Reply to “A resurrection of the Haber-Weiss reaction”

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REPLYING TO Willem H. Koppenol Nature Communications https://doi.org/10.1038/s41467-021-27823-2 (2022)

In our recent published paper1, we presented an entirely new design of a Janus electrocatalytic membrane and demonstrated its efficient water decontamination performance. The Janus electrocatalytic membrane demonstrated in situ singlet oxygen (1O2) formation inside the membrane porous structure, enabling enhanced removal of contaminants from water in a single-pass electrofiltration at very low energy consumption and without the addition of chemical precursors. The enhanced water decontamination performance was ascribed to the electrocatalytic membrane design. The Janus membrane integrates both the anodic and cathodic reactions within the membrane porous structure during flow-through filtration. This unique membrane structure induces spatial confinement within the membrane inner pores and enhances convective mass transport of reactants. In contrast to traditional electrofiltration designs with membranes functioning either as cathode or anode, using a Janus membrane makes full use of electrical energy, thus promoting energy efficiency.

In the accompanying Comment, Dr. Koppenol raised concerns regarding the 1O2 formation pathways in the Janus electrocatalytic membrane. In our work, we proposed potential 1O2 formation pathways in the membrane. Due to limitations of in situ characterization techniques inside a porous membrane, we were not able to provide the exact reaction pathways for 1O2 formation without solid experimental evidence. We appreciate Dr. Koppenol’s effort in proposing an alternative hypothesis for the 1O2 formation pathway in the Janus electrocatalytic membrane, which involves O2−• generation at the cathode followed by anodic O2−• oxidation for 1O2 formation.

The second concern raised by Dr. Koppenol is whether •OH exists in the Janus electrocatalytic membrane. As stated in our manuscript, the Pt anode is inherently an “active” anode. With its low oxygen evolution overpotential, the “active” anode readily transforms the generated physisorbed •OH into a higher oxide. This analysis has been proven by both theoretical and experimental studies2,3. If •OH is generated in the Janus electrocatalytic membrane, it would be readily converted to the higher oxide PtO. Therefore, free •OH would not be detected in the membrane.

The third concern raised by Dr. Koppenol is the suitability of electron paramagnetic resonance (EPR) measurement using 2,2,6,6-tetramethylpiperidine (TEMP) as the trapping agent for 1O2 detection. The general consensus is that TEMP is able to react with 1O2, forming 2,2,6,6-tetramethyl-1-piperidinylkoxy (TEMPO). The TEMPO product exhibits a characteristic 1:1:1 triplet signal in the EPR spectrum, serving as an indicator for 1O2 existence. This method has been widely applied in the field of environmental science as an indicator method for 1O2 detection4,5. Nevertheless, the EPR-TEMP detection method is currently being discussed6, as it cannot exclusively indicate 1O2 formation. This is because TEMPO may possibly be generated by another route, wherein TEMP++ intermediate radical is first formed, then undergoes deprotonation and reaction with molecular oxygen6.

As we stated above, in situ characterization techniques of stepwise transformations of the intermediates inside the porous membrane structure are challenging. Hence, at present, we cannot confirm the TEMP transformation pathway inside the membrane. Given this situation, we employed other detection agents—furfuryl alcohol (FFA) and sulfamethoxazole (SMX)—to confirm 1O2 formation. The oxidized products of FFA and SMX by 1O2 (Figs. S11 and S17 in the Supporting Information of our article1) were in agreement with previously reported results7,8. Overall, we adopted different detection methods to collectively confirm 1O2 formation in the membrane.

Regarding the ROS terminology, Dr. Koppenol states that neither O2−• nor H2O2 are reactive. We clarify that although H2O2 and O2−• are not highly reactive species as •OH, they are reactive with contaminants in water. H2O2 has been demonstrated as an effective disinfectant for inactivating bacteria and mitigating membrane fouling in water treatment9. In addition, the use of the term “ROS” or “reactive oxygen species” for describing H2O2, O2−•, •OH, and 1O2 is widely known in the fields of chemistry and environmental science10.
The current Janus electrocatalytic membrane module has limitations in determining reaction pathways (i.e., ROS formation and pollutant degradation) occurring inside the membrane. These limitations are also found in conventional electrofiltration modules, where flat-sheet membranes function only as cathode or anode. We attribute these limitations to two main causes. First, the membrane electrode and the counter electrode coexist in the same chamber of the membrane module. Reactants and intermediates produced by the membrane electrode will flow to the counter electrode, inducing additional electrochemical reactions. Hence, analyzing the reactions developed exclusively by the electrocatalytic membrane could be interfered by the counter electrode. Second, unlike a heterogeneous batch reaction system, real-time, on-site monitoring of molecules in nanoscale membrane pores during electrofiltration is challenging. Due to spatial and temporal restrictions, advanced detection techniques for elucidating the dynamic and instantaneous transformation of reactants (e.g., stopped-flow spectrophotometry11) cannot be deployed in systems with confined and pressure-driven liquid transport.

Refining membrane module design is critical for clarifying the reaction mechanisms in electrocatalytic membranes. To scrutinize the two half-cell reactions independently, isolating the membrane electrode and the counter electrode (or the cathodic and anodic regions of the Janus membrane) during electrofiltration is necessary. Selective barriers, such as vertically aligned single-walled carbon nanotube membranes12, could be inserted between the two electrodes/regions. Such barriers allow electron transfer while blocking other substances (i.e., H₂O, ROS, and organic pollutants). More importantly, exploiting materials and configurations of membrane modules that are integrated with time-resolved detection devices is of practical significance. The development of microfluidic chips compatible with advanced sensing techniques, such as luminescence13 and ion beam pulse14, is beneficial for in situ observation of phenomena (e.g., catalytic reaction, ROS generation, and ion solvation) occurring inside membrane pores.

In conclusion, we thank Dr. Koppenol for raising these issues. The answer to the main issue raised, i.e., unraveling O₂ formation pathways, is very challenging to fully clarify by experiments at present. Like any newly developed materials and technologies, the Janus electrocatalytic membrane shows unique advantages, but also presents challenges and requires more study to fully understand its detailed molecular mechanisms. Importantly, compared with conventional electro-active membranes, the Janus electrocatalytic membrane is a sustainable and energy-efficient method for water purification. In addition, the Janus electrocatalytic membrane extends electro-active membrane functionalities beyond water purification, with potential applications in resource recovery and environmental sensing15. We hope the present work and the discussion with Dr. Koppenol can inspire more research to promote the development of the Janus electrocatalytic membrane and related in situ detection techniques.

**Data availability**

No new data were generated for this reply.

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