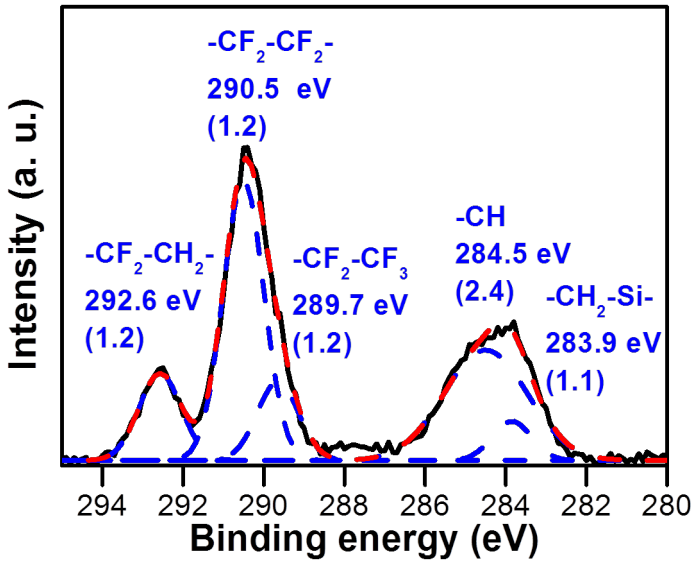

Figure S2. XPS spectrum of the SiO_2-F nanoparticles for C1*s* peaks, where the contribution from each individual peak is described by the dashed line.

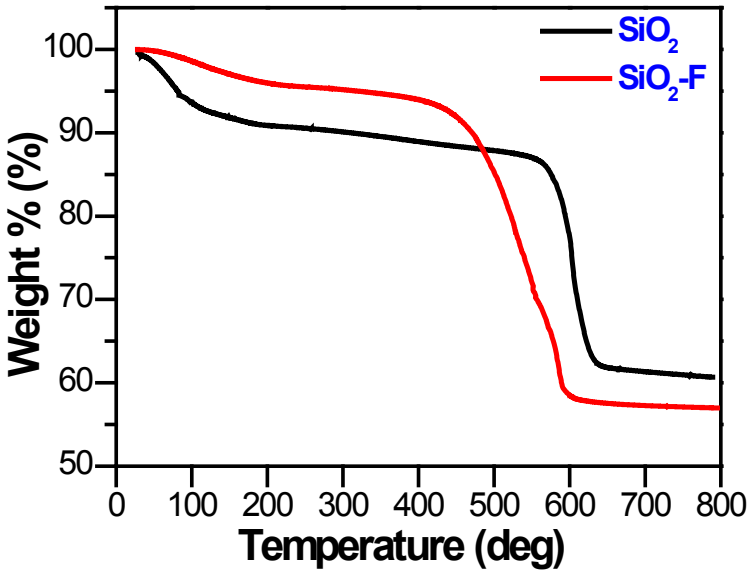

Figure S3. TGA curves for the SiO_2-F and SiO_2 nanoparticles.

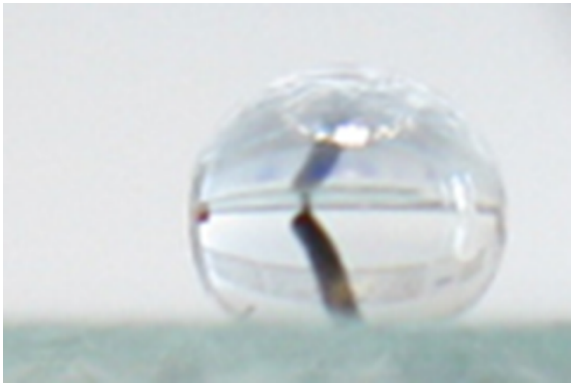

Figure S4. Water droplet (15 μL) on the surface of the SiO_2-F coated glass slide showing the superhydrophobicity.

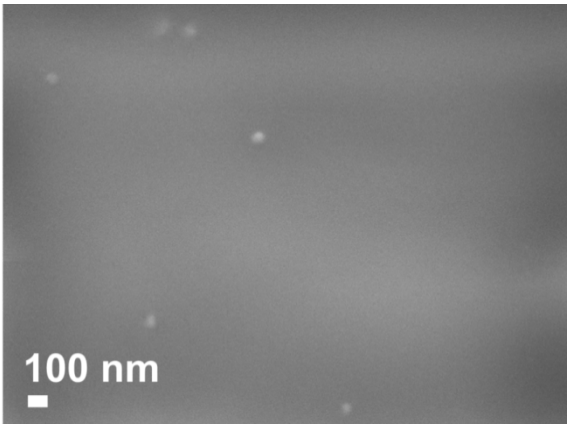

Figure S5. A HRSEM image for the SiO_2-F@Nafion membrane.

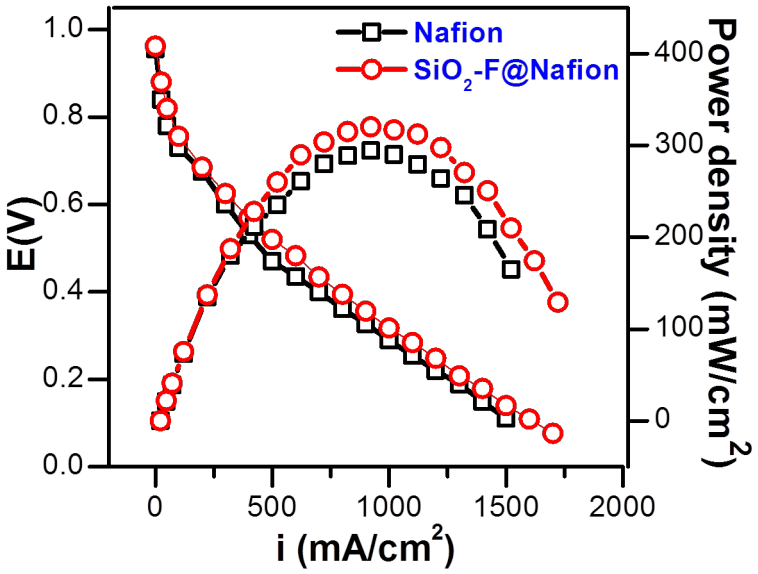

Figure S6. The polarization curves and power outputs for the SiO_2-F@Nafion and Nafion proton conduction membrane at 25 °C.

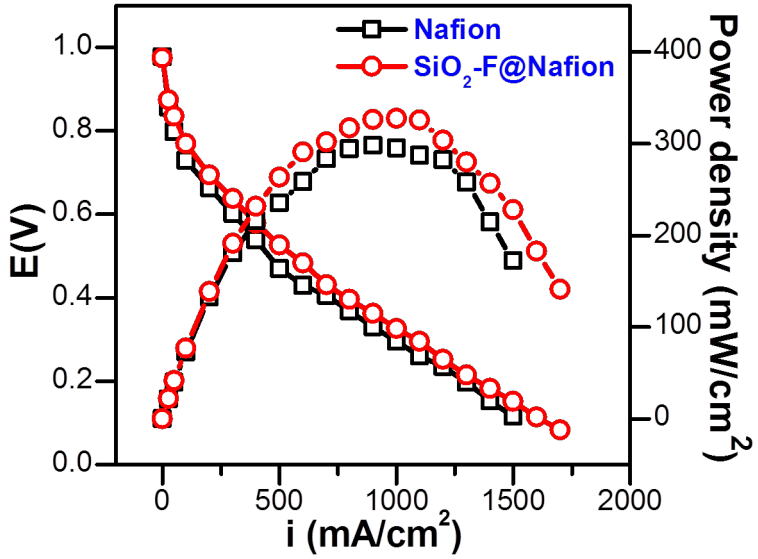

Figure S7. The polarization curves and power outputs for the SiO_2-F@Nafion and Nafion proton conduction membrane after running for 48 h at 25 °C.

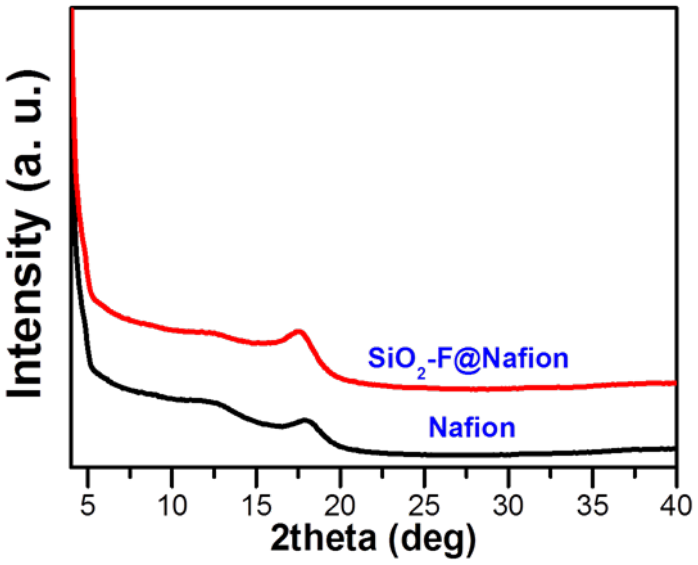

Figure S8. Wide angle X-ray diffraction patterns of the Nafion and SiO_2-F@Nafion membranes. The diffraction peak corresponding to the crystalline perfluoro domains sharped with the addition of SiO_2-F, i.e., the decreasing FWHM from 1.98 to 1.71 °, which indicates larger crystalline sizes in the SiO_2-F@Nafion membrane. Also, this diffraction peak shifted towards lower angle, which indicates a larger lattice spacing for the crystalline domains in the SiO_2-F@Nafion membrane.

Table S1. Comparison of cell performance of various SiO_2@Nafion proton conducting membranes.

Proton conduction membrane	Thickness (μm)	Operation condition	Conductivity ($S \cdot cm^{-1}$)	Output power intensity ($mW \cdot cm^{-2}$)	Reference
SiO_2-F@Nafion	60 ± 1	80 °C, 100 kPa, No humidification		~580 at 1400 $mA \cdot cm^{-2}$	this work
SiO_2@Nafion 115	~ 120	110 °C,	0.0107	320 at ~300 $mA \cdot cm^{-2}$	Ref 1
SiO_2-phosphotungstic acid@Nafion 115	~ 120	1.3 kPa, 70% RH	0.0267	540 at ~520 $mA \cdot cm^{-2}$	
SiO_2@Nafion 112	73	95 °C, 90% RH	~ 0.01	~ 40 at 60 $mA \cdot cm^{-2}$	Ref 2
SiO_2@Nafion	-	110 °C, 300 kPa 59% RH,	~ 4.2	~ 375 at 600 $mA \cdot cm^{-2}$	Ref 3
Mesoporous SiO2-phosphoric acid@Nafion	220	190 °C, no humidification	~ 0.06	689 at ~ 1600 $mA \cdot cm^{-2}$	Ref 4
		110 °C,		~ 75 at ~ 300	

	no humidification	$mA \cdot cm^{-2}$

Table S2. Fitting results from deconvolution on C1*s* and O1*s* XPS peaks of Nafion and SiO_2-F@Nafion.

	Nafion			SiO_2-F@Nafion		
Peak	Position (eV)	FWHM (eV)	Area percentage (%)	Position (eV)	FWHM (eV)	Area percentage (%)
-CH	284.9	1.1	31.6	285.2	1.1	45.9
-CO	286.3	2.3	9.5	286.5	2.1	16.8
-CS	289.6	2.3	4.2	289.4	2.1	6.3
$-CF_2$	292.0	1.1	42.9	292.1	1.2	24.9
$-CF_3$	293.5	1.6	11.8	293.7	1.7	6.1
-OS/OH	533.0	1.9	59.7	532.9	2.1	82.6
-OC	535.7	1.7	40.3	535.7	1.8	17.4

References

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