

Role of H₂O in CO₂ Electrochemical Reduction As Studied in a Water-in-Salt System

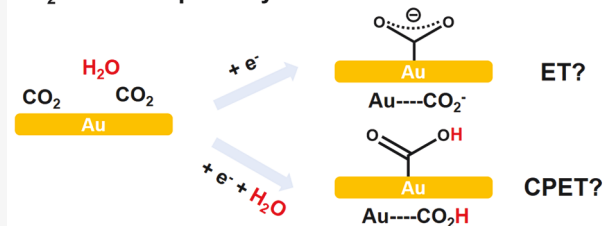
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S Supporting Information

ABSTRACT: CO₂ electrochemical reduction is of great interest not only for its technological implications but also for the scientific challenges it represents. How to suppress the kinetically favored hydrogen evolution in the presence of H₂O, for instance, has attracted significant attention. Here we report a new way of achieving such a goal. Our strategy involves a unique water-in-salt electrolyte system, where the H₂O concentration can be greatly suppressed due to the strong solvation of the high-concentration salt. More importantly, the water-in-salt electrolyte offers an opportunity to tune the H₂O concentration for electrokinetic studies of CO₂ reduction, a parameter of critical importance to the understanding of the detailed mechanisms but difficult to vary previously. Using Au as a model catalyst platform, we observed a zeroth-order dependence of the reaction rate on the H₂O concentration, strongly suggesting that electron transfer, rather than concerted proton electron transfer, from the electrode to the adsorbed CO₂ is the rate-determining step. The results shed new light on the mechanistic understanding of CO₂ electrochemical reduction. Our approach is expected to be applicable to other catalyst systems, as well, which will offer a new dimension to mechanistic studies by tuning H₂O concentrations.

CO₂ reduction pathways on Au



INTRODUCTION

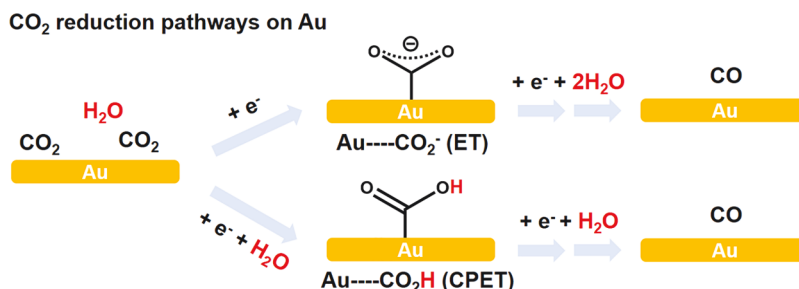
Direct CO₂ reduction by methods such as electrochemistry has attracted significant attention.^{1,2} On the one hand, as a key culprit for the greenhouse effect, using CO₂ for chemical synthesis holds promises for decreasing its concentrations in atmosphere.³ On the other hand, CO₂ reduction ensures severe thermodynamic and kinetic penalties, often leading to a myriad of products (e.g., hydrocarbons and hydrogen).⁴ How to steer the reaction toward desired products represents a fundamentally important challenge.⁵ The intense research has indeed greatly advanced our understanding on this reaction.^{6–10} Just within the context of electrochemical reduction of CO₂, for instance, we have learned that the product selectivity is highly sensitive to at least two parameters, namely, the nature of the catalyst and the electrolyte.^{2,11,12} The relative adsorption energy of the intermediates, most notably M-CO (where M represents a metal center), has been understood to dictate the subsequent chemical steps and, hence, the product selectivity.^{13–15} Along this line, various metallic or compound catalysts have been studied,^{16–18} with the oxide-derived metal (e.g., Au and Cu) being perhaps the most notable.^{19–21} The role played by the electrolyte has been examined, as well.^{22,23} For example, the mass transport of protons was exploited by Sargent et al. to suppress hydrogen evolution reactions (HER) in highly concentrated alkaline solutions.^{24,25} In parallel, the ionic effect was recognized to exert a profound influence on the product selectivity,²⁶ which was attributed to how the ions impact the interactions between H₂O and the substrates (and/or the reaction intermediates).^{23,27–31} These progresses

notwithstanding, much remains unknown about the detailed processes in a CO₂ electrochemical reduction reaction, especially at the molecular level. To illustrate this point, let us next consider the first steps of the initial electron and proton transfer in CO₂ reduction as an example. While concerted proton electron transfer (CPET) has been often used as a basis for kinetic discussions,^{15,19,32–34} the details of this process were not studied until recently. Already, diverging views have been developed.^{35–39} Using Au as a prototypical catalyst platform and by studying the kinetics relative to CO₂ partial pressure (*P*_{CO₂}) and [HCO₃[–]], Surendranath et al. observed no apparent dependence of the reaction rate on [HCO₃[–]], implying that electron transfer (ET) is the rate-determining step (RDS), followed by proton transfer (PT) (Scheme 1).^{38,40} Similar experiments by Xu et al., however, reported apparent dependence of the reaction rate on [HCO₃[–]], which the authors attributed to possible fast pre-equilibrium between CO₂, H₂O, and HCO₃[–].^{37,41} The latter results could be interpreted as evidence to support the CPET rather than the ET pathway. Conflicting views like this highlight the need for additional research to elucidate the details of CO₂ reduction. Examinations of the literature reveal that a key constituent of the reaction, H₂O, has not been varied in previous studies. On the one hand, as an important proton donor, suppression of H₂O concentration ([H₂O]) could greatly limit HER so as to promote carbonaceous product selectivity.²⁴ On the other

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Scheme 1. Schematics Illustrating Possible Reaction Pathways of Two Different Mechanisms during CO₂ Electrochemical Reduction on Au Catalyst^a



^a(top) ET is RDS. (bottom) CPET is RDS. Examinations on how the reaction rate depends on H₂O concentration could help discern which route is more likely.

hand, as a solvent, H₂O participates in nearly every aspect of the reaction; studies on how the reaction kinetics changes as a function of H₂O concentration, for example, will contribute to settling debates as mentioned above. We are, therefore, prompted to conduct the present study in which H₂O concentration is varied for the understanding of CO₂ electrochemical reduction reactions.

The key enabling factor of this work is the “water-in-salt” (WiS) electrolyte, in which ultrahigh concentrations of salt (LiTFSI, where TFSI represents bis-(trifluoromethanesulfonyl)imide) is mixed with H₂O (up to 21 *m*, where *m* is molality, or mole of LiTFSI in 1 kg of H₂O).⁴² Previous research by others and us has shown that such an electrolyte behaves differently from bulk H₂O in that the activity of H₂O is significantly suppressed.^{42,43} We are, therefore, offered an opportunity to perform electrochemical reactions such as CO₂ reduction in an aqueous solution, whose H₂O concentration is no longer constant. Two immediate benefits would be expected from such a system. First, we would be able to significantly suppress HER due to the limited supplies of H₂O, so as to promote selectivity toward carbonaceous products, similar to what has been achieved by Sargent et al.,²⁴ albeit in a milder, near neutral condition in our case. Second, we would be able to interrogate the electrokinetics of the system by varying the H₂O concentration, a feature that has not been assessed by prior studies.⁴⁰ Thus, our results are expected to shed new light onto the mechanistic details of the CO₂ electrochemical reduction processes. Indeed, selectivity toward CO up to 80% was measured in WiS on planar Au catalyst, comparable to the reported values measured on carefully modified Au such as oxide-derived or nanostructured Au catalysts.^{19,32,34,44–46} Moreover, our electrokinetic analyses revealed that the reaction rate appeared independent of H₂O concentration at low overpotentials, further supporting that ET is the RDS in the initial reduction of CO₂. Importantly, as our approach exploits a new dimension of the reaction parameters, it offers a new route to highly selective CO₂ reduction for practical applications.

RESULTS

We elected to use Au as a model catalyst for this study, as it features high selectivity toward CO production as opposed to other carbonaceous products.⁴⁵ For instance, it has been reported that, under common experimental conditions, the cathodic currents on Au electrode mainly constitute of CO and H₂ production.^{45,47} As such, it is convenient to interpret the electrochemical data for kinetic analyses of the elemental steps

during CO₂ electrochemical reduction. Another reason we chose Au for this study is the broad knowledge on Au-based CO₂ reduction, which will allow for easy comparison of our results with the literature.^{19,32,34,37–41,44,46} As shown in Figure 1, the most prominent feature of the cyclic voltammogram

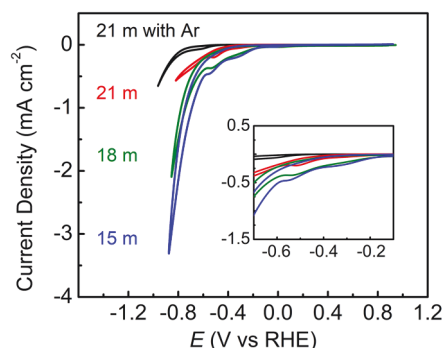


Figure 1. CVs of Au catalyst in WiS of different concentrations; the WiS electrolytes are saturated with either Ar or CO₂.

(CV) in different electrolytes was the suppression of the cathodic currents with the gradual increase of salt concentration from 15 to 21 *m* (the home-designed electrochemical cell is shown in Figure S1 in the Supporting Information). We hypothesize that the suppression is due to limited hydrogen evolution as a result of decrease in H₂O concentration,^{42,43} more discussions of which will be presented in the next section. Here, we wish to direct the readers’ attention to the reduction features as magnified in the inset of Figure 1 (the conversion of potentials using a calibrated pseudoreference electrode is listed in Table S1). The cathodic peaks, which are likely due to CO₂ reduction reactions, remained at ca. −0.52 V (vs reversible hydrogen electrode, RHE; unless noted, all potentials henceforth are relative to RHE) for different salt concentrations. The onset potentials at which CO₂ was reduced are consistent with literature reports on various Au catalysts.^{38,45} It is also consistent with that measured in 0.5 M NaHCO₃ electrolyte (Figure S2). Moreover, substitution of CO₂ with Ar eliminated these features, strongly supporting that these reduction peaks are indeed due to CO₂ electrochemical reduction. It is important to note that, other than at the highly negative potentials (e.g., lower than −0.9 V), the combined Faradaic efficiencies of CO plus H₂ were consistently measured to be greater than 90%. Additional control experiments confirmed that the WiS electrolyte was not decomposed under our experimental conditions (vide infra). Taken as a

whole, we established that the WiS system is a reliable platform that offers electrochemical features of CO₂ reduction by Au similar to other electrolyte systems.

Next, we aimed to delineate the main contributions to the cathodic current by performing potentiostatic electrolysis and product analyses. The percentage of CO production relative to the overall yield (CO plus H₂) was plotted against the applied potentials (Figure 2). No liquid product or decomposition of

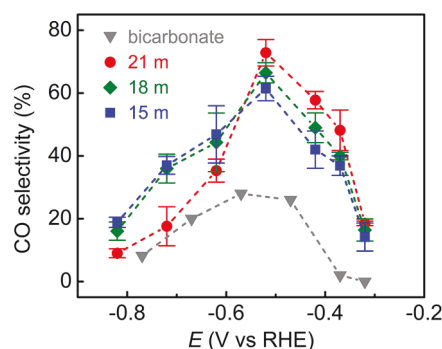


Figure 2. CO selectivity measured in WiS of different concentrations and in 0.5 M NaHCO₃ electrolyte. All electrolytes were saturated with CO₂.

electrode and electrolyte were observed upon electrolysis (Figures S3–S5). One sees from this set of data that the maximum selectivity toward CO on planar Au catalyst in CO₂-saturated 0.5 M NaHCO₃ electrolyte (pH 7.2) was relatively poor, lower than 30%, which would serve as a basis for the following comparisons. Similarly low selectivity has been reported on Au without special treatments.^{19,38,48} When WiS was used, however, the maximum selectivity was readily increased to up to ca. 72% in 21 *m* WiS. The performance is close to the best reported in the literature.^{19,32,34,45,46} Most

notably, the high selectivity was achieved at near neutral pH of the electrolyte (measured using a double-junction pH electrode as shown in Figure S6) and on Au catalyst without special treatments.^{24,25}

The second feature in Figure 2 worth highlighting concerns the trend of selectivity as measured against the applied overpotentials. At high overpotentials (e.g., potentials lower than −0.52 V), the reaction is believed to be mass-transport limited, where relatively low solubility of CO₂ and its poor diffusivity greatly limit CO production in comparison to HER;^{42,45} at low overpotentials (e.g., potentials greater than −0.52 V), the reaction is believed to be more kinetically controlled, in which region higher applied overpotential leads to increased CO production rates.^{13,15,19,47} In other words, the low selectivity of CO at high overpotentials is mainly due to the increase of HER but not the decrease of CO production.⁴⁵ This understanding is confirmed by the data as shown in Figure S7, more details of which will be discussed next. Here, however, let us focus on the data shown in Figure 2. It is observed that the maximum selectivity was achieved at −0.52 V for all three WiS electrolytes. Maximum CO selectivity at comparably low overpotentials has been reported in the literature, and the reasons have been mainly attributed to suppressed HER and catalyst surface modifications.^{19,32,46} Given that our planar Au catalysts for all experiments were unmodified and the same, whose inherent CO selectivity as tested in NaHCO₃ is poor (<30%), we are inspired to understand the data as an indication that low H₂O concentrations (e.g., 21 *m*) greatly suppress HER. The effect is most pronounced for the most concentrated solution and, hence, the highest selectivity.

The realization that the H₂O concentration may be modulated in WiS through altering the salt concentrations (Table S2) prompted us to next study the electrokinetics of CO₂ reduction. For this purpose, we extracted the partial currents due to CO production (Figure 3a). In the low

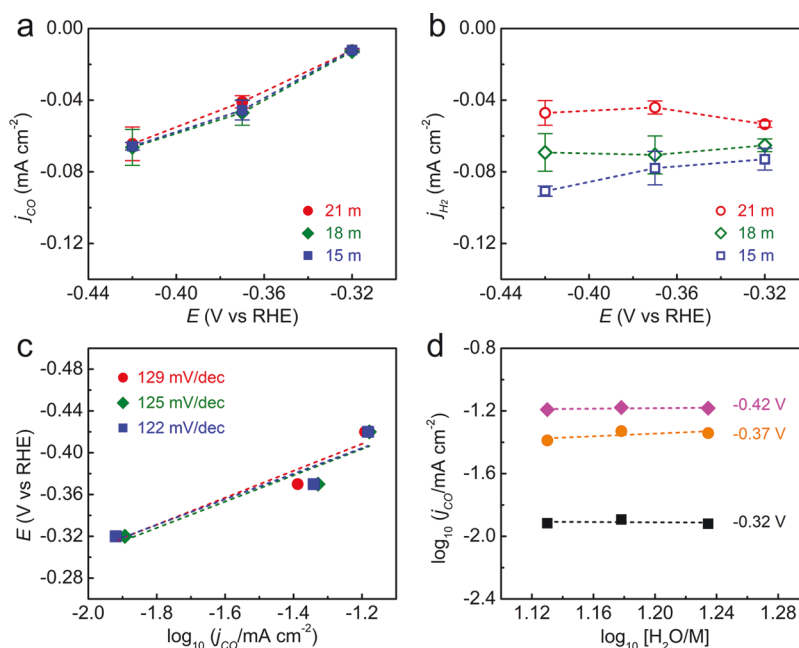


Figure 3. Electrokinetic analyses on CO₂ reduction to CO in WiS of different H₂O concentrations. (a) Partial current densities due to CO production at different potentials. (b) Partial current densities due to H₂ production at different potentials. (c) Tafel analyses in WiS of different H₂O concentrations. (d) Partial current densities due to CO production at fixed potentials for different [H₂O].

overpotential region (-0.42 V to -0.32 V), the partial current of CO increased with the increase of cathodic potentials. The partial current of CO remained at a relatively constant level at high overpotentials due to mass transport limitations of CO_2 (Figure S7), consistent with literature reports.^{19,45,48} Most intriguingly, comparable current densities were measured for WiS electrolytes of different concentrations in the kinetically controlled region (-0.32 V to -0.42 V). The data imply that CO_2 electrochemical reduction kinetics is independent of H_2O concentrations. This observation is in contrast to the partial current densities due to H_2 formation, which increased with the increase of H_2O concentration monotonically (Figure 3b). Tafel analyses indicated that in the low overpotential region, the RDS is an electrochemical step rather than a chemical step, as the Tafel slopes close to a theoretical value of 118 mV/dec were measured (Figure 3c). To better understand the data, we plotted the partial current densities of CO (j_{CO}) at different potentials as a function of $[\text{H}_2\text{O}]$ in Figure 3d. As expected, a pseudo-zeroth-order dependence was confirmed. Inspired by efforts by Surendranath et al.,^{38,40} we examined the possible dependence of the reaction rates on $[\text{CO}_2]$ and $[\text{H}_2\text{O}]$ in four different scenarios and tabulated the results in Table S3. It is seen that only under the circumstances where ET is the RDS should one expect a zeroth-order dependence of the reaction rate on $[\text{H}_2\text{O}]$. The insight is consistent with Noda et al.'s electrokinetic study,³⁹ as well as Surendranath et al.'s understanding, where the authors studied the partial current of CO as a function of P_{CO_2} and $[\text{HCO}_3^-]$.^{38,40} The zeroth-order dependence of the reaction rate toward CO formation on $[\text{H}_2\text{O}]$ can be observed with other planar Au catalyst as well (Figure S7).

A key distinction between our approach presented here and those by Surendranath et al. and Xu et al.,^{37,38,40,41} separately, is whether bicarbonate (HCO_3^-) is involved as a buffer. In the presence of a HCO_3^- buffer, the fast equilibrium between it and CO_2 and H_2O could make the interpretation of electrokinetic data as a function of P_{CO_2} challenging, as has been pointed out by Xu et al.^{37,41} Our results provide a new dimension for the understanding of the electrokinetics of CO_2 reduction. We envision, for instance, more results supporting our understanding may be drawn from future studies similar to those by Surendranath et al. and Xu et al. but without using HCO_3^- buffer. Nevertheless, the presence of HCO_3^- due to the $\text{CO}_2/\text{H}_2\text{O}$ equilibrium is ubiquitous in aqueous electrolytes. Our results could be readily corroborated with previous studies using HCO_3^- buffer.^{37,38,40,41} In addition, we note a potential caveat of our data interpretation. In deriving the rate-law expressions (Table S3) and analyzing the data as shown in Figure 3, we assumed a constant $[\text{CO}_2]$ at fixed P_{CO_2} (1 atm). At the present stage, we cannot rule out the possibility that the solubility of CO_2 could be slightly different for WiS of different H_2O concentrations, despite our efforts of using a constant P_{CO_2} (1 atm) throughout our experiments.⁴⁹ It has been previously reported that $[\text{CO}_2]$ may be sensitive to ionic strength.⁴⁹ To understand whether changing $[\text{CO}_2]$ in WiS of different concentrations may be a complicating factor in our studies, we performed a systematic study by measuring the partial current densities of CO (j_{CO}) as a function of CO_2 partial pressure (P_{CO_2}). As shown in Figure S8, we see that there is a clear first-order dependence of j_{CO} on P_{CO_2} . This result indicates that measurable changes in $[\text{CO}_2]$ would be reflected in j_{CO} . That j_{CO} is independent of $[\text{H}_2\text{O}]$ in our experiments strongly suggests the variation of $[\text{CO}_2]$ in

different WiS electrolytes is insignificant. Notwithstanding, additional research would be needed to fully address this concern.

As a proof-of-concept to demonstrate the potential utility of the WiS in a practical system, we next employed a flow cell design with gas diffusion layer (GDL) as an electrode (Figure S9), and our goal was to study whether the partial current density due to CO production could be further improved in WiS.^{45,48,50–52} We see from Figure 4 that, in 21 *m* WiS, a trend

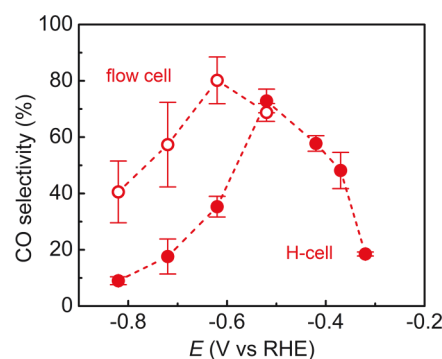


Figure 4. CO selectivity measured in 21 *m* WiS electrolyte in a flow cell using a GDL electrode with sputtered Au catalyst, shown as hollow circles in red. For comparison, the selectivity as measured in a H-cell in 21 *m* WiS electrolyte with Au foil catalyst from Figure 2 is replotted here as solid red circles. All electrolytes were saturated with CO_2 .

of CO selectivity as a function of applied potential similar to that in a H-cell was obtained, with a slightly higher maximum selectivity (ca. 80%). Importantly, a significantly higher CO partial current density (up to ca. 1.3 mA/cm^2 at -0.82 V in a flow cell using a GDL electrode as compared to less than 0.1 mA/cm^2 at the same applied potential in a H-cell using sputtered Au catalyst, Figure S10) was measured. This result further supports that the decrease of CO selectivity in Figure 2 and the saturation currents as shown in Figure S7 were indeed due to CO_2 mass transport limitation.^{48,50} While the flow cell approach appeared to help address this issue, we are mindful that significant research is needed to bring the current density to a level that is of practical value. Further engineering optimization on the cell design and electrode modification is likely to contribute to this matter (Figures S11–S13).^{53,54} Another important issue to address before WiS can be used for practical CO_2 reduction is the high cost of LiTFSI when scaling up the volume of the electrolyte in a flow cell.⁴³ Nevertheless, the most important value generated by this body of research is the advancement of our understanding of the CO_2 reduction mechanisms and the demonstrated potentials toward practical CO productions. Although the present study focused on CO_2 reduction at nearly neutral pH, we envision it is readily applicable to other pH values, as well, for mechanistic studies by other systems.

Safety Statement: No unexpected or unusually high safety hazards were encountered in this study.

DISCUSSIONS

The above results demonstrated the promises of using WiS to understand the mechanism of CO_2 electrochemical reduction reactions, as well as to improve its performance such as selectivity and current densities toward practical applications.

Notwithstanding, we are mindful of the potential limitations of the system. For example, one question that may arise from analyzing our results is whether the knowledge generated here is transferable to systems where different electrolytes (e.g., bicarbonate-based ones) are used. Indeed, the composition of the electrolyte could play critical roles in defining the detailed mechanisms. For instance, the nature of the proton donor (e.g., H₂O or bicarbonate) may exert a profound influence on the electrokinetics. Encouraged by two important considerations, however, we expect the understanding presented here to be readily transferable. First, despite the apparent difference, H₂O is the overwhelming majority chemical in both cases (bicarbonate vs WiS). As such, we do not expect the role played by H₂O to be fundamentally different. Second and more importantly, the conclusion supported by our results is readily corroborated with those obtained using other methods.^{36,38,40} Taken as a whole, we conclude that ET but not CPET is the RDS during the initial steps of CO₂ reduction on Au in both WiS and bicarbonate-based electrolytes. Nevertheless, we caution against taking this conclusion out of the context. Whether the understanding is universally conclusive requires additional research that is beyond the scope of this work.

Moreover, we caution that a more accurate electrokinetic analysis will need to be performed using the activity but not concentration of H₂O. At the present time, however, we do not have quantitative information on the H₂O activity in WiS electrolytes. It is, therefore, envisioned that future research will be needed to correct this deficiency and to further refine the electrokinetic studies for a more complete understanding of the CO₂ to CO electrochemical reduction mechanisms.

CONCLUSIONS

We have performed a mechanistic study of CO₂ electrochemical reduction in the unique water-in-salt electrolyte on a Au prototypical catalyst platform. The strong solvation effect to the high concentration of the salt locks down the H₂O molecules to change their behaviors drastically different from bulk H₂O. As a result, the H₂O reduction activity is greatly reduced, increasing the selectivity toward CO production. Up to 80% selectivity was measured, which is to be compared with ca. 30% in the conventional electrolyte at nearly neutral pH. More importantly, electrokinetic studies in the kinetically controlled potential region revealed that the reaction rate exhibits a pseudo-zeroth-order dependence on [H₂O]. The results imply that an electron transfer process is rate-determining. The information helps resolve diverging views on the initial steps of CO₂ reduction on Au catalyst and may find implications for future catalyst and electrochemical cell designs for practical CO₂ reduction applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.9b00519.

Additional experimental details, electrochemical characterizations, spectroscopic and microscopic analyses, additional schematics, detailed mathematical derivations, and tables of additional data (PDF)

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Author Contributions

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Author Contributions

Q.D. and D.W. conceived the idea. Q.D. prepared the materials and designed the electrochemical cell. Q.D. and X.Z. conducted electrochemical measurements. D.H. and Q.D. conducted the product analyses. C.L. performed the electrokinetic derivations. All authors participated in the data analyses. Q.D. and D.W. wrote the manuscript together with input from all authors. D.W. supervised the research.

Notes

The authors declare no competing financial interest.

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