nature portfolio

Peer Review File

Sulfophenylated centimeter-size graphene membrane in a direct methanol fuel cell

Corresponding Author: Professor Gregory Schneider

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
In the DMFC, the 2D framework of graphene film shows the possibility to realize the proton permeability while stopping methanol crossover, however it faces many challenges. In this manuscript, authors using the chemical modification way to functionalize the monolayer graphene film with sulfophenylated sp3 dislocations by diazotization. This method maintains the integrity of 2D graphene and makes the graphene only permeate proton. The results are attractive. Follows are comments for this manuscript.
1. According to the theoretical calculation, the sulfophenylated sp3 dislocations can reduce the energy barrier of cross-plane transportation of proton. However, the reduction in the energy barrier is not the direct evidence for the high proton conductivity. The energy barrier for the cross-plane transportation of proton should be provided.
2. Measurements reveal that the monolayer graphene is highly functionalized, and why these functional groups can't be directly seen in the high-resolution TEM images?
3. The pristine graphene shows a high proton conductivity of 6.9 ±1.1 S·cm-2, and authors thought it comes from the defects in the form of pinholes or cracks in CVD graphene. As we know the chemical modification can reduce the mechanical strength once many sp3 carbon atoms are produced on the graphene plane, the functionalized graphene will become more vulnerable during transfer and MEA preparation. Thus, authors should confirm that such large enhancement in proton conductivity of the SO3-graphene isn't originated from the defects.
4. Using the proton-accessible 2D materials in the DMFC is attractive for solving the problem of methanol crossover. Some reports using 2D graphdiyne with intrinsic atomic-level pores have close concept with this manuscript, and should not be ignored in this manuscript. (Angew. Chem. Int. Ed DOI: 10.1002/anie.201910588; Nano Today 202. 39, 101213).

Reviewer #2

(Remarks to the Author)
The authors have demonstrated the approach by functionalization of CVD graphene with sulfophenyl groups, which not only enhanced the proton transport rate, but also maintained good selectivity to methanol. This work is interesting, the paper itself is well-written and almost ready for publication. But I have some concerns:
1. The calculation in Figure 1 seems to be a strong support to show that this functionalization is much better than hydrogenation, especially the proton flux can be 7 to 8 orders of magnetite higher than that of H-Gr. As I understand this is also correlated to the energy barrier change compared to pristine graphene. However, from Ref 36, the energy barrier difference from pristine to H-Gr is already very large (>2 eV), but in Figure 1B, the difference is only 0.15 eV, why there is a such big difference? This needs to be checked, otherwise will be misleading.
2. The measured energy barrier for proton transport from Figure 4D for the sample of 4d treatment is only 0.072 eV, which is really very small. This is far below any case that have been reported for proton transport so far. The authors need to check if this fitting is really meaningful as if the conductance change is small, you can fit to any equation.
3. As now the demonstration of using the functionalized Gr membrane for methanol fuel cell is core for this paper, a clear comparison with other state-of-art membrane systems on this field is necessary to show the merit of this approach.
4. The results for the reverse assembly (Fig. S28) shows almost similar performance to that of forward one, does this in consistent to the calculations made for Figure 1?
minor points:
no D' peak was not found, no shall be deleted

No scale bar information for Fig. S13

Reviewer #3

(Remarks to the Author)
Zhang et al. report on Sulfophenylated centimeter-size graphene membrane for a direct methanol fuel cells. The manuscript is well written and seems to present detailed characterization for graphene and with an anchor around the main claim of covalent functionalization of single crystalline graphene.

The lack of novelty and incomplete support for conclusion publication at this stage is premature (see below for details).

Firstly, the use of graphene for methanol fuel cells has been reported by several groups.
DOI: 10.1002/aenm.201601216
DOI: 10.1016/j.jpowsour.2016.02.030
DOI 10.1149/MA2018-01/30/1763

Secondly, some major scientific things to consider are:

1. The core claim of sulfonation allowing for enhanced proton transport is unsupported. Intrinsic defects exist within the individual CVD domains forming the film. How do the authors rule the presence of defects and the etching of these defects with longer sulfonation times or processing during membrane fabrication? Authors should show direct evidence of expansion of the ring with covalent functionalization e.g. TEM images with increased bond length or distorted rings and Raman spectra.

2. The authors use CVD grown single crystalline graphene - how do they rule out defects in single crystalline graphene over centimeter scale areas? Several reports have shown that single crystalline graphene are not devoid of defects. These aspects appear to have been overlooked.

3. Point 1 and 2 are supported by the so called "pristine" graphene in this study showing > 3mS/cm2 (value for exfoliated graphene).

4. How do the authors rule out the formation of crack or tears in graphene as the spin coated Nafion film swells during removal of Cu while etching in acid?

5. The data for 4 day treatment shows better power density than 6 days. This further indicates defects and not covalent functionalization and a trade-off.

6. Referencing is inadequate and several key papers in the field on centimeter scale graphene PEMs are not cited.

Reviewer #4

(Remarks to the Author)
The manuscript describes chemical modification by sulfophenylation as a strategy to (selectively) tune proton conductivity through graphene membranes. Specifically, unless the mechanically exfoliated membrane is properly clamped, the possibility that edge leakage from lifted membranes contributes to the ~5000-fold increase in conductance cannot be excluded. Moreover, the modest selectivity between H+ to K+ ions transport across the membrane does not adequately address this concern. I suggest that perhaps a conclusion based on the CVD graphene data, where sulfophenylation demonstrably helps seal defects, is adequate. As it stands, the indirect approach of ruling out leakages for measurements on sulfophenylated mechanically exfoliated graphene membranes is not sufficiently convincing. I recommend the manuscript for publication as long as this limitation of measurements made on mechanically exfoliated membrane is not dribbled around but clearly acknowledged. In my opinion, the merits of the improvement made by the chemical modification to graphene are worth publishing in Nature Communications.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This paper is well revised according to reviewer's suggestions. Now, it can be acceptable.

Reviewer #2

(Remarks to the Author)
The paper presents a promising and attractive approach for controlling ion transport through chemically functionalized graphene, and now I recommend its publication.

Reviewer #3

(Remarks to the Author)
Previous comments in italics and new comments in normal text
Zhang et al. report on Sulfophenylated centimeter-size graphene membrane for a direct methanol fuel cells and the reviewer appreciates the effort to clarify some of the finer points.
However, this reviewer lack of novelty based on prior work (that have now been cited) and incomplete support for the core claims as alluded to by reviewer 1 – point 3.

1. The core claim of sulfonation allowing for enhanced proton transport is unsupported.
Note reviewer #1 also bring up this point #3 The pristine graphene shows a high proton conductivity of 6.9 ±1.1 S·cm-2,
The authors responded with optical images and Raman which simply doesn't have adequate resolution for quantifying all kinds of defects. Raman below a certain level of defect density is not adequate.
The authors report proton conductance 20 times more than pristine graphene at 3mS cm-2, there is no explanation for this. (Nature volume 516, pages227–230 (2014); ACS Nano 2019, 13, 10, 12109–12119; J. Mater. Chem. A, 2022,10, 19797-19810) crack and tears in centimeter scale membranes are known to enhance transport.
Caution should be exercised in attributing all of it to doping without direct evidence, considering point 2 below.
The devices have Nafion so they won't show up in the performance. The nitrogen doping data actually supports the reviewer's claim that increased proton transport is not from small defects but from sporadic cracks and tears in the graphene for the SO2- case.

2. Intrinsic defects exist within the individual CVD domains forming the film. How do the authors rule the presence of defects and the etching of these defects with longer sulfonation times or processing during membrane fabrication? Authors should show direct evidence of expansion of the ring with covalent functionalization e.g. TEM images with increased bond length or distorted rings and Raman spectra.
Since the authors cannot confirm these aspects with HRTEM or find evidence of sp3 in Raman, they should avoid speculative claims.
They should try to find out the real reason for enhanced transport as suggested by 2 independent reviewers instead of trying to push through this manuscript in its current state.

2. The authors use CVD grown single crystalline graphene - how do they rule out defects in single crystalline graphene over centimeter scale areas? Several reports have shown that single crystalline graphene are not devoid of defects. These aspects appear to have been overlooked.
The authors misunderstood the point the reviewer was making. The pristine graphene they refer to is made via CVD! That also have defects that manifest even in single crystalline graphene membranes. Characterizing these intrinsic defects over centimeter scale areas is challenging with HRTEM, AFM, and Raman, and several groups around the world have developed diffusive transport as an alternative solution that provides information in a few hours with reliable statistics. The authors may want to look into those works and try to characterize their materials thoroughly with relevant techniques that will un-ravel the science behind the effects seen here – instead of claiming it comes from doping, SO3- without direct evidence.

3. Point 1 and 2 are supported by the so called "pristine" graphene in this study showing > 3mS/cm2 (value for exfoliated graphene).
The authors missed the point that even CVD graphene has shown 3-4 mS cm-2 similar to exfoliated graphene. (Nature volume 516, pages227–230 (2014); ACS Nano 2019, 13, 10, 12109–12119; J. Mater. Chem. A, 2022,10, 19797-19810).
Does this mean the CVD single crystalline graphene made here is not as high in quality as even polycrystalline graphene used in other studies? Or is the higher transport from cracks and tears?
In light of points 1 and 2 the reviewer urges extreme caution from making claims without evidence by the authors.

4. How do the authors rule out the formation of crack or tears in graphene as the spin coated Nafion film swells during removal of Cu while etching in acid?

Although the authors used a rigid PC membrane and used Raman these don't allow for probing over macroscopic areas with high resolution.

5. The data for 4 day treatment shows better power density than 6 days. This further indicates defects and not covalent functionalization and a trade-off.
The authors mention they don't see defects but no HR TEM is provided as evidence.
The reviewer is merely point to defects and variability might be responsible for this since one would not expect a reduction after saturation if this was purely functionalization.

6. Referencing is inadequate and several key papers in the field on centimeter scale graphene PEMs are not cited.
The reviewer recommends citing relevant papers in the field focusing on proton transport using CVD graphene to benchmark and contextualize the current work.

Reviewer #4

(Remarks to the Author)

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)
The reviewer appreciates the efforts by Zhang et al. to clarify some aspects including addition of HRTEM images and changes to the manuscript to factor in several aspects that were previously overlooked.

The author's response seems to broadly agree with the reviewer's concerns:

"The method we employed introduces sp^3 distortions, -SO3- groups, and a polymerized layer simultaneously, making it challenging to isolate any single factor as the direct cause of the increased transport of protons, as questioned by the reviewer. A comprehensive analysis of this correlation exceeds the scope of a single manuscript, given the need to carefully isolate all these contributing factors. However, we are confident that our observations, along with the control experiments we have conducted, provide sufficient evidence to demonstrate that sulfophenylated graphene exhibits performance comparable to Nafion polymer membranes in a direct methanol fuel cell."

Comments:
1. Proton conductance increased by ~5x after sulfophenylation and attributed to presumably lower energy barrier. But this should be straightforward to measure with temperature to get activation energy barriers. Flushing this out completely will provide detailed insights and position this paper for a high impact journal.

2. How do the authors rule out formation of additional proton permeable defects in the CVD graphene lattice upon functionalization but hindering methanol transport? The ID/IG ratio in Raman clearly increases for upto 4 days of functionalization indicating defect formation in graphene. The polymer from functionalization layer or transfer contamination will preferentially cover defects preventing observation in HRTEM images. Reviewer notes authors do mention HRTEM doesn't show defects >1nm but polymer/contamination covered defects won't be visible in HRTEM and doesn't mean they don't exist. In fact no defect is seen in the HRTEM images presented!

3. In the context of the above, reviewer urges caution and closer analysis of data and including formation of additional defects as a possibility along with "With our hypothesis that the combination of a sp3 distortion and a charged SO3- group contributes to an increased proton transport"
Authors already allude to this "This is because sulfophenylation may effectively seal and passivate grain boundaries, guiding protons through them."

Version 3:

Reviewer comments:

Reviewer #3

(Remarks to the Author)
No further comments. Congrats on the paper!

Response to reviewers

We thank all the reviewers for their valuable feedback and comments. In response to the growing demand for broadening the applications of large-area 2D materials, we developed a chemical functionalization strategy to enhance proton conductance through centimeter-scale CVD graphene while preserving its proton selectivity. The performance of our DMFC serves as direct evidence of the membrane's efficiency, as it is sensitive to proton conductivity—reflected by the internal circuit resistance and proton selectivity—indicated by the methanol crossover current. The DMFC exhibits superior power output resulting from the sulfophenylation of graphene which we attribute to a high proton conductivity and selectivity.

We characterized the sulfophenylated graphene to confirm the functionalization using state-of-the-art techniques: Raman spectroscopy, high-resolution transmission electron microscopy, atomic force microscopy, and X-ray photoelectron spectroscopy. Additionally, we conducted theoretical studies that describe the chemical states of the functionalized graphene, providing insight into the improved proton conductance.

We understand that the reviewers' primary concerns are whether the increased proton conductance is solely due to the functionalized sites and how these sites contribute to the overall proton conductance. To address this, we have included additional evidences in the manuscript (detailed below). Our findings confirm that the enhanced proton conductance and selectivity are attributed to sulfophenylation, supported by analyses that rule out potential damage from treatment/operations and comparisons with defected graphene.

We hope our response will satisfactorily address the reviewers' questions and concerns.

Point-by-point response

Reviewer #1 (Remarks to the Author):

In the DMFC, the 2D framework of graphene film shows the possibility to realize the proton permeability while stopping methanol crossover, however it faces many challenges. In this manuscript, authors using the chemical modification way to functionalize the monolayer graphene film with sulfophenylated sp3 dislocations by diazotization. This method maintains the integrity of 2D graphene and makes the graphene only permeate proton. The results are attractive. Follows are comments for this manuscript.

We thank the reviewer for his-her report and we answered the questions below.

1. *According to the theoretical calculation, the sulfophenylated sp3 dislocations can reduce the energy barrier of cross-plane transportation of proton. However, the reduction in the energy barrier is not the direct evidence for the high proton conductivity. The energy barrier for the cross-plane transportation of proton should be provided.*

We agree with the reviewer that the energy reduction does not directly relate to the proton conductivity. In fact, we have not simulated the conductivity, but the proton flux through a 6-fold ring in a graphene model. The flux was estimated from the WKB approximation, which we used to calculate tunnelling effects and estimate the classical vs. quantum components of the flux, as we did before in another work (An et al., *Adv. Mater.* **2020**, 2002442).

If we understand the request of the reviewer correctly, below, we provide the correlation between the energy barrier and the ring area, which should correspond to the cross-plane for proton transport. We find a linear correlation between the two except for pristine graphene (*). We excluded this point from the fitting because this is the only system that retains the perfect π-conjugation, which is disrupted in the functionalized graphene models. We added the following content to the revised supplementary material (Fig. S2, Page 4 in supplementary material).

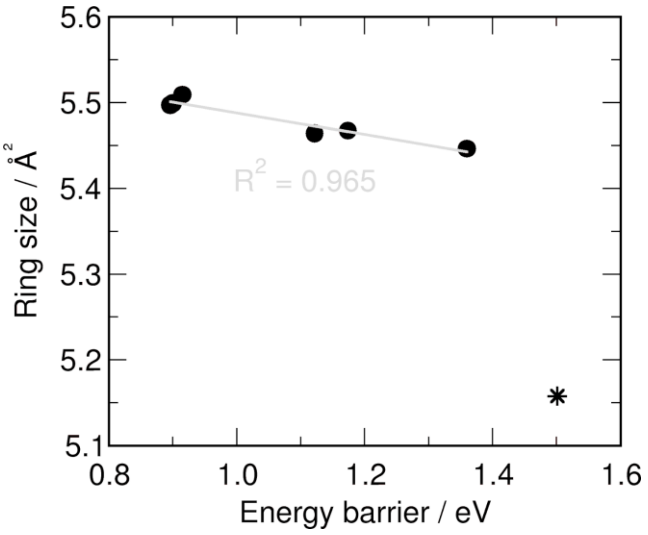

Figure R1. Correlation between ring area and the energy barrier for proton transfer through graphene (using circumcoronene model structure). Energy barrier calculated at the DFT/PBE0/MDB level of theory; ring area calculated via triangle area summation in a 6-fold ring. Pristine graphene is marked with a star, the functionalized graphene with black circles. For the set of points for functionalized graphene, we find a linear correlation between the ring area and the energy barrier.

2. *Measurements reveal that the monolayer graphene is highly functionalized, and why these functional groups can't be directly seen in the high-resolution TEM images?*

We attempted to observe the functionalized sites of graphene using HRTEM, however we could not image individual carbon atoms grafted by SBD (Figure 2E, Figure S10-22). However, as previously reported (Nature Chem, **2011**, 3, 279–286), identifying individual functionalized sites on a graphene lattice with low functionalization levels proved challenging (using Raman, we measured a I_D/I_G of ~0.4, indicating a L_d of ~16 nm corresponding to 1 sp^3 out of >3000 sp^2 carbon atoms, by $L_d=\sqrt{A/(I(\mathrm{D})/I(\mathrm{G})}$, where A is 102 nm^2, Nano Letters, **2012**, 12, 3925-3930). We could not observe such sp^3 by electron microscopy, nor using the diffraction mode. Additionally, the potential effects from the transmission electron microscopy beam on the conversion of sp^3 to sp^2 (Journal of Applied Physics, **2010**, 107 (1), 013709 and the electron-beam induced cleavage (Nanomaterials, 2022, 3 (12)) make the observation on isolated grafting site more challenging. Additionally, this type of functionalization typically does not display a measurable change in the local crystalline structure nearby the distortion. Even for high functionalization degrees (J. Mater. Chem., **2012**, 22, 2063-2068) a direct observation by HRTEM of the grafted sites was not possible.

3. *The pristine graphene shows a high proton conductivity of 6.9 ±1.1 S·cm-2, and authors thought it comes from the defects in the form of pinholes or cracks in CVD graphene. As we know the chemical modification can reduce the mechanical strength once many sp3 carbon atoms are produced on the graphene plane, the functionalized graphene will become more vulnerable during transfer and MEA preparation. Thus, authors should confirm that such large enhancement in proton conductivity of the SO3-graphene isn't originated from the defects.*

The observed increases in proton conductance can be attributed to the inherent properties of pristine graphene. Given the higher proton selectivity over methanol after treatment and considering that methanol molecules are neutral and subnanometer in size, the defects responsible for this selectivity must also be subnanometer in scale. Unlike mechanically introduced defects, which tend to propagate and cause tearing, the sulfophenylation process does not cause mechanical damage. This explains the improved proton conductance while maintaining structural integrity.

While it is true that covalent functionalization can compromise the stability of the graphene lattice and significantly reduce its mechanical strength, such as chlorination and hydrogenation, this was not the case in our study. Given the modest level of functionalization, we did not observe any degradation in the overall integrity of the graphene lattice, as shown in Figure R2.

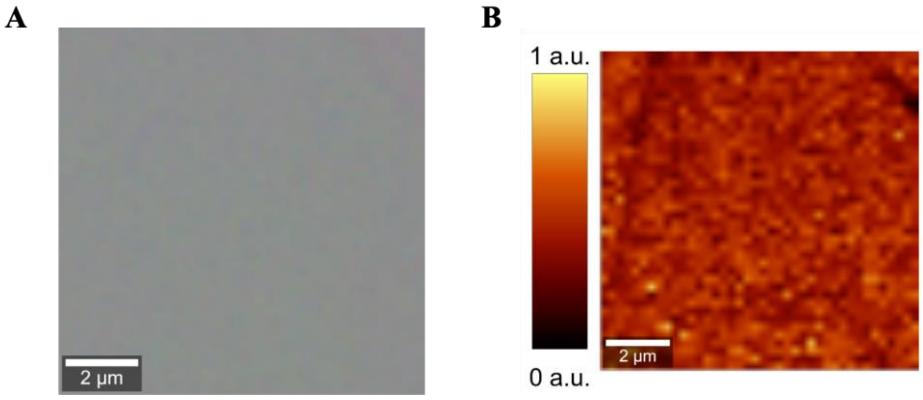

Figure R2. Optical image (A) and I_D/I_G (B) mapping of Raman spectra of corresponding area for a ***Nafion-casted*** graphene floated on 0.1 mg/ml SBD solution for 3 days.

During the chemical treatment, the structural integrity of the graphene lattice was maintained over several days, as demonstrated by the fact that graphene floated at the water-air interface without cracking with only a Nafion-casted layer. Upon sulfophenylation, Raman spectroscopy showed a gradual increase in the D peak, indicating functionalization, which plateaued after 4 days of treatment with no further increase observed during the subsequent 2 days (Fig. 3A). This trend was consistent with our observations on a rigid SiO_2/Si substrate (Fig. S16). From this, we ruled out the likelihood of significant mechanical damage during treatment. Unlike the floated graphene, which exhibited a flat surface, the graphene transferred onto a rigid substrate displayed more wrinkles, with these regions showing a lower I_D/I_G ratio. Consequently, the SBD treatment primarily affected the monolayer areas and did not influence the wrinkles or multilayer islands.

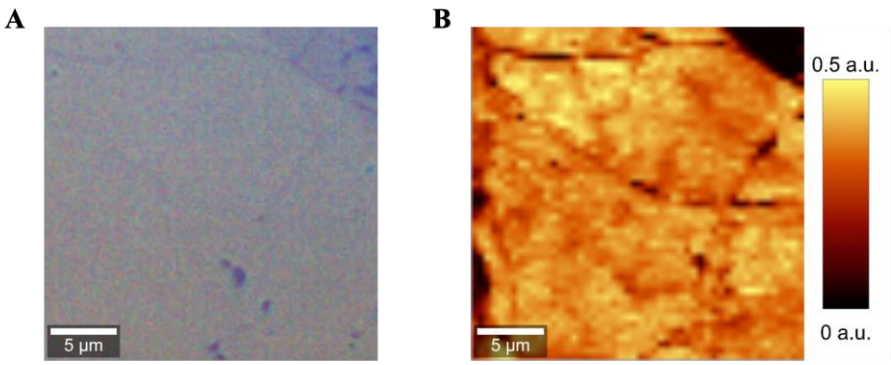

Figure R3. Optical image (A) and I_D/I_G (B) mapping of Raman spectra of corresponding area for a graphene on ***SiO_2/Si substrate*** immersed in 0.1 mg/ml SBD solution for 3 days.

The second phase of our study involved the membrane-electrode assembly. If any damage had occurred during this step, it would have manifested as large cracks rather than small pinholes. Such cracks would have been evident from the start-up of the cell, resulting in a significantly reduced open-circuit voltage and a very low power output, owing to the methanol leakage (as shown in Figure R4, compromised membranes). In contrast, small pinholes would still permit effective methanol selectivity. Our Arrhenius analysis confirmed that membrane conductance remained linear after 4 days of SBD treatment, indicating robust thermal stability. Additionally, we observed a reduced methanol/proton permeation rate, further supporting the integrity of the treated membrane.

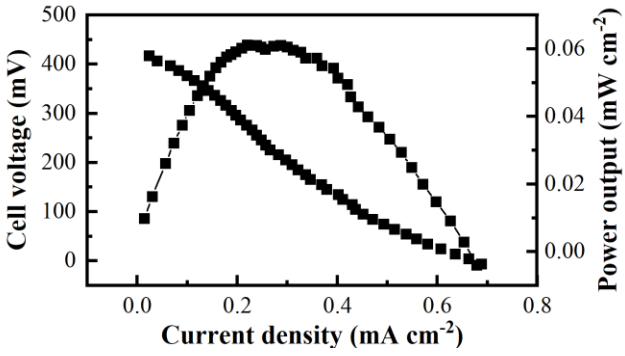

Figure R4. DMFC performance of a graphene membrane with cracks.

Additionally, we explored the role of active sites and defects by functionalizing graphene using nitrogen plasma treatment. This exposure led to an increase in defect density, which initially boosted the DMFC power output (Figure R5). However, despite the defect density being significantly higher than that of sulfophenylated graphene (Figure R6) with an I_D/I_G ratio of ~1.2 (0.4~0.6 for sulfophenylated graphene), the maximum power output achieved was only one-third of that seen with sulfophenylated graphene.

This finding further substantiates that the enhanced proton conductance results from sp^3 dislocations and the presence of ph-SO_3^- functional groups.

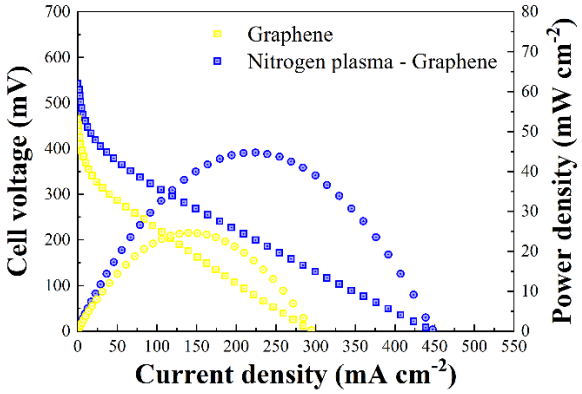

Figure R5. DMFC performance with a membrane made of defected graphene by nitrogen plasma.

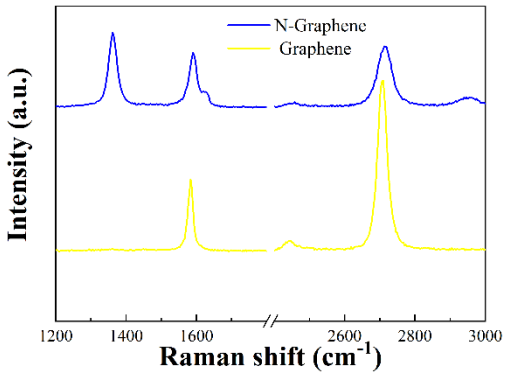

Figure R6. Raman spectrum of defected graphene by nitrogen plasma.

4. *Using the proton-accessible 2D materials in the DMFC is attractive for solving the problem of methanol crossover. Some reports using 2D graphdiyne with intrinsic atomic-level pores have close concept with this manuscript, and should not be ignored in this manuscript. (Angew. Chem. Int. Ed DOI: 10.1002/anie.201910588; Nano Today 2021. 39, 101213).*

We thank the reviewer for referring to these publications. We have now incorporated these references into the introduction.

Reviewer #2 (Remarks to the Author):

The authors have demonstrated the approach by functionalization of CVD graphene with sulfophenyl groups, which not only enhanced the proton transport rate, but also maintained good selectivity to methanol. This work is interesting, the paper itself is well-written and almost ready for publication. But I have some concerns:

We thank the reviewer's positive feedback.

1. *The calculation in Figure 1 seems to be a strong support to show that this functionalization is much better than hydrogenation, especially the proton flux can be 7 to 8 orders of magnetite higher than that of H-Gr. As I understand this is also correlated to the energy barrier change compared to pristine graphene. However, from Ref 36, the energy barrier difference from pristine to H-Gr is already very large (>2 eV), but in Figure 1B, the difference is only 0.15 eV, why there is a such big difference? This needs to be checked, otherwise will be misleading.*

The differences between our results and those reported in Ref. 46 can be explained as we functionalize only two C atoms with hydrogen, whereas Ref. 46 reports results for complete 6-fold ring functionalization. In our previous work (An et al., *Adv. Mater.* **2020**, 2002442), we investigated how varying degrees of hydrogenation (2, 4, or 6 H atoms on a 6-fold ring) affect the energy barrier and proton flux. For these cases, we observed that the energy barrier changes from 1.41 eV for pristine conditions to 1.23 eV for 2 H, 0.79 eV for 4 H, and 0.70 eV for 6 H. In comparison, Ref. 36 reports energy changes from 3.65 eV for pristine graphene down to 3.24 eV (a decrease of only 0.41 eV) for 2 H, 3.07 eV for 4 H, and 1.82 eV for 6 H. The discrepancy in absolute values is due to the transition state in Ref. 36, which involves a bound proton that stabilizes both the product and reactant, leading to a higher energy barrier. Also, we did not consider water capturing the proton in the form of hydronium. However, the relative trend remains similar, with 6 H atoms reducing the barrier by roughly half compared to pristine graphene.

Full hydrogenation in Ref. 46 results in lowering of energy barrier to about 1 eV for chair confirmation and to 0.76 eV for boat one.

2. *The measured energy barrier for proton transport from Figure 4D for the sample of 4d treatment is only 0.072 eV, which is really very small. This is far below any case that have been reported for proton transport so far. The authors need to check if this fitting is really meaningful as if the conductance change is small, you can fit to any equation.*

The activation energy of our 4-day treated samples is approximately 30% to 65% lower than that reported for polymeric proton exchange membranes, which typically show values around 0.1 eV for high-performance PEMs. Activation energies of 0.075 eV (J. Mater. Chem. A, **2020**, 8, 1147-1153), 0.085 eV (J. Mater. Chem. A, **2023**, 11, 3446-3453), and 0.17 eV for Nafion HP (J. Solid State Electrochem, **2019**, 23, 2639–2656) were previously reported.

We have therefore verified our calculations. The conductance of our samples increased from 4.9 S cm^{-2} to 6.5 S cm^{-2} when the temperature was raised from 20 to 60 °C. Under this temperature range, the conductance of a Nafion 117 membrane increased from 2.4 S cm^{-2} to 3.1 S cm^{-2}, with reported activation energies ranging between 9 to 14 kJ mol^{-1} (J. Electrochem. Soc. **2014**, 161, F1395). For the linear fitting, the R^2 is 0.9935, 0.9986, 0.9887, 0.9724 for 1-4 days sample. The R^2 for 0-day sample is 0.7311, as we observed a poor linearity and thermal stability. The following table was added to the supplementary material for the clarification of our calculations (Table S3, page 37).

Table R1. Datasheet of Arrhenius behavior analysis

T (K)	1000/T (K^{-1})	0-day		1-day		2-day		3-day		4-day		5-day	
		σ (S cm^{-2})	ln(σ*T*)	σ (S cm^{-2})	ln(σ*T*)	σ (S cm^{-2})	ln(σ*T*)	σ (S cm^{-2})	ln(σ*T*)	σ (S cm^{-2})	ln(σ*T*)	σ (S cm^{-2})	ln(σ*T*)
293.15	3.41	1.13	5.81	1.86	6.30	3.15	6.83	4.08	7.09	4.94	7.28	3.93	6.70
313.15	3.19	1.39	6.08	2.39	6.62	3.77	7.08	4.91	7.34	5.75	7.50	4.41	6.93
323.15	3.09	2.30	6.61	2.65	6.75	4.04	7.17	5.22	7.43	6.12	7.59	4.53	7.00
333.15	3.00	2.19	6.59	2.83	6.85	4.32	7.27	5.50	7.51	6.29	7.65	4.54	7.02
343.15	2.91	1.81	6.43	3.01	6.94	4.55	7.35	5.68	7.58	6.35	7.69	4.41	7.04

3. *As now the demonstration of using the functionalized Gr membrane for methanol fuel cell is core for this paper, a clear comparison with other state-of-art membrane systems on this field is necessary to show the merit of this approach.*

We appreciate the reviewer's suggestion and have expanded the introduction to highlight recent advancements in the field of DMFCs, with an emphasis on membrane technologies. This elaboration underscores the progress made in improving membrane performance to enhance the overall efficiency and power output of DMFCs. We also removed a sentence from the abstract which may be a speculative perspective of the work: 'Selective to protons, transmembrane areal conductances surpass those of polymer membranes, while providing proton selectivity over methanol through such an atomically thin layer.'

The main challenge for polymeric membranes lies in balancing proton conductivity and selectivity, with methanol crossover posing an additional obstacle due to its high solubility in water and uncharged nature, which facilitates migration from the anode to the cathode. To mitigate this issue, various strategies have been pursued to enhance the power output of direct methanol fuel cells (DMFCs) (J Polym Res., **2024** 31, 125). For instance, incorporating layered additives has been shown to improve performance; the power output increased to 35 mW cm^{-2} with nano-silica additives (Electrochemistry Communications, **2004**, 6(10), 1069–1074) and to 39 mW cm^{-2} with graphene oxide (ACS Appl. Eng. Mater., **2023**, 1(3), 947–954). The power output of DMFCs using a Nafion 117 membrane was enhanced to 79 mW cm^{-2} by impregnating the membrane with Pd (Electrochemistry Communications, **2003**, 5(7), 571–574). Additionally, recasting the Nafion membrane with blended additives has been shown to boost DMFC power output to over 100 mW cm^{-2} (Electrochimica Acta, **2018**, 292, 855–864; Journal of Membrane Science, 2017, 541, 127–136). The power output of DMFCs was enhanced to 25 mW cm^{-2} by sandwiching single-layer graphene between two layers of Nafion membrane (Journal of Power Sources, **2016**, 311, 188-194) and increased to 120 mW cm^{-2} by incorporating single-layer graphene onto the electrode (Adv. Energy Mater., **2017**, 7 (5), 7).

4. *The results for the reverse assembly (Fig. S28) shows almost similar performance to that of forward one, does this in consistent to the calculations made for Figure 1?*

We originally aimed to test whether a directional DFMC performance dependency would stand from mounting the sulfophenylated graphene membrane in the reverse direction. As shown in Figure S29, the reverse assembly demonstrated a nearly identical performance to the forward assembly, confirming that the proton conductance is non-directional. In the simulations in Figure 1, the proton flux is influenced primarily by the energy barrier associated with proton tunneling across the functionalized sites, irrespective of the direction.

minor points:

no D' peak was not found, no shall be deleted

The D' peak is not visible in our case due to the relatively low I_D/I_G ratio.

No scale bar information for Fig. S13

The scale bar is added.

Reviewer #3 (Remarks to the Author):

Zhang et al. report on Sulfophenylated centimeter-size graphene membrane for a direct methanol fuel cells. The manuscript is well written and seems to present detailed characterization for graphene and with an anchor around the main claim of covalent functionalization of single crystalline graphene.

The lack of novelty and incomplete support for conclusion publication at this stage is premature (see below for details).

To our knowledge, no prior studies have reported similar observations on proton transport through chemically functionalized graphene lattices. We also provided comprehensive evidence for the functionalized membrane, including Raman spectroscopy, HRTEM, AFM, XPS, and full-scale fuel cell tests conducted with over 30 samples. The characterizations were conducted by the most state-of-art techniques. We believe our work is new and important.

Firstly, the use of graphene for methanol fuel cells has been reported by several groups.
DOI: 10.1002/aenm.201601216
DOI: 10.1016/j.jpowsour.2016.02.030
DOI 10.1149/MA2018-01/30/1763

We incorporated the top two references into a comprehensive paragraph that introduces recent advancements in membrane technology for DMFCs.

The last reference, however, is a conference abstract which we did not added. See our addition below:

The main challenge for polymeric membranes lies in balancing proton conductivity and selectivity, with methanol crossover posing an additional obstacle due to its high solubility in water and uncharged nature, which facilitates migration from the anode to the cathode. To mitigate this issue, various strategies have been pursued to enhance the power output of direct methanol fuel cells (DMFCs) (J Polym Res., **2024** 31, 125). For instance, incorporating layered additives has been shown to improve performance; the power output increased to 35 mW cm^{-2} with nano-silica additives (Electrochemistry Communications, **2004**, 6(10), 1069–1074) and to 39 mW cm^{-2} with graphene oxide (ACS Appl. Eng. Mater., **2023**, 1(3), 947–954). The power output of DMFCs using a Nafion 117 membrane was enhanced to 79 mW cm^{-2} by impregnating the membrane with Pd (Electrochemistry Communications, **2003**, 5(7), 571–574). Additionally, recasting the Nafion membrane with blended additives has been shown to boost DMFC power output to over 100 mW cm^{-2} (Electrochimica Acta, **2018**, 292, 855–864; Journal of Membrane Science, 2017, 541, 127–136). The power output of DMFCs was enhanced to 25 mW cm^{-2} by sandwiching single-layer graphene between two layers of Nafion membrane (Journal of Power Sources, **2016**, 311, 188-194) and increased to 120 mW cm^{-2} by incorporating single-layer graphene onto the electrode (Adv. Energy Mater., **2017**, 7 (5), 7).

Secondly, some major scientific things to consider are:

1. The core claim of sulfonation allowing for enhanced proton transport is unsupported. Intrinsic defects exist within the individual CVD domains forming the film. How do the authors rule the presence of defects and the etching of these defects with longer sulfonation times or processing during membrane fabrication?

Intrinsic defects in CVD graphene are unavoidable, which contrasts with the controlled introduction of functionalized graphene samples. To better understand these intrinsic properties, we conducted studies on non-functionalized CVD graphene. We did not observe that intrinsic defects were further etched

during the functionalization process, as evidenced by HRTEM (Figure 2E). Raman spectroscopy (Figure R2), and AFM (refer to Figures S19). HRTEM observations revealed no discernible alterations beyond the pristine lattice structure. In fact, despite our efforts, we could not directly visualize the sp^3 defects as intended (refer to our previous response regarding the imaging challenges of distortion).

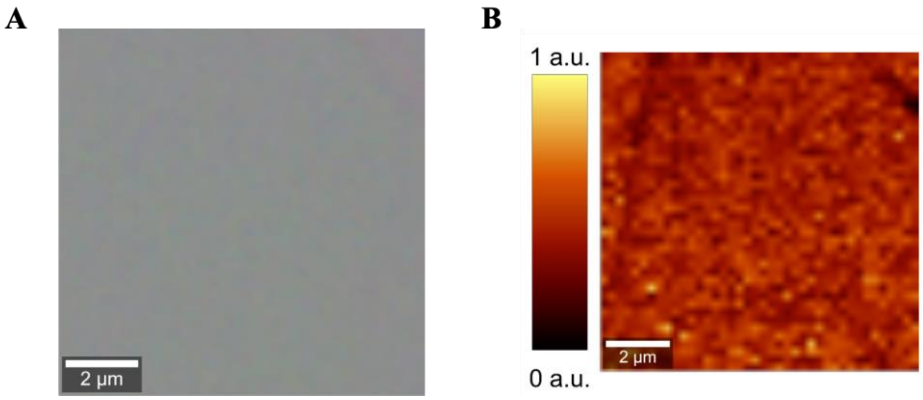

Figure R2. Optical image (A) and I_D/I_G (B) mapping of Raman spectra of corresponding area for a ***Nafion-casted*** graphene floated on 0.1 mg/ml SBD solution for 3 days.

Authors should show direct evidence of expansion of the ring with covalent functionalization e.g. TEM images with increased bond length or distorted rings and Raman spectra.

What the referee is asking is not possible with current techniques. And samples are not yet compatible to carry STM. Efforts have been made to directly observe the distortion after SBD treatment. As previously reported (Nature Chem, **2011**, 3, 279–286), identifying individual functionalized sites on a graphene lattice with low functionalization levels proved challenging.

2. The authors use CVD grown single crystalline graphene - how do they rule out defects in single crystalline graphene over centimeter scale areas? Several reports have shown that single crystalline graphene are not devoid of defects. These aspects appear to have been overlooked.

We did not overlook the potential defects from pristine graphene. Instead, all the analysis/characterization involve the untreated graphene as a control to compare the changes in transport properties upon the chemical treatment (Figure 2, observations by HRTEM and AFM with pristine graphene included, Figure 3 Raman and XPS characterizations include the pristine samples, Figure 4 fuel cell tests with all parameters from pristine graphene discussed).

We are also curious about the proton transport through the intrinsic graphene lattice (Nature, **2023**, 620, 782-786) *vs.* sulfophenylated sites (arXiv:2308.16112)

Observing and measuring sparsely distributed active sites vs non-functional defects sites is inherently challenging, especially when they are spread over a large surface area. An operando system is required to correlate the changes in the lattice and resulting proton conductance. Therefore, we will build an on-chip platform allowing us to observe the introduced changes (by electron beam, electrochemical reaction and electrical field) and the correlated changes in the chemical states by spectroscopy (Raman and IR), ideally with a probing system similar to SECCM. But this is beyond the content this manuscript and the work of the team of PD and PhD students authoring this manuscript.

3. Point 1 and 2 are supported by the so called "pristine" graphene in this study showing > 3mS/cm2 (value for exfoliated graphene).

We added in the main text that the 3mS/cm2 were measured for exfoliated flakes as a graphene 2D crystal.

4. How do the authors rule out the formation of crack or tears in graphene as the spin coated Nafion film swells during removal of Cu while etching in acid?

During the membrane fabrication process, the graphene was supported by a rigid PC membrane, which mitigated any potential impact from size variations in Nafion during DMFC operation. The casted Nafion layer was approximately tens nanometers thick and exhibited an amorphous structure, unlike reinforced membranes such as Nafion 117. This configuration provided sufficient space among the polymer chains to allow for hydration and dehydration without significant size changes in the composite membrane. To confirm this stability, Raman spectroscopy and optical observations were conducted on the Nafion-casted graphene. Figure R2 shows the graphene floating on the SBD solution for three days, revealing only homogeneous D peaks without any evidence of cracks, alleviating concerns about structural integrity.

5. The data for 4 day treatment shows better power density than 6 days. This further indicates defects and not covalent functionalization and a trade-off.

The referee refers to defects which we do not see in HRTEM. We respectfully disagree with the assertion that the oligomerization of SBD is responsible for the improvement in DMFC power output. Instead, the enhancement in proton conductance is the primary factor driving this improvement. The proton conductance increased after SBD treatment, whereas one would expect a decline in conductance if only an additional layer had formed atop the graphene while no functionality of the lattice was changed. An additive mechanism could only justify an improvement in power output if the reduction in methanol crossover would be the main contributor.

Our findings show that diazonium groups graft onto the basal plane within the initial 4-day treatment, followed by oligomerization in extended treatments. This conclusion is supported by Raman spectroscopy and AFM observations (Figure S19). Specifically, after 4 days of treatment, the D peak no longer increased, indicating minimal changes to the lattice with prolonged exposure. However, AFM imaging revealed that longer treatments resulted in a polymer-like layer developing on the graphene surface, rather than discrete grafted sites. This explains the observed decrease in power output after 6 days of treatment.

Experimentally, we ensured that the membrane floated on the treatment solution, making it unlikely for non-covalently bound layers to adhere to the graphene surface, especially without external electron to initiate further polymerization (as it would be, for example, by electrografting). Additionally, the treated graphene was floated on water before being assembled with the electrode, further ruling out residual surface-bound layers.

6. Referencing is inadequate and several key papers in the field on centimeter scale graphene PEMs are not cited.

As the reviewer noticed, the single-layer graphene as a membrane in fuel cells is relevant to our work, showing the proton/methanol transport through the lattice. All crucial works featuring proton transport through a (pristine) graphene lattice have been discussed in our manuscript.

Reviewer #4 (Remarks to the Author):

The manuscript describes chemical modification by sulfophenylation as a strategy to (selectively) tune proton conductivity through graphene membranes. Specifically, unless the mechanically exfoliated membrane is properly clamped, the possibility that edge leakage from lifted membranes contributes to the ~5000-fold increase in conductance cannot be excluded. Moreover, the modest selectivity between H+ to K+ ions transport across the membrane does not adequately address this concern. I suggest that perhaps a conclusion based on the CVD graphene data, where sulfophenylation demonstrably helps seal defects, is adequate. As it stands, the indirect approach of ruling out leakages for measurements on sulfophenylated mechanically exfoliated graphene membranes is not sufficiently convincing. I recommend the manuscript for publication as long as this limitation of measurements made on mechanically exfoliated membrane is not dribbled around but clearly acknowledged. In my opinion, the merits of the improvement made by the chemical modification to graphene are worth publishing in Nature Communications.

We appreciate the valuable feedback provided by the reviewer. At this stage, we cannot entirely exclude the possibility of leakage in our experiments involving exfoliated graphene, as reported in our preprint on (arXiv:2308.16112). In this preprint manuscript, we investigated proton transport through chemically functionalized exfoliated graphene. While the presence of leakage cannot be ignored, which makes the confirmation of proton conductance less certain, we submitted the fuel cell part separately (this manuscript under review).

Acknowledging the recent advancements in understanding proton transport through graphene lattices, we have also highlighted the recent work by our colleagues (Nature, **2024**, 630, 619-624; Proceedings of the National Academy of Sciences, **2024**, 120, e2300481120). Additionally, we believe that for exfoliated graphene, a form of clamping is beneficial. Here, clamping is achieved using Nafion in combination with a rigid polymer support.

Response to reviewers

We sincerely appreciate the additional comments from Reviewer #3. We understand that his/her primary concerns are on proton permeation through CVD graphene and the correlation between enhanced proton permeation and chemical functionalization *vs.* the presence of defects and cracks. We can not exclude the presence of defects in CVD graphene. In response, we have revised our manuscript to provide additional explanations on these points. We also confirm that the observed effects originate from chemical functionalization, proposing that the chemical functionalization with SBD does not bring additional defects, such as treatment-induced cracks or pinholes.

The method we employed introduces sp^3 distortions, $-SO_3^-$ groups, and a polymerized layer simultaneously, making it challenging to isolate any single factor as the direct cause of the increased transport of protons, as questioned by the reviewer. A comprehensive analysis of this correlation exceeds the scope of a single manuscript, given the need to carefully isolate all these contributing factors. However, we are confident that our observations, along with the control experiments we have conducted, provide sufficient evidence to demonstrate that sulfophenylated graphene exhibits performance comparable to Nafion polymer membranes in a direct methanol fuel cell.

In the laboratory, we are currently isolating the influence of individual factors, including sp^3 defects, sulfonate groups, and vacancy-type defects, for exfoliated graphene flakes and CVD graphene. These studies require careful statistics before we can conclusively isolate and identify which factors influence proton/ion transport through chemically functionalized graphene.

We believe this revision adequately addresses now the reviewer's questions and concerns.

Point-by-point response

Reviewer #3 (Remarks to the Author):

Previous comments in italics and new comments in normal text

Zhang et al. report on Sulfophenylated centimeter-size graphene membrane for a direct methanol fuel cells and the reviewer appreciates the effort to clarify some of the finer points.

However, this reviewer lack of novelty based on prior work (that have now been cited) and incomplete support for the core claims as alluded to by reviewer 1 – point 3.

1. The core claim of sulfonation allowing for enhanced proton transport is unsupported.

The claim that sulfophenylation enhances the fuel cell performance is supported. That the increased performance of the fuel cell is attributed to the selective transport of protons is not the claim of this manuscript; instead, it is a hypothesis we formulate. The verification of this hypothesis requires further investigation, not using a fuel cell but on freestanding graphene. We revised the manuscript where our description of the results may have conveyed that we conclude on the selective transport of protons caused through sulfophenylation (see our detailed answer below).

Note reviewer #1 also bring up this point #3 The pristine graphene shows a high proton conductivity of 6.9 ±1.1 S·cm-2,

For pristine graphene, this conductivity is caused by either defects intrinsically present in the CVD graphene or (what we now believe most) the interfacial chemistry between graphene and the fuel cell membrane assembly components.

The authors responded with optical images and Raman which simply doesn't have adequate resolution for quantifying all kinds of defects. Raman below a certain level of defect density is not adequate.

We agree. We extended the original description of the HRTEM results. See below in the detailed answer.

The authors report proton conductance 20 times more than pristine graphene at 3mS cm-2, there is no explanation for this. (Nature volume 516, pages227–230 (2014); ACS Nano 2019, 13, 10, 12109–12119; J. Mater. Chem. A, 2022,10, 19797-19810) crack and tears in centimeter scale membranes are known to enhance transport.

For dry Nafion a conductance of 3mS/cm^2 was indeed reported in 2014. We noted in our manuscript that intrinsic defects, along with interfacial contacts in a membrane fabricated from CVD graphene, could contribute to higher proton conductance. This value could be up to three orders of magnitude greater than 3 mS/cm^2 (*Science*, **2021**, 374, eabd7687). Details of our modifications are provided in response to the following specific questions.

Caution should be exercised in attributing all of it to doping without direct evidence, considering point 2 below.

We believe that we now have revised the manuscript by taking into consideration our results carefully. We formulated hypothesizes to explain our data.

Modification we made following the comments above:

L39-47: ~~Selective to protons, transmembrane areal conductances surpass those of polymer membranes, while~~ The membrane conductance of pristine graphene in direct methanol fuel cells, derived mainly from intrinsic defects, is 6.9 ± 1.1 S·cm^{-2}. After chemical functionalization, the proton conductance increases to 30.9 ± 2.3 S·cm^{-2}, normalized to the free-standing graphene area, indicating that covalently functionalizing graphene with sulfophenyl groups efficiently lowers the membrane resistance presumably because the sulfophenylation lowers the energy barrier for protons to transport across graphene. ~~By creating proton-conductive and selective paths through graphene, we unveil a covalent chemical route to rationalize transmembrane~~

~~proton transport through 2D materials.~~

We modified the introduction by adding more references discussing proton transport through CVD graphene, especially the defects

L84-96: ~~Defects in graphene, such as seven- and higher-member rings, together with small lattice disorders such as sp^3 distortions and polar functional groups are promising approaches for enhancing proton conductivity, while maintaining the impermeability of the basal plane to other substances, which are particularly of interests in energy devices such as fuel cells.~~ In CVD graphene, for example, cracks and defects are commonly observed at the microscale[46], influencing proton transport properties. At a smaller scale than larger sized cracks, theoretical studies indicate that small lattice disorders, such as hydrogenated graphene seven- and higher-membered rings, effectively lower the proton permeation barrier through graphene[47-49]. Diffusive proton conductance experiments also demonstrate improved proton transport through graphene with eight-membered rings[50], vacancy defects[33], and other structural modifications such as nitrogen-doped graphene[51]. Therefore, due to the presence of intrinsic defects, the proton conductance of CVD graphene was reported up to three orders of magnitude higher than that of defect-free graphene 2D crystals[52].

The devices have Nafion so they won't show up in the performance. The nitrogen doping data actually supports the reviewer's claim that increased proton transport is not from small defects but from sporadic cracks and tears in the graphene for the SO2- case.

Nitrogen doping does not create cracks but nanopores. We ruled out the possibility that the enhanced proton conductance originates from enlarged cracks and tears caused by chemical functionalization. This conclusion is supported by tests on stand-alone spin-coated Nafion ionomer and extensive HRTEM observations.

We spin-coated a Nafion ionomer layer onto a flat Cu foil without graphene and then transferred it onto a porous PC membrane by etching away the Cu, floating the

Nafion/Cu/PC stack on a Cu etchant. The Nafion/PC membrane was subsequently rinsed in ultrapure water and 0.1 M HCl, following the same procedure used for fabricating the Nafion/graphene/PC membranes in our study. Our results showed that the Nafion ionomer alone was highly permeable to the methanol/water mixture. In DMFC tests, this led to significant methanol crossover, causing near-zero cell current and complete activation failure (see Fig. R1). Thus, the spin-coated Nafion layer alone had negligible impact on membrane performance, particularly in sealing leaks. Based on this, we conclude that any cracks or tears in the graphene would be detectable through methanol crossover measurements.

We added this observation to the following discussion:

L258-262: To assess the contribution of the spin-coated Nafion ionomer, we tested the Nafion ionomer/PC membrane in DMFCs. The membrane exhibited high permeability to the methanol/water mixture, resulting in almost no cell current (Fig. S24). This confirms that the graphene layer serves as the primary selective barrier, and the DMFC observations effectively demonstrate the selective proton conductance of graphene.

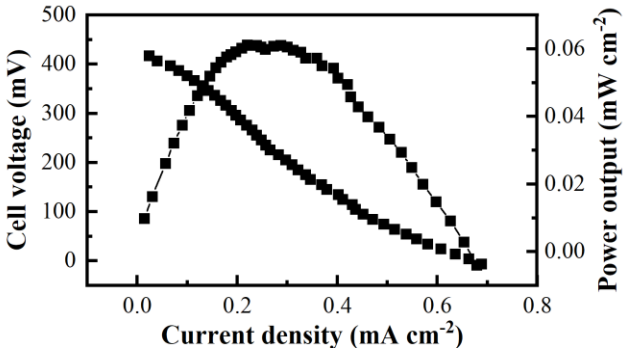

Figure R1 (S24). DMFC performance of a Nafion spin-coated PC membrane.

If the original proton-conducting sites had developed larger cracks or tears, methanol crossover would have increased, but we did not observe such an effect (also for nitrogen doped graphene as shown in our previous response, pasted below for information). Secondly, we aimed to investigate the presence of smaller openings, such as pinholes.

However, extensive HRTEM observations of three batches—comprising a total of eleven independent samples—did not reveal any pinholes or vacancy-type defects after chemical functionalization. To maintain a more neutral perspective, we have revised the following discussion accordingly.

Our comments on N-doped graphene

Additionally, we explored the role of active sites and defects by functionalizing graphene using nitrogen plasma treatment. This exposure led to an increase in defect density, which initially boosted the DMFC power output (Figure R5). However, despite the defect density being significantly higher than that of sulfophenylated graphene (Figure R6) with an I_D/I_G ratio of ~1.2 (0.4~0.6 for sulfophenylated graphene), the maximum power output achieved was only one-third of that seen with sulfophenylated graphene. This finding further substantiates that the enhanced proton conductance results from sp^3 dislocations and the presence of ph-SO_3^- functional groups.

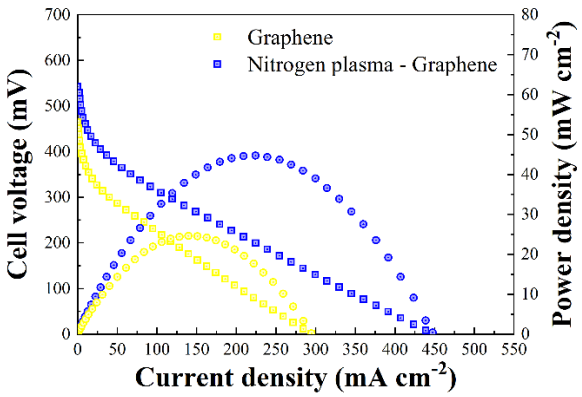

***Figure R'5**. DMFC performance with a membrane made of defected graphene by nitrogen plasma.*

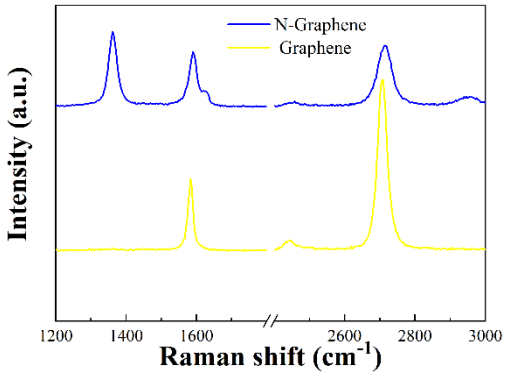

Figure R'6*. Raman spectrum of defected graphene by nitrogen plasma.*

L164-166: We checked the potential damage induced by the chemical functionalization at the nanometer scale. HRTEM images of graphene after 4-day and 6-day of SBD treatment did not show the apparition of large >1 nm pores (Fig. 2E)

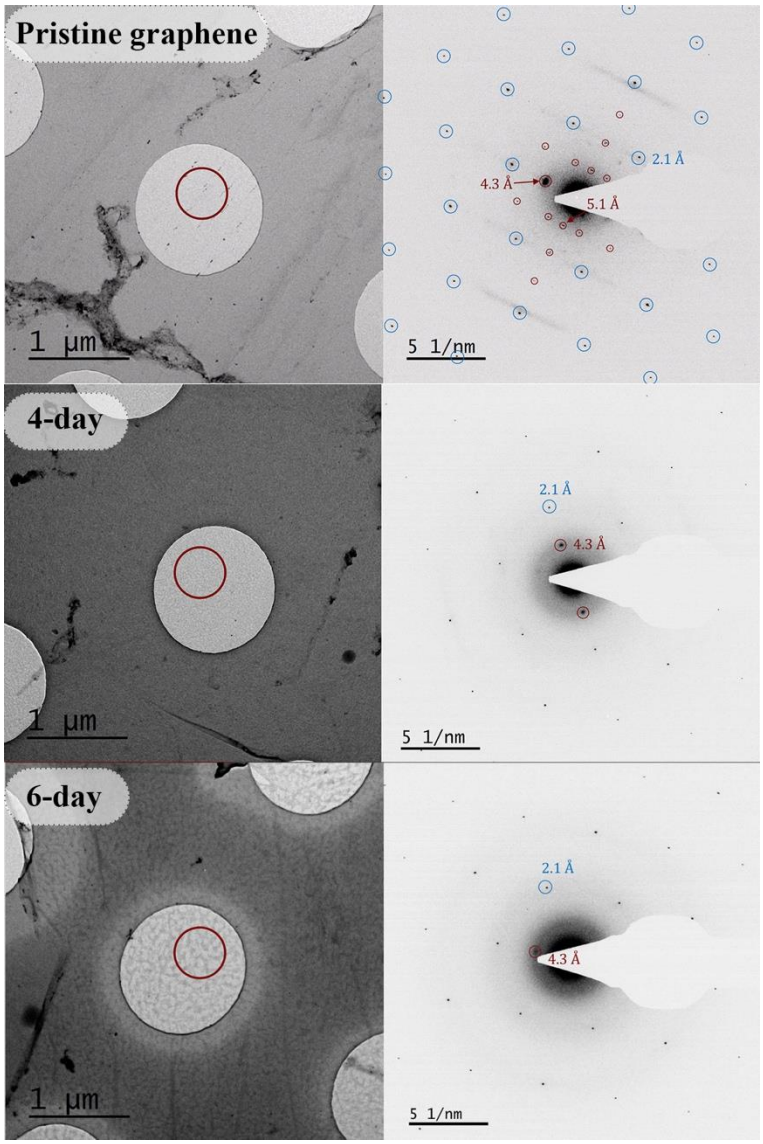

Fig. R2 (S20) TEM image with diffraction pattern of pristine CVD graphene and SO_3^--graphene after 4 days and 6 days 4-SBD (**batch 1**, 1 mg·ml^{-1} in 0.1 M HCl) treatment.

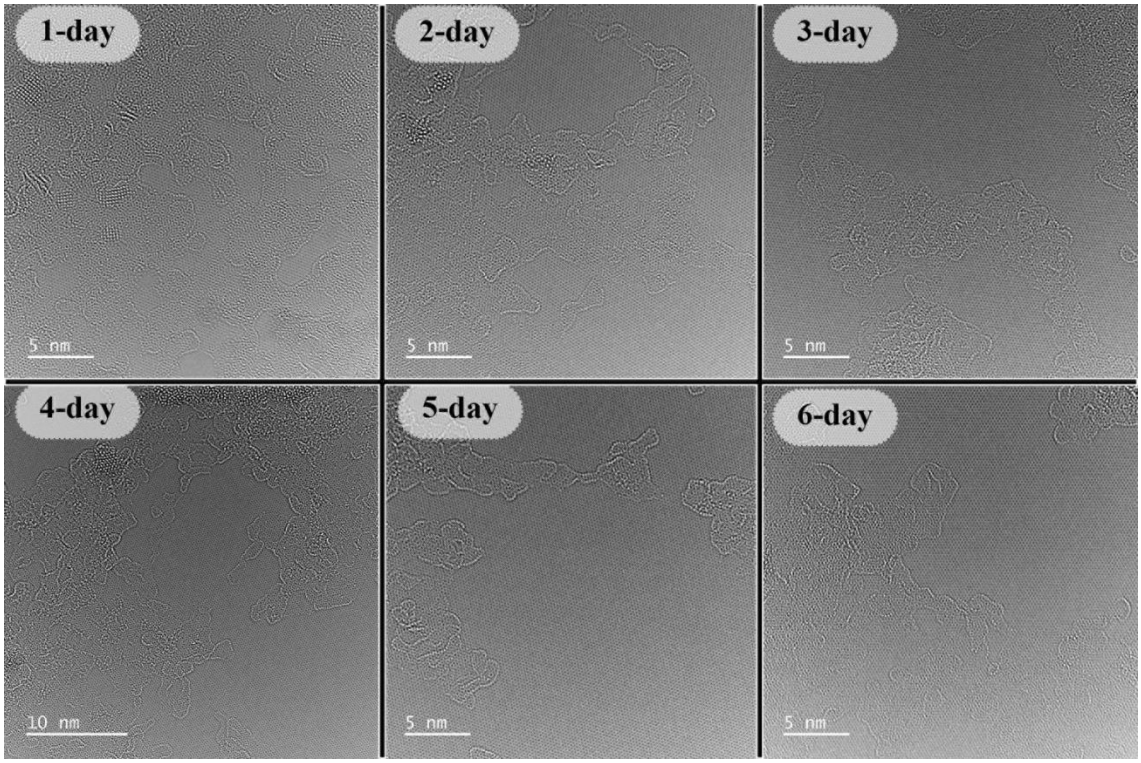

Fig. R3 (S21) HRTEM images of CVD graphene after 1 to 6 days of 4-SBD (**batch 2**, 1 mg·ml^{-1} in 0.1 M HCl) treatment.

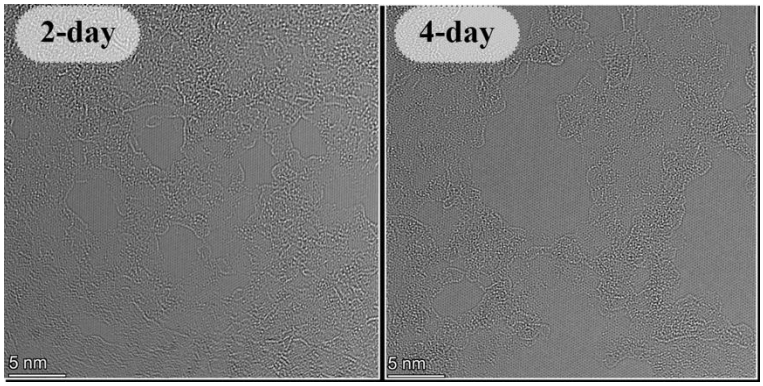

Fig. R4 (S22) HRTEM images of CVD graphene after 2 and 4 days of 4-SBD (**batch 3**, 1 mg·ml^{-1} in 0.1 M HCl) treatment.

Moreover, during the functionalization with SBD, graphene floats on 0.1M HCl in water. We carried control experiment where graphene was floated on pure water and water containing 0.1M HCl and mounted in the DMFC. We did not measure significant improvement in power density, membrane resistance and open circuit voltages for those

samples, ruling out the possibility that the enhanced proton conductance was due to graphene degradation due to water or 0.1M HCl during the treatment.

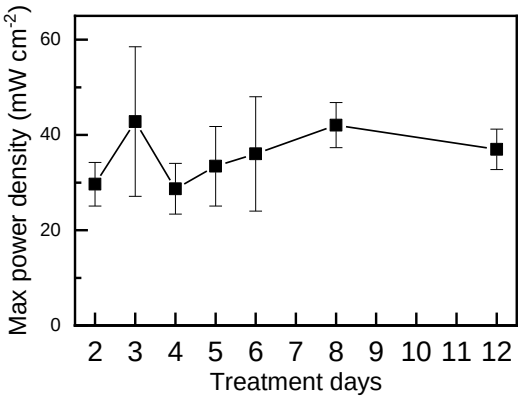

Fig. R5 (S25) Maximum power output of Direct Methanol Fuel Cells (DMFCs) with graphene membranes floated on pure water. Graphene membranes were floated on ultrapure water using the same conditions applied for the SBD treatment. The fuel cell tests were operated at 60 °C, with same flow rate of 1 M methanol solution and oxygen as tests conducted with SO_3^--graphene membranes.

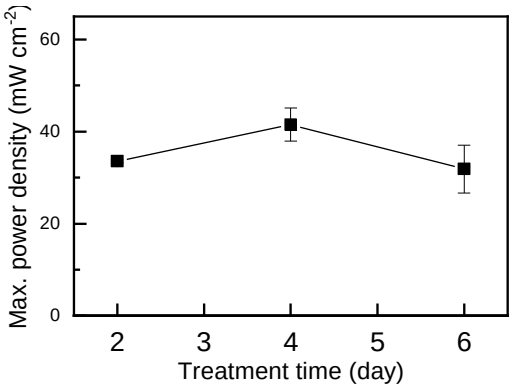

Fig. R6 (S26) Maximum power output of Direct Methanol Fuel Cells (DMFCs) with graphene membranes floated on 0.1 M HCl solution. Graphene membranes were floated on 0.1 M HCl using the same conditions applied for the SBD treatment. The fuel cell experiments were performed at 60 °C, with same flow rate of the 1 M methanol solution and oxygen as experiments conducted with SO_3^--graphene membranes.

2. Intrinsic defects exist within the individual CVD domains forming the film. How do the authors rule the presence of defects and the etching of these defects with longer sulfonation times or processing during membrane fabrication? Authors should show direct evidence of expansion of the ring with covalent functionalization e.g. TEM images with increased bond length or distorted rings and Raman spectra.

Since the authors cannot confirm these aspects with HRTEM or find evidence of sp3 in Raman, they should avoid speculative claims.

Sulfophenylation does not cause the etching of original defects into larger one. We have performed extensive TEM characterization, and we could not observe any holes forming upon functionalization. We recognize that once the fuel cell is mounted, additional damage may occur, however, still, sulfophenylated graphene membranes yield better fuel cell performances than pristine graphene or Nafion alone. We have revised the discussion to leave room for an open dialogue on the potential influence of defects to the increased fuel cell performances.

Modification in the manuscript:

CVD graphene, **L146-149** : Fig. 2B shows scanning electron microscopy (SEM) images of >200 μm wide CVD graphene single crystals grown on a copper foil with minimized grain boundaries and intrinsic defects. Multilayer patches were negligibly observed in the samples. However, the sparsely distributed defects and cracks introduced during membrane manipulation cannot be entirely prevented and may contribute to additional permeation in contrast to the proton conductance measured with a perfectly defect-free graphene 2D crystal.

HRTEM, **L164-170**: We checked the potential damage induced by the chemical functionalization at the nanometer scale. HRTEM images of graphene after 4-day and 6-day of SBD treatment did not show the apparition of large >1 nm pores (Fig. 2E). Instead, the large defect-free graphene area suggests that individual grafting sites could

not be observed on the monolayer regions (Fig. 2E). Additionally, no apparent expansion of the graphene lattice due to sp^3 distortion was observed. To confirm covalent functionalization, we conducted Raman spectroscopy and elemental analysis and the results are discussed in the next section.

Raman, **L193-206** : The increasing value of the D peak intensity ratio (~1350 cm^{-1}) over the G peak (~1580 cm^{-1}) (I_D/I_G) indicates the formation of defects upon 4-SBD treatment~~, primarily the introduction of sp^3 distortions~~[58]. Since the I_D/I_G peak remains similar after the 4-day treatment, we speculate that the introduced defects are unlikely to be vacancies or cracks. Additionally, after mounting in the fuel cell, the presence of active edges that could further enlarge over time would yield to an increase of methanol crossover, which we did not measure. We cannot rule out that sulfophenylation could seal grain boundaries, or sp^3 distortions, however, we could not observe such an effect in HRTEM images. With our hypothesis that the combination of a sp^3 distortion and a charged SO_3^- group contributes to an increased proton transport. A more favorable functionalization of grain boundaries and defects could enhance proton transport selectivity through these regions, rather than decreasing it. This is because sulfophenylation may effectively seal and passivate grain boundaries, guiding protons through them. However, our analysis showed no clear preference for functionalization at grain boundaries on the microscale, as indicated by the homogeneous distribution of Raman signals across the graphene surface (Fig. S14-S15).

They should try to find out the real reason for enhanced transport as suggested by 2 independent reviewers instead of trying to push through this manuscript in its current state.

We formulate hypothesis that could possibly explain our results wherever this is possible. Besides the modifications mentioned above, we refined the conclusion accordingly:

L343-360: To conclude, the functionalization of centimeter-size CVD graphene ~~with~~

~~an out-of-plane polar group and an sp^3 distortion by diazotization~~ with a sulfophenyl radical increases the membrane conductance of CVD graphene in a working DMFC from 6.9 ± 1.1 $S \cdot cm^{-2}$ to 30.9 ±2.3 $S \cdot cm^{-2}$ at room temperature, with a power density of 127 $mW \cdot cm^{-2}$ at 60 °C, which is more than twice the power density measured with Nafion 117. ~~which yielded highly selective proton conductivity (30.9 ±2.3 $S \cdot cm^{-2}$) and also enabled application in a direct methanol fuel cell delivering a power density more than twice higher than its Nafion™ counterpart according to the electrode area (127 $mW \cdot cm^{-2}$ at 60 °C).~~ However, further investigations are required to understand the factors contributing to enhancing the proton conductance, particularly defects, sp^3 distortions, and functional groups at the interface between graphene and the electrolyte. Controlling how functional groups are oriented on both side of the membrane could play a crucial role in modulating the transport of protons across the membrane. The creation of active sites as intrinsic proton pathways on graphene, as well as controlling the polarization of 2D membranes via these active sites – particularly in more complex two-dimensional polymer architectures[62,63] – would be a natural next step of this research, to establish correlations between the chemistry of the graphene and electrolyte interface and the efficiency of proton transport, for example using performance parameters of a fuel cell or using ion transport measurements.

2. The authors use CVD grown single crystalline graphene - how do they rule out defects in single crystalline graphene over centimeter scale areas? Several reports have shown that single crystalline graphene are not devoid of defects. These aspects appear to have been overlooked.

The graphene we use is single crystalline over centimeter scales. Still it shows a conductance of 6.9 S/cm2 with wet Nafion in its pristine state. This conductance increases to 30.9 S/cm2 after SBD functionalization. We discussed the possible role of defects in the revised manuscript:

L84-96: ~~Defects in graphene, such as seven- and higher-member rings, together with small lattice disorders such as sp^3 distortions and polar functional groups are promising~~

~~approaches for enhancing proton conductivity, while maintaining the impermeability of the basal plane to other substances, which are particularly of interests in energy devices such as fuel cells.~~ In CVD graphene, for example, cracks and defects are commonly observed at the microscale[46], influencing proton transport properties. At a smaller scale than larger sized cracks, theoretical studies indicate that small lattice disorders, such as hydrogenated graphene seven- and higher-membered rings, effectively lower the proton permeation barrier through graphene[47-49]. Diffusive proton conductance experiments also demonstrate improved proton transport through graphene with eight-membered rings[50], vacancy defects[33], and other structural modifications such as nitrogen-doped graphene[51]. Therefore, due to the presence of intrinsic defects, the proton conductance of CVD graphene was reported up to three orders of magnitude higher than that of defect-free graphene 2D crystals[52].

L264-267: Pristine graphene showed a maximum power density of 25.8 ±15.4 mW·cm^{-2}, at 212 mV, which is about half (~ 45%) compared to Nafion 117. ~~These results can be attributed to defects and cracks, resulting from the membrane electrode assembly (MEA) including CVD graphene.~~ These results can be attributed to the fact that graphene blocks proton transport compare to Nafion.

The authors misunderstood the point the reviewer was making. The pristine graphene they refer to is made via CVD! That also have defects that manifest even in single crystalline graphene membranes. Characterizing these intrinsic defects over centimeter scale areas is challenging with HRTEM, AFM, and Raman, and several groups around the world have developed diffusive transport as an alternative solution that provides information in a few hours with reliable statistics. The authors may want to look into those works and try to characterize their materials thoroughly with relevant techniques that will un-ravel the science behind the effects seen here – instead of claiming it comes from doping, SO3- without direct evidence.

In our manuscript we do not perform ion transport measurements and do not systematically try to make correlations between the active site types and the fuel cell

performance. To address the misunderstanding regarding CVD graphene, we have revised the following sections to discuss the presence of cracks in CVD graphene and the role of defects and how we confirm the contribution of chemical functionalization to the higher fuel cell performances.

Single-crystalline CVD graphene vs. exfoliated graphene:

L84-96: ~~Defects in graphene, such as seven- and higher-member rings, together with small lattice disorders such as sp^3 distortions and polar functional groups are promising approaches for enhancing proton conductivity, while maintaining the impermeability of the basal plane to other substances, which are particularly of interests in energy devices such as fuel cells.~~ In CVD graphene, for example, cracks and defects are commonly observed at the microscale[46], influencing proton transport properties. At a smaller scale than larger sized cracks, theoretical studies indicate that small lattice disorders, such as hydrogenated graphene seven- and higher-membered rings, effectively lower the proton permeation barrier through graphene[47-49]. Diffusive proton conductance experiments also demonstrate improved proton transport through graphene with eight-membered rings[50], vacancy defects[33], and other structural modifications such as nitrogen-doped graphene[51]. Therefore, due to the presence of intrinsic defects, the proton conductance of CVD graphene was reported up to three orders of magnitude higher than that of defect-free graphene 2D crystals[52].

L142-149: The centimeter-size single-crystal CVD graphene films, which were seamlessly stitched into well-aligned domains[57], were used to minimize the defects and grain boundaries. Fig. 2B shows scanning electron microscopy (SEM) images of >200 μm wide CVD graphene single crystals grown on a copper foil with minimized grain boundaries and intrinsic defects. Multilayer patches were negligibly observed in the samples. However, the sparsely distributed defects and cracks introduced during membrane manipulation cannot be entirely prevented and may contribute to additional permeation in contrast to the proton conductance observed with a perfectly structured graphene 2D crystal.

Besides the modifications we made to the original text of the manuscript, we also would like to comment on how we included the contributions of cracks in our original data set:

1. Cracks:

Stability of transferred graphene:

To assess the stability of transferred graphene, we floated the sample on water and a 0.1 M HCl solution for several days. No significant changes were observed, indicating that potential cracks would not enlarge simply due to liquid contact (Fig. R5&R6).

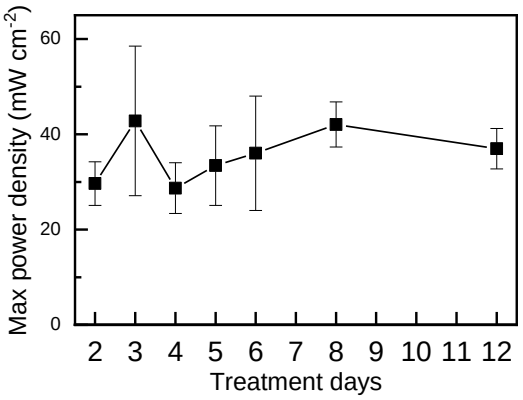

Fig. R5 (S25) Maximum power output of Direct Methanol Fuel Cells (DMFCs) with graphene membranes floated on pure water. Graphene membranes were floated on ultrapure water using the same conditions applied for the SBD treatment. The fuel cell tests were operated at 60 °C, with same flow rate of 1 M methanol solution and oxygen as tests conducted with SO_3^--graphene membranes.

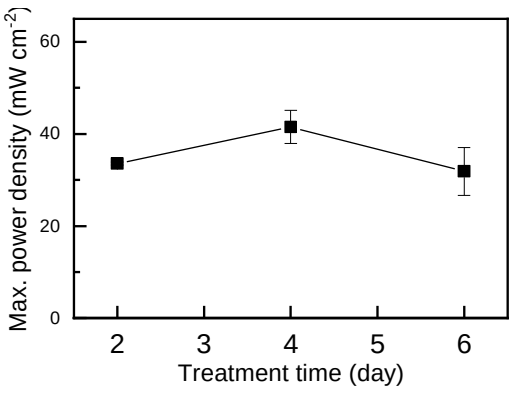

Fig. R6 (S26) Maximum power output of Direct Methanol Fuel Cells (DMFCs) with graphene membranes floated on 0.1 M HCl solution. Graphene membranes were floated on 0.1 M HCl using the same conditions applied for the SBD treatment. The fuel cell experiments were performed at 60 °C, with same flow rate of the 1 M methanol solution and oxygen as experiments conducted with SO_3^--graphene membranes.

Raman study of SBD treatment and controlled defect growth by diazotization:

To evaluate the impact of the chemical treatment, we conducted Raman spectroscopy on Nafion/graphene samples floating in the reactive SBD solution over multiple days. The spectral changes remained homogeneous throughout the treatment period, ruling out the possibility of treatment-induced cracks at the microscale (Fig. R8). The defect density increased only up to four days of treatment, aligning with the expected surface grafting process, where only a limited number of sites could be functionalized. If the D peak were associated with reactive edges, a much more rapid increase in defect density and a significantly larger D peak would be expected.

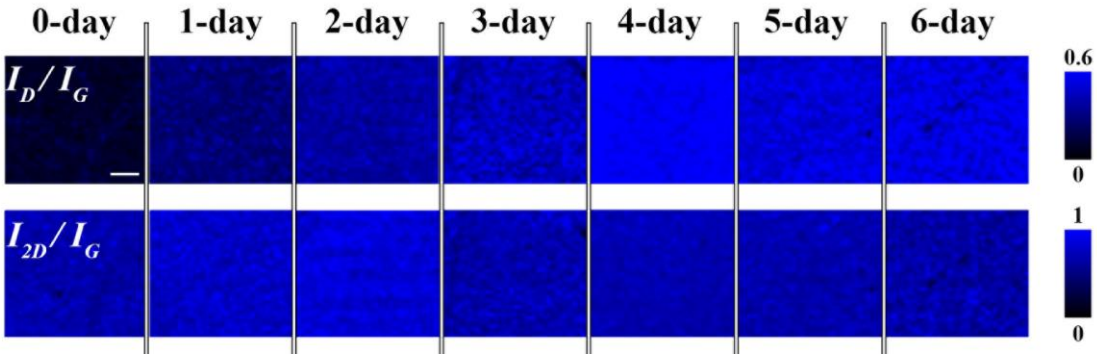

Fig. R8 (S14) Raman mapping of peak intensity ratios, I_D/I_G and I_{2D}/I_G, images of Nafion/graphene after floating on SBD solution for 0 to 6 days. The scale bar is 2 μm.

2. Pinholes

We performed three batches of HRTEM measurements on eleven independent samples after different time of SBD treatment. We did not observe the formation of pinholes

(Fig R2-4).

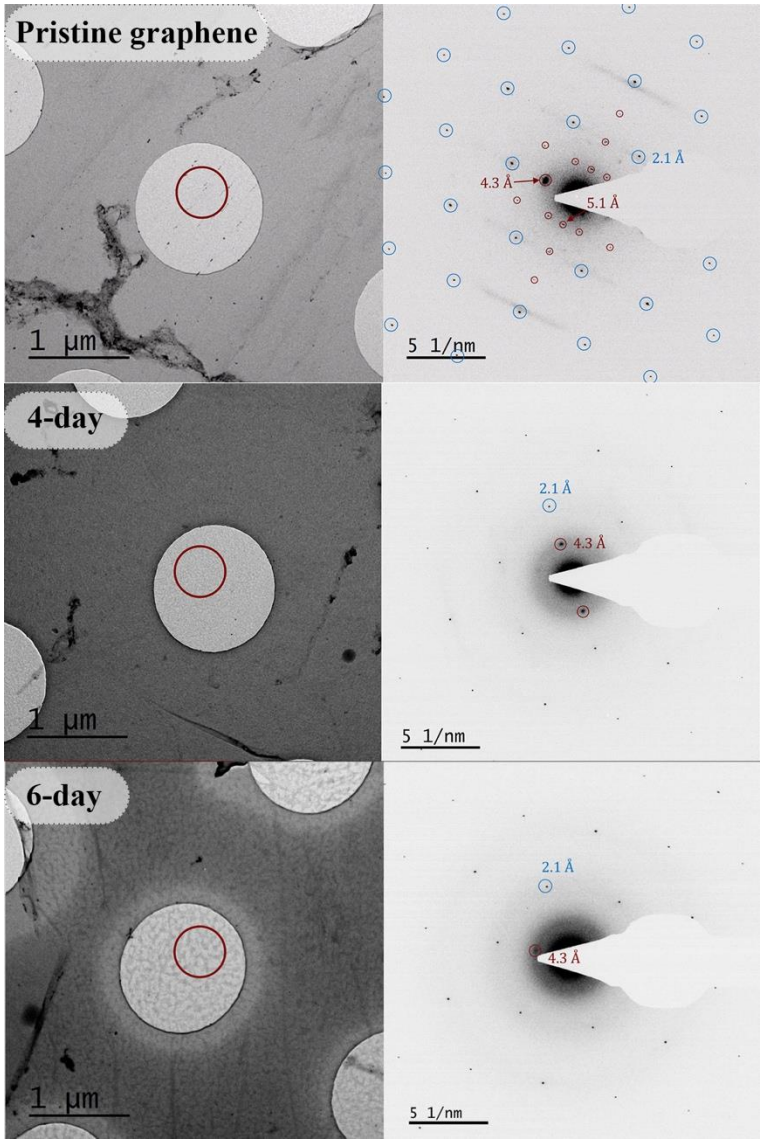

Fig. R2 (S20) TEM image with diffraction pattern of pristine CVD graphene and SO_3^--graphene after 4 days and 6 days 4-SBD (**batch 1**, 1 mg·ml^{-1} in 0.1 M HCl) treatment.

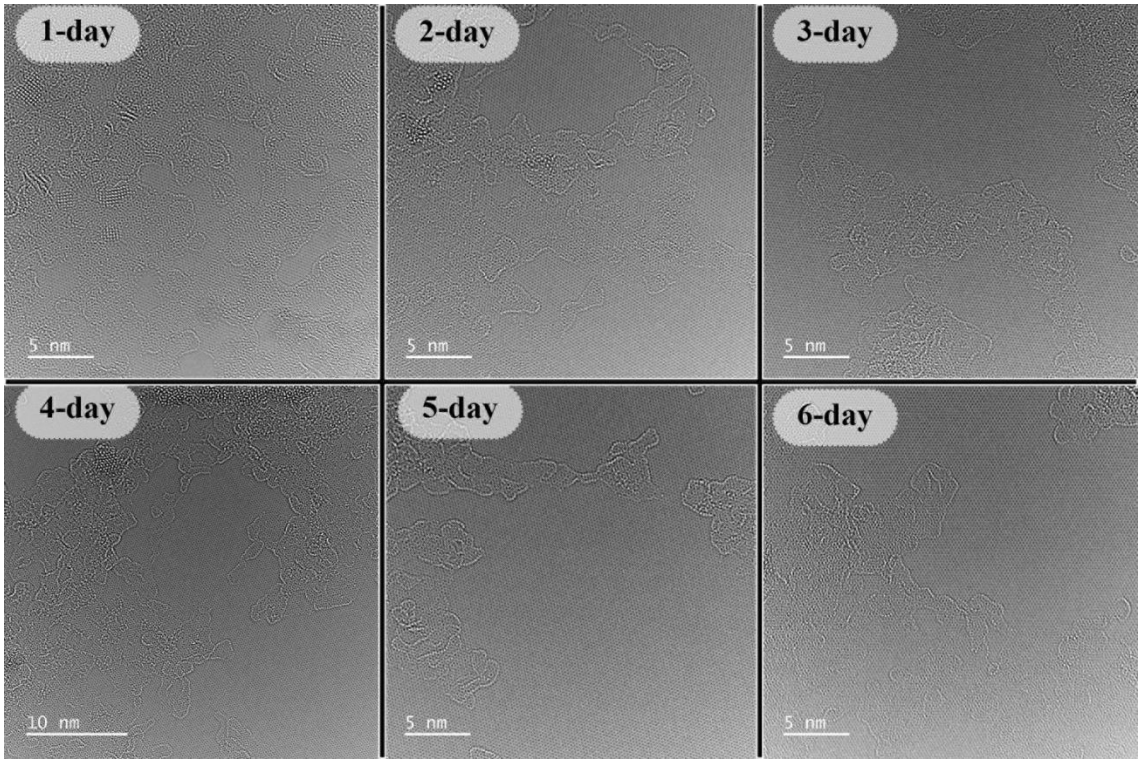

Fig. R3 R10 (S21) HRTEM images of CVD graphene after 1 to 6 days of 4-SBD (**batch 2**, 1 mg·ml^{-1} in 0.1 M HCl) treatment.

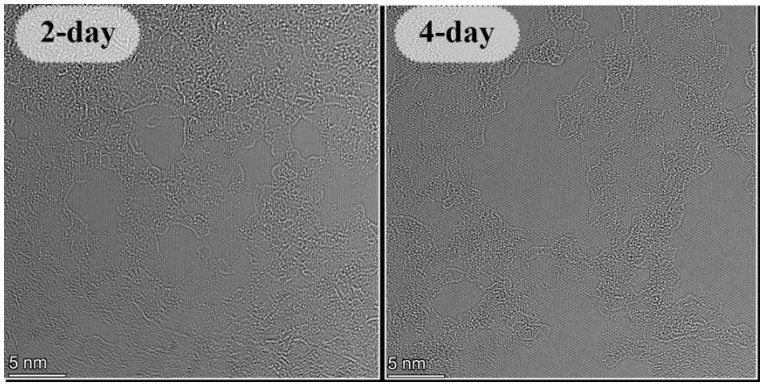

Fig. R4 (S22) HRTEM images of CVD graphene after 2 and 4 days of 4-SBD (**batch 3**, 1 mg·ml^{-1} in 0.1 M HCl) treatment.

3. Point 1 and 2 are supported by the so called "pristine" graphene in this study showing > 3mS/cm2 (value for exfoliated graphene).

The authors missed the point that even CVD graphene has shown 3-4 mS cm-2 similar to exfoliated graphene. (Nature volume 516, pages227–230 (2014); ACS Nano 2019,

13, 10, 12109–12119; J. Mater. Chem. A, 2022,10, 19797-19810).

We pasted our reply this question here again:

For dry Nafion a conductance of 3mS/cm^2 was indeed reported in 2014. We noted in our manuscript that intrinsic defects, along with interfacial contacts in a membrane fabricated from CVD graphene, could contribute to higher proton conductance. This value could be up to three orders of magnitude greater than 3 mS/cm^2 (*Science*, **2021**, 374, eabd7687).

Single-crystalline CVD graphene vs. exfoliated graphene:

L84-96: ~~Defects in graphene, such as seven- and higher-member rings, together with small lattice disorders such as sp^3 distortions and polar functional groups are promising approaches for enhancing proton conductivity, while maintaining the impermeability of the basal plane to other substances, which are particularly of interests in energy devices such as fuel cells.~~ In CVD graphene, for example, cracks and defects are commonly observed at the microscale[46], influencing proton transport properties. At a smaller scale than larger sized cracks, theoretical studies indicate that small lattice disorders, such as hydrogenated graphene seven- and higher-membered rings, effectively lower the proton permeation barrier through graphene[47-49]. Diffusive proton conductance experiments also demonstrate improved proton transport through graphene with eight-membered rings[50], vacancy defects[33], and other structural modifications such as nitrogen-doped graphene[51]. Therefore, due to the presence of intrinsic defects, the proton conductance of CVD graphene was reported up to three orders of magnitude higher than that of defect-free graphene 2D crystals[52].

Does this mean the CVD single crystalline graphene made here is not as high in quality as even polycrystalline graphene used in other studies? Or is the higher transport from cracks and tears?

In light of points 1 and 2 the reviewer urges extreme caution from making claims without

evidence by the authors.

The CVD graphene has single crystalline domains of centimeters and was used to minimize grain boundaries and inherent defects, as highlighted in the manuscript. However, when mounted in the fuel cell, we measured a non-infinite membrane resistance, suggesting that the MEA contributes to the membrane resistance. Compared to polycrystalline graphene, which contains more grain boundaries and multilayer regions, single-crystalline graphene offers a more controlled structure with fewer intrinsic imperfections. We added to the manuscript:

L142-149: The centimeter-size single-crystal CVD graphene films, which were seamlessly stitched into well-aligned domains[57], were used to minimize the defects and grain boundaries. Fig. 2B shows scanning electron microscopy (SEM) images of >200 μm wide CVD graphene single crystals grown on a copper foil with minimized grain boundaries and intrinsic defects. Multilayer patches were negligibly observed in the samples. However, when mounted in the fuel cell, we measured a non-infinite membrane resistance, suggesting that the MEA contributes to the membrane resistance with an original conductance of pristine graphene of 6.9 ± 1.1 $S \cdot cm^{-2}$.

4. How do the authors rule out the formation of crack or tears in graphene as the spin coated Nafion film swells during removal of Cu while etching in acid?

If large cracks and tears would form, the power density of the fuel cell would reach near zero as shown in Figure R1 (Figure S24). But still, we measure a conductance for pristine graphene which accounts for 6.9 ± 1.1 $S \cdot cm^{-2}$.

Although the authors used a rigid PC membrane and used Raman these don't allow for probing over macroscopic areas with high resolution.

After the membrane electrode assembly and fuel cell testing, we can not image the graphene layer. This would be optimal but the graphene is stuck with Nafion and the catalyst layers and can not be taken apart.

5. The data for 4 day treatment shows better power density than 6 days. This further indicates defects and not covalent functionalization and a trade-off.

The polymerization of the diazonium compound occurs as a result of surface grafting, a process confirmed through AFM observations showing that the surface roughness increases with increasing treatment time (see Figure 2C and 2D). The formation of a thick polymer layer is likely responsible for the observed decrease in membrane performance. This outlines the reaction mechanism involved in the chemical treatment with both grafting and polymer growth phases.

The authors mention they don't see defects but no HR TEM is provided as evidence.

We have discussed our HRTEM studies and images in the main text. The complete set of HRTEM results is provided in the supplementary information (Fig. S20-S22). Those do not show defects that appear from the SBD treatment. As such, in fuel cells, we do not expect the SBD treatment itself to create but also can not be compared with graphene after the fuel cell has operated.

The reviewer is merely point to defects and variability might be responsible for this since one would not expect a reduction after saturation if this was purely functionalization.

The sulfophenyl radical reacts with a sp^2 carbon atom on the graphene basal plane, which is converted to sp^3 upon grafting. Meanwhile, side reactions might also occur: 4-SBD can react with an already grafted aryl group (at the ortho position) either via a radical or azo-coupling mechanism, both of which might result in oligomerization[54] of the aryl species on the graphene basal plane.

Pristine graphene is therefore covered by 4-SBD already after 24 h after which the 4-SBD layer becomes thicker and more homogenous. Oligomerization, which is commonly observed during diazonium treatment[53] likely leads to the additional resistance that protons encounter. The spontaneous oligomerization of SBD, giving rise

to agglomerates visible in AFM, were therefore not distinguishable by HRTEM from common hydrocarbon contaminations resulting from the growth of CVD graphene (supplementary material, Fig. S20-S22).

6. Referencing is inadequate and several key papers in the field on centimeter scale graphene PEMs are not cited.

The reviewer recommends citing relevant papers in the field focusing on proton transport using CVD graphene to benchmark and contextualize the current work.

We revised the discussion of graphene PEMs with the following literatures selected for the discussion:

The main challenge for polymeric membranes lies in balancing proton conductivity and selectivity, with methanol crossover posing an additional obstacle due to its high solubility in water and uncharged nature, which facilitates migration from the anode to the cathode. To mitigate this issue, various strategies have been pursued to enhance the power output of direct methanol fuel cells (DMFCs)[22]. For instance, incorporating layered additives has been shown to improve performance; the power output increased to 35 mW cm^{-2} with nano-silica additives[23] and to 39 mW cm^{-2} with graphene oxide[24]. The power output of DMFCs using a Nafion 117 membrane was enhanced to 79 mW cm^{-2} by impregnating the membrane with Pd[25]. Additionally, recasting the Nafion membrane with blended additives has been shown to boost DMFC to over 100 mW cm^{-2} of the maximum power outputs[26,27]. The power output of DMFCs was enhanced to 25 mW cm^{-2} by sandwiching single-layer graphene between two layers of Nafion membrane[28] and increased to 120 mW cm^{-2} by incorporating single-layer graphene onto the electrode[29].

22 Asghar, M. R. & Xu, Q. A review of advancements in commercial and non-commercial Nafion-based proton exchange membranes for direct methanol fuel cells. *Journal of Polymer Research* **31**, 125 (2024). https://doi.org/10.1007/s10965-024-03964-y

23 Kim, D., Scibioh, M. A., Kwak, S., Oh, I.-H. & Ha, H. Y. Nano-silica layered composite membranes prepared by PECVD for direct methanol fuel cells. *Electrochemistry Communications* **6**, 1069-1074 (2004).

https://doi.org/https://doi.org/10.1016/j.elecom.2004.07.006

24 Ruhkopf, J. *et al.* Graphene Coating of Nafion Membranes for Enhanced Fuel Cell Performance. *ACS Applied Engineering Materials* **1**, 947-954 (2023). https://doi.org/10.1021/acsaenm.2c00234

25 Kim, Y.-M., Park, K.-W., Choi, J.-H., Park, I.-S. & Sung, Y.-E. A Pd-impregnated nanocomposite Nafion membrane for use in high-concentration methanol fuel in DMFC. *Electrochemistry Communications* **5**, 571-574 (2003). https://doi.org/https://doi.org/10.1016/S1388-2481(03)00130-9

26 Parthiban, V., Panda, S. K. & Sahu, A. K. Highly fluorescent carbon quantum dots-Nafion as proton selective hybrid membrane for direct methanol fuel cells. *Electrochimica Acta* **292**, 855-864 (2018). https://doi.org/https://doi.org/10.1016/j.electacta.2018.09.193

27 Parthiban, V., Akula, S. & Sahu, A. K. Surfactant templated nanoporous carbon-Nafion hybrid membranes for direct methanol fuel cells with reduced methanol crossover. *Journal of Membrane Science* **541**, 127-136 (2017). https://doi.org/https://doi.org/10.1016/j.memsci.2017.06.081

28 Yan, X. H., Wu, R. Z., Xu, J. B., Luo, Z. T. & Zhao, T. S. A monolayer graphene - Nafion sandwich membrane for direct methanol fuel cells. *Journal of Power Sources* **311**, 188-194 (2016). https://doi.org/10.1016/j.jpowsour.2016.02.030

29 Holmes, S. M. *et al.* 2D Crystals Significantly Enhance the Performance of a Working Fuel Cell. *Adv. Energy Mater.* **7**, 7 (2017). https://doi.org/10.1002/aenm.201601216

While numerous studies have explored the use of nanoflake additives to enhance PEM performance, many of these involve permeation pathways that include interlayer transport rather than purely transmembrane mechanisms. Regarding single-layer graphene used as PEMs, we discuss now also relevant diffusion experiments with particular emphasis on ionic permeation behavior. See below the added paragraph in the revised introduction:

L84-96: ~~Defects in graphene, such as seven- and higher-member rings, together with small lattice disorders such as sp^3 distortions and polar functional groups are promising approaches for enhancing proton conductivity, while maintaining the impermeability of the basal plane to other substances, which are particularly of interests in energy devices such as fuel cells.~~ In CVD graphene, for example, cracks and defects are commonly observed at the microscale[46], influencing proton transport properties. At a smaller scale than larger sized cracks, theoretical studies indicate that small lattice disorders, such as hydrogenated graphene seven- and higher-membered rings, effectively lower the proton permeation barrier through graphene[47-49]. Diffusive proton conductance experiments also demonstrate improved proton transport through graphene with eight-membered rings[50], vacancy defects[33], and other structural modifications such as nitrogen-doped graphene[51]. Therefore, due to the presence of

intrinsic defects, the proton conductance of CVD graphene was reported up to three orders of magnitude higher than that of defect-free graphene 2D crystals[52].

33 Chaturvedi, P. *et al.* Ionic conductance through graphene: Assessing its applicability as a proton selective membrane. *ACS Nano* **13**, 12109-12119 (2019). https://doi.org/10.1021/acsnano.9b06505

46 Arjmandi-Tash, H., Jiang, L. & Schneider, G. F. Rupture index: A quantitative measure of sub-micrometer cracks in graphene. *Carbon* **118**, 556-560 (2017). https://doi.org/https://doi.org/10.1016/j.carbon.2017.03.054

47 Feng, Y. X. *et al.* Hydrogenation facilitates proton transfer through two-dimensional honeycomb crystals. *Journal of Physical Chemistry Letters* **8**, 6009-6014 (2017). https://doi.org/10.1021/acs.jpclett.7b02820

48 An, Y., Oliveira, A. F., Brumme, T., Kuc, A. & Heine, T. Stone-Wales defects cause high proton permeability and isotope selectivity of single-layer graphene. *Adv. Mater.* **32**, 2002442 (2020). https://doi.org/10.1002/adma.202002442

49 Bartolomei, M., Hernandez, M. I., Campos-Martinez, J. & Hernandez-Lamoneda, R. Graphene multi-protonation: A cooperative mechanism for proton permeation. *Carbon* **144**, 724-730 (2019). https://doi.org/10.1016/j.carbon.2018.12.086

50 Griffin, E. *et al.* Proton and Li-Ion Permeation through Graphene with Eight-Atom-Ring Defects. *ACS Nano* **14**, 7280-7286 (2020). https://doi.org/10.1021/acsnano.0c02496

51 Zeng, Z. *et al.* Biomimetic N-Doped Graphene Membrane for Proton Exchange Membranes. *Nano Letters* **21**, 4314-4319 (2021). https://doi.org/10.1021/acs.nanolett.1c00813

52 Kidambi, P. R., Chaturvedi, P. & Moehring, N. K. Subatomic species transport through atomically thin membranes: Present and future applications. *Science* **374**, eabd7687 (2021). https://doi.org/10.1126/science.abd7687

Response to reviewers

We thank Reviewer #3 for the valuable questions which helped to further increase the clarity of our manuscript. Please find our detailed responses to each specific question below. We also amended the manuscript with these revisions (in red).

Reviewer #3 (Remarks to the Author):

The reviewer appreciates the efforts by Zhang et al. to clarify some aspects including addition of HRTEM images and changes to the manuscript to factor in several aspects that were previously overlooked.

The author's response seems to broadly agree with the reviewer's concerns:

"The method we employed introduces sp^3 distortions, -SO3- groups, and a polymerized layer simultaneously, making it challenging to isolate any single factor as the direct cause of the increased transport of protons, as questioned by the reviewer. A comprehensive analysis of this correlation exceeds the scope of a single manuscript, given the need to carefully isolate all these contributing factors. However, we are confident that our observations, along with the control experiments we have conducted, provide sufficient evidence to demonstrate that sulfophenylated graphene exhibits performance comparable to Nafion polymer membranes in a direct methanol fuel cell."

1. Proton conductance increased by ~5x after sulfophenylation and attributed to presumably lower energy barrier. But this should be straightforward to measure with temperature to get activation energy barriers. Flushing this out completely will provide detailed insights and position this paper for a high impact journal.

Thanks you for the suggestion. We agree. Element of this analysis, including the results in Table S3 (now mentioned in the revised manuscript) together with Figure 4D and S28 show, indeed, that the activation energy barrier decreases down to 6.9 $kJ \cdot mol^{-1}$ after 4 days of SBD treatment, which is approximately half of the one reported for Nafion membranes under fully humidified conditions (~13.5 $kJ \cdot mol^{-1}$, Journal of Power Sources, Volume 196, Issue 18, 15 September 2011, Pages 7363-7371).

Now our manuscript states:

By analyzing the measured conductance and temperature-dependence, the proton conductances of SO_3^--graphene membranes exhibit an Arrhenius behavior as described by equation (1):

$$ln(\sigma T) = ln(\sigma_0) - ln(e)E_a/k_B \times T^{-1} \quad (1)$$

where σ is the measured conductance, T is the temperature, E_a is the activation energy and k_B is the Boltzmann's constant. Samples after 1, 2, 3 and 4 days of SBD treatment

show a linear relationship of ln(σT) vs. T^{-1}, with a fitted E_a of 6.9 kJ·mol^{-1} (0.072 eV) after 4 days of SBD treatment (Fig. 4D, and Table S3). Pristine graphene does not show an Arrhenius behavior. The relatively low E_a after 4 days of SBD treatment suggests that protons cross the membrane via a Grotthus mechanism (≤0.4 eV) where the proton hops through the membrane at a faster rate than dissociating from the hydronium ion[61]. After 5-day and 6-day, ln(σT) vs. T^{-1} present a less linear relationship compared to 4-day of treatment (Fig. S28), which could be caused by the polymerization of SBD, therefore hindering proton transport, leaving larger defects/cracks with a lower proton selectivity compared to methanol crossover.

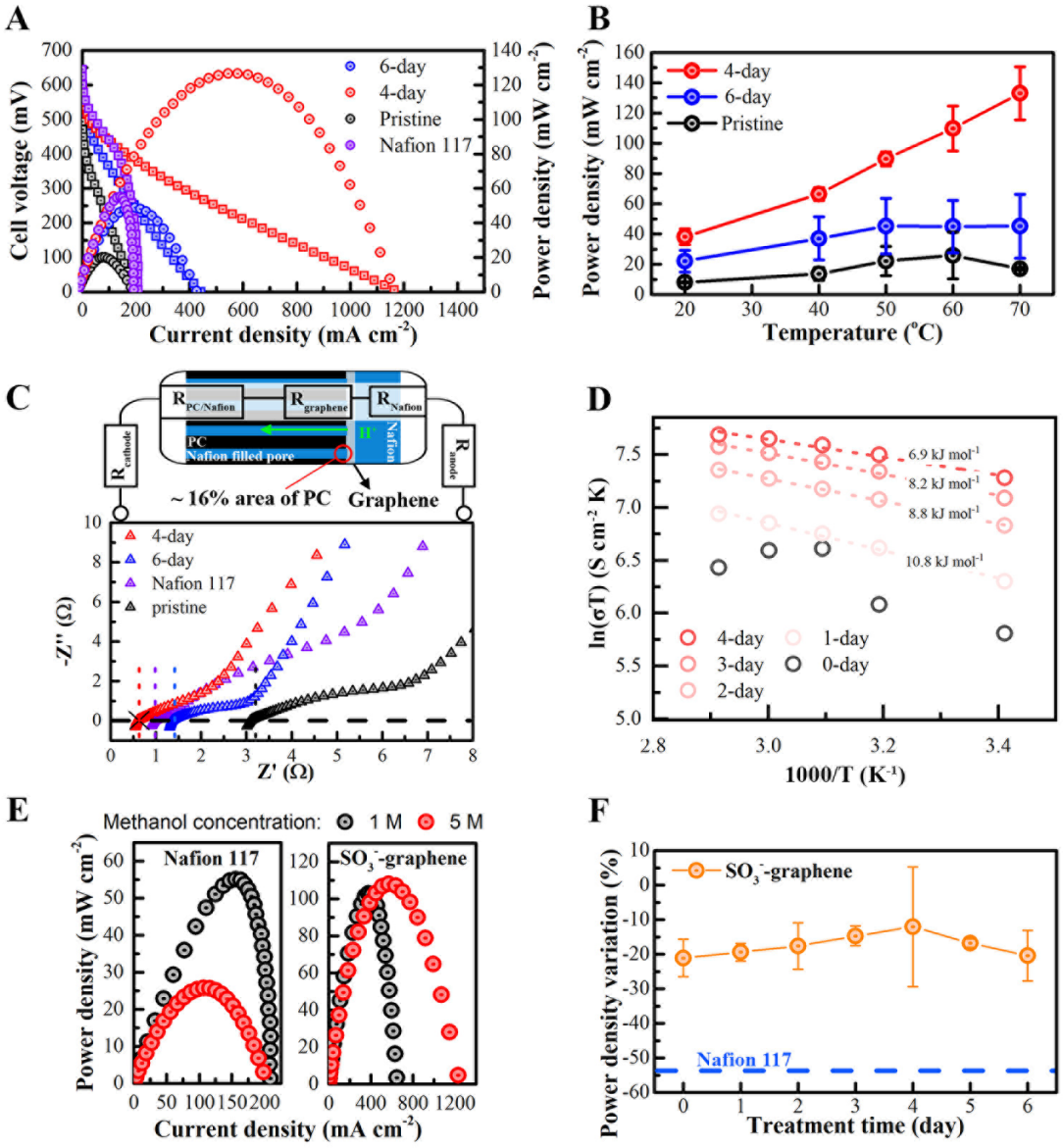

Figure 4 | DMFC performance with CVD graphene and SO_3^--graphene membranes.

(A) *Power-current density (P-I) and voltage-current density (V-I) curves for Nafion 117, pristine graphene, 4-day, and 6-day 4-SBD treated SO_3^--graphene. The cell voltage (V)*

and the power density (P) as a function of current density (I) were measured in a 1 M methanol/water solution at 60 °C. ***(B)*** *Maximum power density as a function of temperature.* ***(C)*** *Equivalent circuit and Nyquist plots of electrochemical impedance spectroscopy (EIS) measured at the open circuit voltage of the DMFC with graphene and SO_3^--graphene membranes. A Nafion™ layer was spin coated on graphene and SO_3^--graphene, and the stack was transferred on a polycarbonate porous support (~16% of PC with ca. 3µm diameter holes) filled with Nafion™.* ***(D)*** *ln(σT) as a function of the inverse of temperature for graphene membranes. The energy barriers were calculated based on eq. (1) following an Arrhenius-type analysis.* ***(E)*** *P-I curves of the DMFC fuel cell operating at 60 °C with aqueous solutions of methanol (respectively 1 and 5 M) for a ~183 µm thick Nafion 117 layer and 4-day SO_3^--graphene.* ***(F)*** *Decreases of maximum power density upon operating the DMFC in 5 M methanol compared to 1 M methanol. The blue dashed line corresponds to the decrease of the power density of a DMFC with only Nafion 117 when switching from 1 M methanol to 5 M methanol.*

We also added the activation energy values, to reflect on the correlation between the activation energy and the increased proton conductance upon sulfophenylation by SBD.

We revised the abstract:

L39-44: The membrane conductance of pristine graphene in direct methanol fuel cells, derived mainly from intrinsic defects, is 6.9 ± 1.1 $S \cdot cm^{-2}$. After chemical functionalization, the proton conductance increases to 30.9 ± 2.3 $S \cdot cm^{-2}$, normalized to the free-standing graphene area, indicating that covalently functionalizing graphene with sulfophenyl groups efficiently lowers the membrane resistance presumably because the sulfophenylation lowers the energy barrier to 6.9 $kJ \cdot mol^{-1}$ for protons to transport across graphene.

We also revised the conclusion:

L341-346: To conclude, the functionalization of centimeter-size CVD graphene with a sulfophenyl radical increases the membrane conductance of CVD graphene in a working DMFC from 6.9 ± 1.1 $S \cdot cm^{-2}$ to 30.9 ±2.3 $S \cdot cm^{-2}$ at room temperature, with a power density of 127 $mW \cdot cm^{-2}$ at 60 °C, which is more than twice the power density measured with Nafion 117. The activation energy barrier of -SO_3^--graphene is as low as 6.9 $kJ \cdot mol^{-1}$, indicating a reduced proton transport barrier, in line with the improved proton conductance through graphene after sulfophenylation.

2. How do the authors rule out formation of additional proton permeable defects in the CVD graphene lattice upon functionalization but hindering methanol transport? The ID/IG ratio in Raman clearly increases for upto 4 days of functionalization indicating defect formation in graphene. The polymer from functionalization layer or transfer contamination will preferentially cover defects preventing observation in HRTEM images. Reviewer notes authors do mention HRTEM doesn't show defects >1nm but polymer/contamination covered defects won't be visible in HRTEM and doesn't mean

they don't exist. In fact no defect is seen in the HRTEM images presented!

We did not observe that the sulfophenylation creates pores larger than a sp^3 distortion. Instead, AFM suggests the polymerization of SBD after 4 days. And as there are no pores to start with, the polymerized layer increases the resistance, which results in the decrease in the power output. If pores larger than a sp^3 distortion were present before SBD functionalization, they would be visible on HRTEM images of pristine graphene. We discuss the grain boundaries below.

3. In the context of the above, reviewer urges caution and closer analysis of data and including formation of additional defects as a possibility along with "With our hypothesis that the combination of a sp3 distortion and a charged SO3- group contributes to an increased proton transport"
Authors already allude to this "This is because sulfophenylation may effectively seal and passivate grain boundaries, guiding protons through them."

At this stage of the research, several parameters may influence the proton transport across functionalized graphene. For example, the distance between the $-SO_3^-$ group and graphene, the presence of a sp^3 site together with a charged group, the combination of a charge and a grain boundary. SBD functionalization does not allow us to disentangle each of these separate contributions. We added in the second round of revision:

However, further investigations are required to understand the factors contributing to enhancing the proton conductance, particularly defects, sp^3 distortions, and functional groups at the interface between graphene and the electrolyte. Controlling how functional groups are oriented on both side of the membrane could play a crucial role in modulating the transport of protons across the membrane. The creation of active sites as intrinsic proton pathways on graphene, as well as controlling the polarization of 2D membranes via these active sites – particularly in more complex two-dimensional polymer architectures[62,63] – would be a natural next step of this research, to establish correlations between the chemistry of the graphene and electrolyte interface and the efficiency of proton transport, for example using performance parameters of a fuel cell or using ion transport measurements.

What we like to convey by '*This is because sulfophenylation may effectively seal and passivate grain boundaries, guiding protons through them.'* is that adding a charged group either next to a lattice distortion or to a grain boundary site may increase proton transport. Any defects larger than the benzene ring sealed by a polymer chain upon polymerization of SBD (for example, a heptagon in a Stone-Wales grain boundary defect) could be yielding a reduced proton conductance. Additionally, the presence of cracks from the membrane electrode assembly can contribute to a baseline conductance (as we measured through the cracks), which we expect to be the same for pristine and SBD functionalized graphene.