# **Supporting Information**

# Engineering of Interfacial Energy Bands for Synthesis of Photoluminescent 0D/2D Coupled MOF Heterostructure with Enhanced Selectivity Towards Proton Exchange Membrane

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# 1. Experimental

# 1.1 Synthesis of Graphite Oxide (GO)

Modified Hummers' method was adapted for preparation of graphite oxide (GO).<sup>1</sup> Accordingly, mixture of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 63 mL) and orthophosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 7 mL) were added to pure graphite flakes (500 mg) and stirred for 30 minutes in an ice bath. This was followed by slow addition of potassium permanganate (KMnO<sub>4</sub>, 3g) and stirred for 30-40 minutes. The mixture was then kept overnight in an oil bath at 323 K. Subsequently, deionized water (DI, 150 mL) was added to the solution, and was kept for 30 minutes in an ice bath, followed by addition of 10 mL of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) accompanied with continuous stirring. The solid was centrifuged and washed successively with 10% hydrochloric acid (HCl) solution for complete removal of sulphate ions and water. The viscous suspension was dried at 323 K under vacuum for 24 h (**Fig. S1**).

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# 1.2 Synthesis of UiO-66

UiO-66 was prepared by solvothermal method according to previously established procedure.<sup>2</sup> In the usual synthesis, BDC (0.983 g) and  $ZrCl_4$  (1.00 g) were dissolved in DMF acidified by HCl. The solution was then transferred to a Teflon-lined stainless steel autoclave and kept in a vacuum oven at 80 °C for 24 h to attain homogenous reaction. The obtained powder was then centrifuged at 12000 rpm and washed with DMF and ethanol to remove any unreacted molecules. It was then dried at 80°C.



Figure S1. Synthesised GO, Pd-GO, UiO-66 and UiO-66/Pd-GO

# **1.3 Sulfonation of PEEK**

The PEEK polymer was sulfonated by adding 5g of PEEK gradually in 98% concentrated  $H_2SO_4$  solution (100 mL) and it was stirred for 5 h using a magnetic stirrer at 323K. The precipitated polymer was then taken and put in ice-cold water and was left to settle overnight (**Fig. S2**). The precipitated SPEEK formed white noodle-like strands. Several filtrations and washing were performed with deionized water to bring the pH to neutral. This was then dried in a vacuum oven for one week at 60 °C.<sup>3</sup>



Figure S2. Schematic representation of sulfonation of PEEK and fabrication of SPEEK membrane.

# 2. Characterization technique

The X-ray diffractometer (XRD, Bruker, D8 Advance) spectra giving out Cu Kα Radiation (power 40kV, 40mA) was used for studying the crystallography of the prepared membranes. The transmission electron microscope (JEOL JEM 2100F) and Field Emission Scanning Electron Microscope (FESEM, Zeiss, Sigma) were used for analysing the surface morphology. The surface chemical composition was characterized by X-Ray electron spectroscopy (XPS) and Fourier Transform Infrared Spectra (FTIR, 4000-400 cm<sup>-1</sup>). Thermogravimetric analysis (Shimadzu TGA-50) was used to study the thermal stability of the samples. The samples were subjected to a heat under N<sub>2</sub> atmosphere, beginning at 30 °C ranging to 800 °C in intervals of 10 °C/min. UV Vis Spectrophotometer (Model No.: UV-2600, Make: Shimadzu, Singapore) has used to measure the light absorption. The photoluminescence (PL) spectra of the samples were performed at 290 nm excitation wavelength using a spectrofluorometer (PerkinElmer, LS 45). Measurement technique of water uptake and ion exchange capacity of fabricated membrane has been described in the supporting information.

#### 2.1 Photo-electrochemical Analysis

The Pristine MOF and the composites were coated on ITO (indium tin oxide) substrate (Sigma Aldrich, India) via spin coating (SpinNXG-P1, Apex Instruments, India). About 10 mg of the samples was dispersed in a solution of isopropanol and Nafion (binder; 0.5 wt. %) and then spin coated at 2000 rpm for 10 s on the ITO substrate [devipriya]. The solvent was removed by drying at room temperature. The photocurrent experiments were performed using a Potentiostat/Galvanostat (AUTOLAB 302N, Metrohm Autolab B.V, Netherlands) equipped with a three-electrode system. Ag/AgCl (3 M KCl), platinum wire, and ITO coated with samples were taken as the reference, counter and working electrodes. 0.5 (M) Na<sub>2</sub>SO<sub>4</sub> solution was taken as the electrolyte. The photocurrent analysis was performed upon illuminating with 500 W halogen lamp in on-off mode. The EIS measurements were performed in the same system by varying frequency from 0.1 to  $10^5$  Hz. The Mott-Schottky analysis was obtained at 10 kHz frequency in the range 0.0 to -1.4 V vs. Ag/AgCl. The dissolved oxygen was removed from the system by purging N<sub>2</sub> gas prior to each experiment.

#### 2.2 Water Uptake

The water uptake of the membrane was calculated using below equation.<sup>4</sup>

Water uptake (%) = 
$$\frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\%$$
 (1)

Where  $m_{dry}$  and  $m_{wet}$  are the mass of the dry membrane and mass of the wet membrane after being completely submerged in water for 24 h. The excess water was carefully wiped off the membrane surface with the help of a tissue-paper.

#### 2.3 Ion Exchange Capacity

The number of counter-ions that are exchangeable in the SPEEK membrane are measured by IEC. For this, 1M HCl was used to dip the membrane for 24h, after it was cut. This was done to protonize the membrane. The excess acid was thoroughly washed with an abundant supply of water. Furthermore, a 2M NaCl solution was used to dip the solution completely for 24 h in order to facilitate the Sodium-proton ion exchange. A 0.1M NaOH solution was used for titrating the solution, post the removal of the membrane. A phenolphthalein indicator was used for the purpose. Below mentioned equation was used for calculating the IEC:<sup>5</sup>

$$IEC = \frac{C_{NaOH} \times V_{NaOH}}{W_d}$$
(2)

Where,  $C_{NaOH}$  is the concentration NaOH solution,  $V_{NaOH}$  is the volume of NaOH used in the titration and  $W_d$  is the weight of the dry membrane.

#### 2.4 Methanol Permeability

The opposition offered against methanol crossover by the membranes was analyzed by evaluating the methanol permeability in the membranes. A glass cell setup was structured which consisted of two identical glass chambers. The membrane (7 cm<sup>2</sup> area) was placed in between the compartments and securely clenched with clamps (**Fig. S3**). The two compartments in the glass setup were namely the "feed" section and the "permeate" section. 5M methanol was poured as the "feed" whereas 250 ml of distilled water was enforced into the "permeate" section. The chambers were mechanically stirred at 110-120 rpm. This permeation experiment was carried out under room temperature. Samples from the "permeate" section were collected and recorded on an hourly basis for 24 hours. The samples were then tested under the High Performance Liquid Chromatography (Prominence HPLC, Shimadzu) setup. The area under the methanol peak obtained from the HPLC chromatogram was observed to deduce the methanol concentration of the samples. Below equation was used for calculating the membrane permeability.<sup>4</sup>

$$P = \frac{\kappa \times V \times L}{A \times C}$$
(3)

Where, k is the slope of the curve between concentration of methanol on the water side and corresponding methanol permeation time, V is the initial Volume of the deionized water, L denote the thickness of the membrane, A is the Area of the membrane and C indicates the initial concentration of methanol.



Figure S3. Schematic of methanol permeability setup

#### **2.5 Proton Conductivity**

The AutoLab PGSTAT204 system was used for the measurement of conductivity ( $\sigma$ ). The protonation was allowed to take place by allowing the membrane to be immersed in 1M H<sub>2</sub>SO<sub>4</sub> solution for 24h, following which the excess acid was thoroughly washed off with deionized water. The single cell system that was used for the ion conductivity measurement has a dimension of 2 cm × 2.5 cm. The 5 cm<sup>2</sup> membranes were kept in water for 24 h prior to being sandwiched between the Cu electrodes of the system. The impedance measurement was carried out under a frequency ranging from 1 Hz to 1 MHz. Below equation was used for calculating the conductivity.<sup>4</sup>

$$\sigma = \frac{L}{R A} \tag{4}$$

Where, A is the area of the membranes, L is the thickness of the membranes and R indicates the resistance obtained from Impedance data.

The selectivity is calculated using the ratio of their ionic conductivity ( $\sigma$  in S cm<sup>-1</sup>) and methanol permeability (P in cm<sup>2</sup> s<sup>-1</sup>) i.e

$$S = \frac{\sigma}{P} \tag{5}$$

A higher selectivity is favorable for an efficient DMFC functioning.

#### 3. Results and Discussion

EDX mapping analysis (**Fig. S4**) of GO shows homogeneous distribution of C and O element on the surface of GO sheet.

EDS Layered Image 5



Figure S4. EDX elemental mapping analysis mapping of GO sheet.

EDX mapping analysis (**Fig. S5**) of Pd-GO shows homogeneous distribution of C , O and Pd element on the surface of Pd-GO sheet.

EDS Layered Image 1



Figure S5. EDX elemental mapping analysis mapping of Pd-GO.



Figure S6. AFM analysis of UiO-66 and UiO-66-Pd-GO composite

The FESEM images for the internal structures of the pure and composite membranes are shown in **Fig. S7.** The newly synthesized UiO-66/Pd-GO mixed SPEEK membrane showed the presence of UiO-66/Pd-GO on the surface of SPEEK. However, the surface of the SPEEK/UiO-66/Pd-GO shows more roughness in nature. The mutual interactions between the SPEEK and UiO-66/Pd-GO nanosheets may be a possible reason for this roughness. The hydrophobic nature and the strong interparticle interactions of the composites makes it particularly difficult to achieve a uniform dispersion.<sup>6</sup> However, a uniform dispersion was seen in the case of UiO-66/Pd-GO particles induced in SPEEK membranes because of the unique hybrid structure of the GO sheets.



Figure S7. FESEM images of (a-b) top surface and (c-d) cross-section of SPEEK and SPEEK/UiO-66/Pd-GO

The energy dispersive X-ray spectroscopy (EDS) mapping (**Fig. S8**) confirms the presence of palladium, zirconium, carbon and oxygen in UiO-Pd-GO composite.

Electron Image 3 C 25µm 25µm Pd 25µm 25µm

Figure S8. EDX elemental mapping analysis mapping of UiO-66/Pd-GO composite.

The energy dispersive X-ray spectroscopy (EDS) mapping (**Fig. S9**) confirms the presence of surfer, palladium, zirconium, carbon and oxygen in SPEE/UiO-Pd-GO composite membrane and all elements are found to be well distributed on the surface of the composite membrane.



Figure S9. EDX elemental mapping analysis mapping of UiO-66/Pd-GO composite membrane.

**Fig. S10** represent the XRD analysis of SPEEK and SPEEK/UiO-66/GO composite membrane. It is can be seen from the figure UiO-66/GO composite membrane shows a strong peak 5<sup>°</sup> and 6.8<sup>°</sup> which is corresponding to the (111) and (002) characteristic peaks from UiO-66. Pure SPEEK membrane exhibited a broad peak on  $18.9^{\circ}$  which is sifted to the high value of  $2\theta$  (21.2<sup>°</sup>) after adding of UiO-66/GO composite.<sup>7</sup> This behaviour of mixed membrane indicates

a strong filler-polymer interaction and also the well dispersion capability of MOF-GO composite with higher specific area.



Figure S10. XRD patterns of SPEEK and SPEEK/UiO-66/Pd-GO composite membrane.

**Fig. S11** shows the FTIR spectra of synthesized composites. The FTIR studies of GO showed peaks at 1393 cm<sup>-1</sup> (stretching vibrations from C-O), at 1742 cm<sup>-1</sup> (stretching vibrations from C=O), at 1632 cm<sup>-1</sup> (stretching vibrations from C=C), 1046 cm<sup>-1</sup> (stretching vibrations from C-O-C) and 3420 cm<sup>-1</sup> (stretching vibrations from -OH). These peaks indicated the presence of functional groups which confirmed the successful oxidation of graphite.<sup>1</sup> In case Pd-GO, all the peak for GO has been found but the peak for C=O at 1742 cm<sup>-1</sup> is shifted to the 1729 cm<sup>-1</sup>. The H-bonding to the carbonyl may be observed by a shift of the C=O stretching mode (decrease of the wavenumber), but the change may be small depending of the interaction.<sup>8,9</sup> The stretching and vibration of C=O bond from the carboxylic acid group causes the weak peak at 1658 cm<sup>-1</sup>, while the asymmetric stretching of the O-C-O group forms the strong band at 1581

cm<sup>-1</sup>. The weak peak at 1505 cm<sup>-1</sup> is attributed to the stretching vibrations of the unsaturated carbon (C=C) in the benzene rings of the BDC ligand, while the strong peak at 1398 cm<sup>-1</sup> is formed by the symmetric stretching of C=O carboxylic acid.<sup>10</sup> The C-H bond's vibrations cause the small peaks at 813 cm<sup>-1</sup> and 753 cm<sup>-1</sup>, whereas the peak at 664 cm<sup>-1</sup> corresponds to the vibrations of the O-H bending. The FTIR spectra of the UiO-66 and the UiO-66-Pd-GO composites are similar, indicating no structural changes during the in-situ growth.



Figure S11. FTIR patterns of GO, Pd-GO, UiO-66 and UiO-66-Pd-GO

Further to verify the inducement effect of sulfonation with quantitative analysis, XPS was performed in the range of 0-700 eV (**Fig. S12**). From the survey scan of SPEEK membrane, three significant spectra perceived were C1s, O1s and s2p. C1s and O1s peaks arise (**Fig. S12a**). The peak attributed in the range of 165 eV to 170 eV (**Fig. S12b**) is due to the s2p orbital from

sulfur in  $-SO_3H$  groups group.<sup>11</sup> After deconvolution of C 1s spectrum, three major peaks at the binding energies of 284.8 eV, 286.7 eV and 289.2 eV has arisen which is corresponds to C atoms with sp2 hybridization, C-O from ether groups and carbon atom in the carbonyl group. There are also two different oxygen environments which are C=O (532.7 eV) and C-OH (533.9 eV). We found the elemental composition of sulfur in the membrane SPEEK is 1.79%.



**Figure S12.** (a) The wide survey scans of SPEEK membrane with high-resolution spectra of (b) S2p, (c) C1s and (d) O1s.

Further XPS analysis was performed to determine the inducement effect of UiO-66/Pd-GO composite in SPEEK membrane (**Fig. S13**). SPEEK membrane generally shows a peak around 168 eV due the presence of sulfur group from  $-SO_3H$  groups<sup>12</sup> but in this case two new small hump arises at 184 eV and 334 ev, which corresponds to Pd 2d (**Fig. S13b**) and Zr 3d (**Fig. S13c**), respectively. The presence of Zr and Pd demonstrated that the UiO-66/Pd-GO composite was successfully doped into the SPEEK membrane.



**Figure S13.** (a) The wide survey scans of SPEEK/UiO-66/Pd-GO with (b) deconvoluted Pd3d spectra and (c) Zr3d XPS spectra.

The thermogravimetric curves of UiO-66, UiO-66/GO, UiO-66-Pd-GO and their composite membranes are shown in **Fig. S14**. UiO-66, UiO-66/GO and UiO-66/Pd-GO samples are exhibited similar turning points (**Fig. S14a**). The decrease in weight due to the loss of physically adsorbed water and solvent molecules was found to be exhibited till 100 °C, following which a stability was exhibited by all of the molecules until 480 °C. This could be inferred from the fact that no significant weight loss was observed till this point. However, structural degradation was found beyond 520 °C based on the significant weight loss and degradation post this period.<sup>13</sup> The TGA showed that inducing Pd-GO into the UiO-66 improved the thermal stability of UiO-66 materials. In case of fabricated membranes, all the samples also showed almost similar trend in the thermal degradation plots. The evaporation of water absorbed by hydrophilic UiO-66/Pd-GO fillers and SO<sub>3</sub>H groups present in the membrane leads to initial weight loss till 100 °C. Desulfonation of SPEEK also contributes to

weight loss in this regime. The decomposition of sulfonic acid group in the temperature up to 380 °C is improved in the composite membrane compared to pure SPEEK.<sup>14</sup> This might be due to the interaction between the hydroxyl groups of the UiO-66/Pd-GO composite and sulfonic acid groups on the polymeric membrane surface, which results in enhancement of the thermal resistance of the membrane. This is followed by a final stage (>450 °C) where degradation of the polymeric backbone occurs. The composite membrane shows an improved stability. Moreover, the residual mass of the composite membrane was found to greater than pure SPEEK membrane, indicating their improved stability.



**Figure S14.** TGA analysis of (a) GO, Pd-GO, UiO-66 and UiO-66-Pd-GO and (b) SPEEK, SPEEK/UiO-66, SPEEK/UiO/GO, SPEEK/UiO-66/Pd-GO composite membranes.

## Leaching test of nanocomposite from polymer matrix

For this statement we have conducted a small experiment. Briefly, a small part of SPEEK/UiO-66/Pd-GO membrane was immersed in aqueous solution of methanol solution and kept for 72 hours. The membrane was then taken out from the methanol solution and dried at room temperature under atmospheric conditions. Then EDX mapping analysis was done where uniform distribution of carbon, oxygen, sulphur, zirconium and palladium was observed. From this, we can conclude that there is no leaching of nanocomposite from the mixed matrix membrane. immersed in aqueous solution of methanol solution



Figure S15. EDX mapping analysis of SPEEK/UiO-66/Pd-GO membrane

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