nature portfolio

Peer Review File

Cationic carbon nanotube modulates surface fields for general acidic CO2 reduction with aqueous organic cations

Corresponding Author: Professor Ruquan Ye

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

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)
The experimental innovation in this work is the application of cationic carbon nanotubes as additives to metal catalysts for enhancing CO2 reduction reaction (CO2RR) in strong acidic media. Through detailed experimental evaluation the authors show high Faradaic efficiency for HCOOH, CO, and modest for C2H4 products on bismuth, silver, and copper oxide electrodes. As compared to pristine, the cationic carbon nanotubes appear to inhibit the competing hydrogen evolution reaction. The experimental work is well documented and the organic cations used by the authors appears to provide a good strategy for avoiding HER which may otherwise limit CO2RR efficiency.
While I find the experimental results interesting and novel, the theoretical explanation is not as convincing since results of classical molecular dynamics simulations depend very much on the force fields that are used. I realize that full ab initio molecular dynamics simulations, particularly in the grand canonical ensemble (which would allow inclusion of the electrode potential in the simulation) is not feasible for system sizes that the authors have considered in their simulation. There is mention of some DFT calculations. Could the authors elaborate on how those simulations were carried out? Did they include the electrode potential and solvent molecules or were they calculations of the total energy without the electrochemical environment? Since a mechanistic understanding would place the work on strong footing, the authors may want to consider providing some insights from ab initio calculations that mimic the electrochemical environment to some extent.

Reviewer #2

(Remarks to the Author)
In this manuscript, the authors propose a strategy using cation-modified carbon nanotubes (CCNTs) as catalyst additives combined with the introduction of organic cations in the electrolyte. This approach aims to reduce H+ diffusion to the catalyst surface, thereby suppressing the hydrogen evolution reaction (HER) and achieving enhanced CO2 electroreduction (CO2RR) activity in acidic electrolytes. However, the strategy of adding organic cations to the electrolyte has been previously reported (Angew. Chem. Int. Ed. 2025, 64, e202504785), which diminishes the novelty of this work. Thus, I recommend reconsideration after major revisions.

1：In Supplementary Figure 10, compared with the data in Figure 2c, why is the current density higher at a lower electrolyte concentration for Bi/CCNT? Additionally, the voltage is expressed as E-iR in some parts of the manuscript but simply E in others; please provide a detailed clarification.

2：When preparing the catalyst ink, the authors still used anionic Nafion as the binder, which contradicts the claimed cation-modified CNT strategy in the manuscript.

3：The authors synthesized a series of CCNT samples with varying cation loadings (CCNT-0.125, CCNT-0.5, CCNT-1.0, and CCNT-2.0). Experimental characterization is required to quantify the actual cation content in these samples.

4：The authors should pay attention to manuscript formatting, as the order of figure citations is inconsistent with their

presentation in many instances.

5：The authors employed both CCNTs and organic cations in the electrolyte. However, based on the stability test results, CCNTs appear to afford no improvement in stability. On the contrary, the previously reported strategy (adding organic cations to the electrolyte) achieves an orders-of-magnitude improvement in stability.

6：Calculating energy efficiency using flow cell data is not valid, which should be done in MEA or other similar cells.

7：For the sake of manuscript completeness, the authors are advised to supplement the stability test of CuO.

8：In the rotating disk electrode (RDE) studies, the limiting diffusion currents of CNTs and CCNTs are nearly identical in the diffusion-limiting region. This contradicts the authors' claim that CCNTs reduce the H+ diffusion coefficient—if CCNTs indeed decreased the H+ diffusion coefficient, the corresponding limiting diffusion current should be lower.

Reviewer #3

(Remarks to the Author)
This manuscript presents an innovative and versatile strategy that employs cationic carbon nanotubes (CCNTs) as a universal additive to achieve efficient CO2 reduction reaction (CO2RR) in strongly acidic media. The cationic modification significantly suppresses the severe hydrogen evolution reaction (HER) typically associated with pristine carbon nanotubes. Furthermore, replacing conventional alkali metal-based electrolytes with an organic cation-based alternative effectively prevents salt deposition, thereby improving long-term stability and energy efficiency without obviously compromising the HCOOH FE. The study is innovative and is well-supported by extensive data. However, major revisions are required before the manuscript can be considered for acceptance.
1. The influence of CO2 flow rate on HCOOH yield should be determined. If a correlation exists, both the flow rate and the corresponding yield should be incorporated into the economic assessment of HCOOH production.
2. The PTFE-coating strategy is selected as a benchmark due to its ability to mitigate flooding. It is suggested to provide the contact angle for both PTFE-coating and CCNT. It would be interesting to investigate whether the hydrophobic environment provided by the long alkyl chains of CCNT contributes to its high performance.
3. The FE values and partial current density curves for the Bi/CCNT-0.5 sample appear to be missing. These data are essential for evaluating the effect of CCNT charge density on acidic CO2RR performance and should be provided.
4. The formula used for calculating the turnover frequency (TOF) should be provided in the manuscript.
5. With the increase of charge density of CCNTs, the operation potential window with high HCOOH FE is increased. The underlying reason for this correlation should be clarified, as it is important for understanding the mechanism.
6. The long-term stability of the Bi/CCNT catalyst in the 0.05 M H2SO4 + 3 M KCl electrolyte should be supplemented to confirm whether salt deposition occurs.
7. The effect of the electrolyte change from KCl to N(CH3)4Cl on the HCOOH formation pathway and rate-determining step requires further investigation.

Version 1:

Reviewer comments:

Reviewer #3

(Remarks to the Author)
The authors have addressed all my concerns and I recommend the manuscript for acceptance in its current form.

Reviewer #4

(Remarks to the Author)
In this manuscript, the authors demonstrate that grafting long alkyl chain organic cations onto carbon nanotubes (CNTs) serves as a universal additive capable of enhancing CO2RR performance of different metal catalysts in acidic media. This approach stands in contrast to previous strategies, which typically involve adding high concentrations of alkali metal cations to the electrolyte or incorporating cationic ionomers into the catalyst layer. It offers a novel pathway to promote acidic CO2RR. The authors support this enhancement with extensive comparative data and provide a detailed analysis of the underlying mechanism. I believe this work is suitable for publication in Nat. Commun.
I have also reviewed the previous referees' comments and the authors' responses. While most concerns have been adequately addressed, a few minor points remain for the authors' consideration:
1. Following the grafting of cationic groups, the CNTs are expected to exhibit both electronic and ionic conductivity. Could the authors separately measure the electronic and ionic conductivities of the modified CNTs? It would be important to consider whether the CCNTs function dually as both conductive agents and ionomers within the catalyst layer, rather than acting merely as an H+ migration suppressor as proposed.
2. In Supplementary Figure 1, to prevent any confusion with the volume of ethylenediamine (EDA) used during synthesis, it is recommended that the grafted alkyl chain be explicitly labeled with its molecular formula C12H25.

Reviewer #5

(Remarks to the Author)
The authors'efforts in addressing the previous concerns are appreciated, but several technical and mechanistic issues remain unresolved. The manuscript still lacks the rigor required for Nature Communications and is likely better suited for a more specialized journal.

1. While the authors have now included iR-compensated data in the SI, Figure 2 still presents uncompensated potentials. Since uncompensated data makes it difficult to evaluate and compare intrinsic catalytic activity, the authors should provide a clear explanation for why this was retained for the primary results.

2. The authors attributed the poor stability of Bi/CNT in acidic N(CH3)4Cl to electrode flooding, yet this raises a fundamental question. Flooding is an inherent property of porous CNTs (J. Am. Chem. Soc. 2024, 146, 16348), how cation modification suddenly mitigates this intrinsic mass transport problem? Since stability is a key claim of this study, the authors should provide specific evidence and explanation for this underlying mechanism.

3. In the RDE studies, the authors observed suppressed HER current density on CCNTs in the kinetic-limited regime, yet attempted to justify this using decreased H+ diffusion. The interpretation of HER suppression is conceptually inconsistent. Additionally, the negligible difference in diffusion coefficients between CNTs and CCNTs cannot explain the significant HER activity difference, even in the mixed kinetic-mass transport regime. This confusion between fundamental surface kinetics and diffusion processes undermines the core mechanistic claims of the work.

4. The authors proposed an electric field mechanism to explain enhanced CO2RR and suppressed HER, yet supporting evidence such as detection of the local electric field at electrochemical interface is missing. Importantly, as the CCNTs and metal catalysts are only physically mixed, it is unclear how an electric field localized on CNTs effectively modulates spatially separated metal active sites. Without clarifying this interaction, the proposed mechanism remains speculative.

Reviewer #6

(Remarks to the Author)
The authors have adequately addressed the concerns regarding the theoretical explanation, and the computational details that separating the roles of DFT (providing accurate electrostatics via ESP charges) and classical MD (capturing long-timescale CO2 mass transport) have added to the revised manuscript, confirming that the key conclusions are governed by the DFT-derived charges, reducing the sensitivity to the specific choice of force-field parameters, and thus robust enough for the current study.

Version 2:

Reviewer comments:

Reviewer #4

(Remarks to the Author)
The authors have addressed all my concerns. I believe it is ready for publication.

Reviewer #5

(Remarks to the Author)
The authors have addressed my concerns. The manuscript is now recommended for publication.

Response to Reviewers' comments

Dear reviewers,

Thank you for your precious time to constructive comments on our manuscript titled "Cationic carbon nanotube modulates surface fields for general acidic CO_2 reduction with aqueous organic cations" (Manuscript number: NCOMMS-25-91536-T) for *Nature Communications*. We sincerely appreciate your comments and suggestions on our work, which are highly important for further improvements to the manuscript. According to all the comments, we have made a detailed response and substantial revisions to our revised manuscript. We sincerely hope that our response will fully address your concerns about our work.

To facilitate reading, we use blue color for the reviewers' comments, black color for our replies, and red color for our change in manuscript.

Reviewer #1

Comment 1.1: The experimental innovation in this work is the application of cationic carbon nanotubes as additives to metal catalysts for enhancing CO_2 reduction reaction (CO_2RR) in strong acidic media. Through detailed experimental evaluation the authors show high Faradaic efficiency for HCOOH, CO, and modest for C_2H_4 products on bismuth, silver, and copper oxide electrodes. As compared to pristine, the cationic carbon nanotubes appear to inhibit the competing hydrogen evolution reaction. The experimental work is well documented and the organic cations used by the authors appears to provide a good strategy for avoiding HER which may otherwise limit CO_2RR efficiency.

Response: We thank you so much for your constructive and thoughtful evaluation of our manuscript, as well as for highlighting its intriguing aspects. Below is our detailed response to the comments.

Comment 1.2: While I find the experimental results interesting and novel, the theoretical explanation is not as convincing since results of classical molecular dynamics simulations depend very much on the force fields that are used. I realize that full ab initio molecular dynamics simulations, particularly in the grand canonical ensemble (which would allow inclusion of the electrode potential in the simulation) is not feasible for system sizes that the authors have considered in their simulation. There is mention of some DFT calculations. Could the authors elaborate on how those simulations were carried out? Did they include the electrode potential and solvent molecules or were they calculations of the total energy without the electrochemical environment? Since a mechanistic understanding would place the work on strong footing, the authors may want to consider providing some insights from ab initio calculations that mimic the electrochemical environment to some extent.

Response: We appreciate the reviewer's thoughtful comments and the opportunity to clarify the scope and limitations of our simulations, as well as the role of DFT in our work.

1. **Why we chose classical MD instead of AIMD / grand canonical AIMD**

As the reviewer correctly points out, a fully ab initio treatment of the electrochemical interface (e.g., grand canonical AIMD including explicit electrode potential and solvent) would be ideal for mechanistic insight. However, in our system this is computationally prohibitive for the following two main reasons:

- System size

The organic cation used in this work already contains more than 50 atoms as a single molecule. If we include:

  - explicit solvent molecules
  - gas molecules and multiple dissolved ions
  - substrate for the molecular cation

the total atom count grows rapidly beyond the typical range of tractable AIMD simulations. Using MD, we can include all of the subsystems described above with multiple cationic molecules in a single simulation cell (**> 4500 atoms**) which allows dynamic interaction between them in realistic local environment

- Required timescale:

The central objective of our theoretical study is to understand **mass transport of neutral CO_2** in the presence of cationic carbon nanotubes and molecular cations, not the details of reaction on the catalyst surface based on the observation of **similar HER suppression regardless of the catalyst types**.

- Reliable statistics on diffusion and spatial distributions in such heterogeneous environments require at least **tens to hundreds of nanoseconds** of trajectory.
- In our experience, standard AIMD can require weeks of wall time for only **a few tens of picoseconds** of trajectory even **for a few hundred atoms**.
- Grand canonical AIMD that explicitly includes the electrode potential typically incurs an additional factor of ~ 3 or more in computational cost.

Consequently, the trajectories needed to capture mass transport physics (> ns) and minimum system size (thousands of atoms) are far beyond the accessible time window of DFT-based dynamics. Given these constraints, we consider classical MD to be the only practical route for exploring CO_2 diffusion and mass transfer in the complex environment including the cationic additives.

2. How the DFT calculations were used

We agree with the reviewer that the reliability of classical MD depends critically on the quality of the underlying parameters. In our work, DFT calculations are **not** used to simulate the full electrochemical interface, but rather to provide a **quantitatively reliable electrostatic description** for the classical MD since introducing Coulombic interaction in the system is our main purpose of introducing cationic molecules.

We performed DFT calculations on isolated molecular cations with (H-passivated) finite graphene fragment with charge of +1.0. The **ESP charge** is obtained **for accurate quantitative intermolecular interaction**. Resulting total charge on molecular cation is +0.9 while +0.1 is broadly distributed on finite graphene fragment. This aligns with the results from Bader charge analysis using a periodic model with the plane-wave DFT code as we mentioned in the manuscript. The ESP charges are used for all atoms for the additives to parameterize the Coulombic interactions in the classical MD force field. In this way, the electrostatics around the cationic components (which strongly affect CO_2 distribution and mass transfer) are grounded in first-principles electronic structure, even though the trajectories themselves are propagated with classical MD.

3. Choice and robustness of the force field

We employ the Universal Force Field (UFF, *JACS* **1992**, 114, 10024), which explicitly accounts for atomic hybridization and connectivity. UFF provides parameters for all elements in the periodic table, enabling its broad use in a wide range of molecular dynamics simulations (cited over 12,000 times). It is sufficiently flexible to capture room-temperature conformational dynamics of large organic structures while maintaining computational efficiency for large-scale systems.

In our study, UFF is mainly responsible for bonded terms (bond stretching, angle bending, torsions) and generic van der Waals interactions while the key physics of interest (electrostatic landscape experienced by CO_2) is primarily controlled by DFT-based ESP charges as described above).

Because of this division of labor, the main qualitative conclusions are not strongly sensitive to the specific choice of generic bonded force-field parameters, as long as the electrostatics are accurately represented with DFT-based ESP charges.

To further elaborate our computation method, we have revised our Computational Method part:

"We constructed a theoretical model for CCNT comprising two graphene layers with a 14 × 14 supercell, with the top graphene layer decorated by 8 molecular cations ($[NR_4]^+$). To simulate a 0.05 M H_2SO_4 electrolyte (pH 1), we included four hydronium cations (H_3O^+), two sulfate anions (SO_4^{2-}), and 1096 water molecules (H_2O). Eight chlorine anions (Cl^-) were added to maintain charge balance against the 8 $[NR_4]^+$, and five CO_2 molecules were incorporated. Periodic boundary conditions were applied in all three dimensions.

Atomic charges for molecular cations were obtained from electrostatic potential (ESP) charges[72] calculated via DFT calculation with the PBE-D3 functional[73] as implemented in Jaguar software[74]. To assign charges to the CCNT, we first constructed a finite molecule model (Supplementary Fig. 63a) yielding a net of charges of +0.90 on the molecular cation moiety. This value closely matched the +0.91-value obtained from the Bader charge analysis[75] using a periodic model (Supplementary Fig. 63b) with the plane-wave DFT code (VASP)[76]. For all charged species, we used a 0.75 scaling factor for the electronic continuum correction[77,78]. Classical molecular dynamics simulations were performed to equilibrate the constructed systems using LAMMPS[79] with a 1 fs timestep. We employed the TIP3P force field[63] for the water molecules, utilizing the Ewald summation scheme[64], while the Universal Force Field (UFF)[80] was applied to the rest of the system. UFF explicitly accounts for atomic hybridization and connectivity and provides parameters for all elements in the periodic table. It is sufficiently flexible to capture room-temperature conformational dynamics of large organic structures while remaining computationally efficient for large systems, and in our case the key electrostatic interactions are governed by DFT-derived partial charges, reducing the sensitivity of our conclusions to the specific choice of bonded force-field parameters.

The initial models were relaxed by steepest-descent energy minimization, followed by heating to 298.15 K in the NPT ensemble for 100 ps. Subsequently, NPT equilibration was performed for 80 ns at room temperature. The temperature was controlled using the Nose-Hoover thermostat[81,82] with a damping constant of 100 fs. We allowed only the z dimension of simulation box to be adjusted for stable dynamics. Starting from the last snapshot from the equilibration, we applied a uniform electric field along z axis and further equilibrated for 20 ns."

Reviewer #2

General Comment: In this manuscript, the authors propose a strategy using cation-modified carbon nanotubes (CCNTs) as catalyst additives combined with the introduction of organic cations in the electrolyte. This approach aims to reduce H^+ diffusion to the catalyst surface, thereby suppressing the hydrogen evolution reaction (HER) and achieving enhanced CO_2 electroreduction (CO_2RR) activity in acidic electrolytes. However, the strategy of adding organic cations to the electrolyte has been previously reported (Angew. Chem. Int. Ed. 2025, 64, e202504785), which diminishes the novelty of this work. Thus, I recommend reconsideration after major revisions.

Response: We greatly appreciate the effort and time you put into reviewing our work. We highly appreciate your encouraging feedback and constructive comments on our work, which are important for us to improve the quality and clarity of this manuscript.

However, in terms of novelty, we appreciate your recommendation of previous report (*Angew. Chem. Int. Ed.* 2025, 64, e202504785). However, we believe the strategy, significance and impact of our work are different. The listed work attained a Faradaic efficiency (FE) of 90% for formate along with a stability of over 20 h on a polycrystalline Cu catalyst by adding 1 ppm octadecyl trimethyl ammonium ($C_{18}TA^+$) cations into near-neutral electrolyte (0.1 M $KHCO_3$). Furthermore, their electrocatalytic CO_2 reduction was performed entirely in an H-type cell with small current density (~10 mA cm^{-2}).

In comparison, the pH of electrolyte, the use of different catalysts to show versality, and the operation under high current densities highlight the difference. For our work, the cationic carbon nanotube (CCNT)-additive strategy can be compatible with organic cation (tetraalkylammonium). Even if the alkali metal cation (K^+) is totally replaced with the tetraalkylammonium cation in the acidic electrolyte (0.05 M H_2SO_4 + 3.0 M $N(CH_3)_4Cl$), our Bi/CCNT catalyst also exhibits a remarkable FE of formic acid (HCOOH) of >90% over a wide current density range of 40 to 400 mA cm^{-2} in the flow cell, comparable to that of K^+. In stark contrast, organic cations usually show moderate activity in near-neutral electrolyte (*Nat. Energy* 2022, 7, 835-843) and mild acids (*Nat. Catal.* 2021, 4, 645-662).

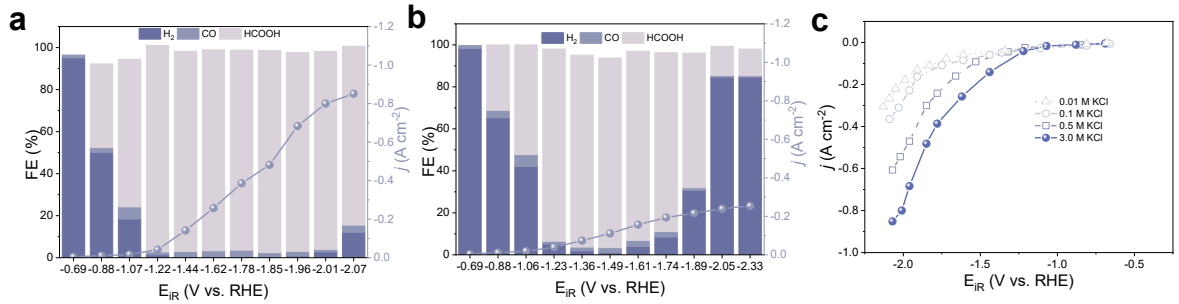
In conclusion, we demonstrate that CCNT can serve as a universal conductive matrix for metal catalysts, enabling efficient and selective CO_2RR in strong acids. We show this strategy yields high efficiency across a broad range of electrocatalysts (e.g., bismuth, silver, and copper oxide). Furthermore, we extend the concept beyond alkali cations, demonstrating that our CCNT platform also activates organic cations, which were previously reported to be negligibly active in mild acids. The above is a brief discussion highlighting the novelty and contributions of our work compare with the listed work.

Comment 2.1: In Supplementary Figure 10, compared with the data in Figure 2c, why is the current density higher at a lower electrolyte concentration for Bi/CCNT? Additionally, the voltage is expressed as E-iR in some parts of the manuscript but simply E in others; please provide a detailed clarification.

Response: We thank you very much for raising this important question. In **Original Supplementary Fig. 10**, it displays the total current density curves and FE values of CO_2RR products in 0.05 M H_2SO_4 + 0.5 M KCl for Bi/CCNT. The applied potential is converted to the reversible hydrogen electrode (RHE) with *iR* compensation. While for the **Fig. 2c**, it shows the total current density and FE values but in 0.05 M H_2SO_4 + 3.0 M KCl for Bi/CCNT, and the applied potential is not compensated. Therefore, this might cause the misinterpretation that Bi/CCNT has a higher current density at lower concentration of electrolyte. Actually, after *iR* compensation, Bi/CCNT does exhibit a higher current density in the acidic electrolyte of 0.05 M H_2SO_4 with 3.0 M KCl compared to 1.5 M KCl (**Supplementary Fig. 13**).

We have added the **Supplementary Fig. 13** in our revised Supplementary Information, and also added some discussion on Page 6 in our revised manuscript, as shown below.

"With increase K^+ concentrations in acidic electrolytes, the total current density dramatically increases at the same applied potential in the order of 0.01 M<0.1 M<0.5 M<3.0 M (Supplementary Fig. 13)."



Supplementary Figure 13. Total current density curves and FE values of CO_2RR products in 0.05 M H_2SO_4 + 3.0 M KCl for (a) Bi/CCNT and (b) Bi/CNT, (c) Total current density curves of Bi/CCNT in 0.05 M H_2SO_4 with various K^+ concentrations.

According to your valuable suggestion, we have provided a detailed clarification of the voltage (E) for better understanding. The detailed explanation has been added on Page 6 in our revised manuscript, as shown below.

"The applied potential without *iR* compensation is abbreviated as $E_{iR\text{-}free}$, while the applied potential with *iR* compensation is abbreviated as E_{iR}."

Comment 2.2: When preparing the catalyst ink, the authors still used anionic Nafion as the binder, which contradicts the claimed cation-modified CNT strategy in the manuscript.

Response: We thank you for your careful observation. When preparing the catalyst ink, we still used the anionic Nafion as the binder because

(1) its zeta potential is small (-3.58 mV) at the 7.5 μL dosage used in our experiments (**Supplementary Fig. 62**), extremely lower than that of our CCNT (27.8 mV-51.2 mV).

(2) The ionomer is needed to prepare the catalyst film, but the total amount is negligible in reference to the catalyst (20 mg catalyst *vs* 1.5 μg Nafion). Thus, the perturbation of Nafion is small.

(3) Our control experiments with different surface charge densities, and CCNT vs CNT, further highlight the role of surface potentials.

Thus, we have elaborated in the method part, as shown below.

"While Nafion shows a small zeta potential of -3.48 mV (Supplementary Fig. 62), its perturbation to CCNT potential is negligible since its loading is 10000 times lower."

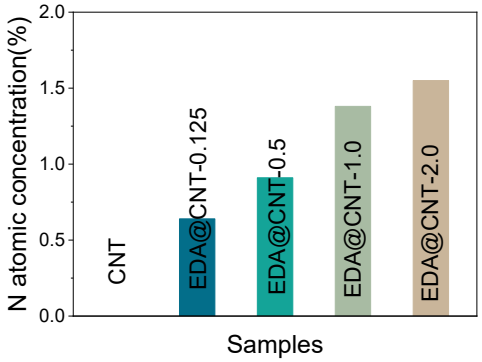
Comment 2.3: The authors synthesized a series of CCNT samples with varying cation loadings (CCNT-0.125, CCNT-0.5, CCNT-1.0, and CCNT-2.0). Experimental characterization is required to quantify the actual cation content in these samples.

Response: We sincerely thank you for your insightful comments on the experimental characterization required to quantify quaternary ammonium cations ($-NR_4^+$). X-ray photoelectron spectroscopy (XPS) of EDA@CNT-n (n=0.125, 0.5, 1.0 and 2.0) was used to investigate the atomic concentration of N to eliminate the influence of long alkyl chains and methylation. In this way, the experimental results can more objectively quantify the actual cation content in these samples. The XPS results indicate that the atomic concentration

of N increases in the order of EDA@CNT-2.0 (1.55%) > EDA@CNT-1.0 (1.38%) > EDA@CNT-0.5 (0.91%) > EDA@CNT-0.125 (0.64%), confirming the highest cationic density for CCNT-2.0 and also consistent with the zeta potential and KPFM tests (**Supplementary Fig. 19**).

We have added the **Supplementary Fig. 19** in our revised Supplementary Information, and also added some discussion on Page 8 in our revised manuscript, as shown below.

"XPS results shows that the N atom concentration increases in the order of EDA@CNT-2.0 (1.55%) > EDA@CNT-1.0 (1.38%) > EDA@CNT-0.5 (0.91%) > EDA@CNT-0.125 (0.64%), confirming that EDA@CNT-2.0 has the densest -NH_2 density, which was consistent with the highest -NR_4^+ density for CCNT-2.0 (Supplementary Figure 19)."



Supplementary Figure 19. The N atom concentration of various samples measured by XPS tests.

Comment 2.4: The authors should pay attention to manuscript formatting, as the order of figure citations is inconsistent with their presentation in many instances.

Response: We thank you so much for your kind suggestion and apologize for our mistake. We have thoroughly checked and corrected the inappropriate order of figure citations.

Comment 2.5: The authors employed both CCNTs and organic cations in the electrolyte. However, based on the stability test results, CCNTs appear to afford no improvement in stability. On the contrary, the previously reported strategy (adding organic cations to the electrolyte) achieves an orders-of-magnitude improvement in stability.

Response: We thank you for your valuable comment. Compared with unmodified CNTs, the CCNTs additives permit organic cations' use as electrolytes for selective acidic CO_2RR with more efficient FE and larger current density (**Fig. R1**). The FE_{HCOOH} of CCNTs exceeds 90% over a wide current density range of 40-400 mA cm^{-2}, while for CNTs, a lower current density and product selectivity are observed. As for stability, Bi/CCNT remains at a steady FE_{HCOOH} value of over 91% during the 130-h electrolysis at 280 mA cm^{-2} in the acidic electrolyte of 0.05 M H_2SO_4 + 3.0 M $N(CH_3)_4Cl$ (**Fig. R2**). Importantly, this CCNT strategy achieves an orders-of-magnitude improvement in stability, far exceeding these related works on CO_2RR based on metal-free, namely (alkyl)ammonium cations as electrolytes (**Supplementary Table 5**). We also assess the operation stability of Bi/CNT in 0.05 M H_2SO_4 + 3.0 M $N(CH_3)_4Cl$. Given its inferior FE at industrial current density (>200 mA cm^{-2}), a limited current density (~130 mA cm^{-2}) is chosen to run the stability test for Bi/CNT. The FE_{HCOOH} gradually decreases from 88% to 60%, and the total current density also drops from 135 mA cm^{-2} to 90 mA cm^{-2} during the 30-h electrolysis due to the flooding, which again shows the significant role of CCNTs in improving stability (**Fig. R3**).

Indeed, there are some previously reported works using strategy of adding organic cations to electrolytes to achieve an efficient CO_2RR process (**Supplementary Table R1**). Some of them have a decent operation stability of over 20 hours with good product selectivity. However, all of them have an extremely limited current density because of the higher impedance after adding organic cations into catholytes. And a decreased current density will hamper product formation, posing substantial challenge for the industrial application of CO_2 electrolysis. Furthermore, their addition of organic cations could be only applied for one metal catalyst. While for the CCNTs strategy, it can be generally applied as a matrix to enable efficient CO_2RR in strong acids for various metal catalysts, operating for longer periods even at an industrial current density.

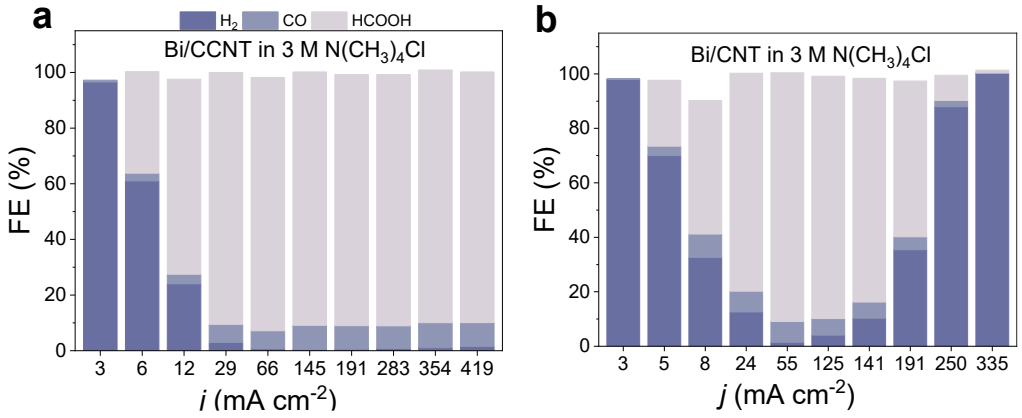


Figure R1. FE values for (a) Bi/CCNT and (b) Bi/CNT in 0.05 M H_2SO_4 + 3.0 M $N(CH_3)_4Cl$ at various current densities.

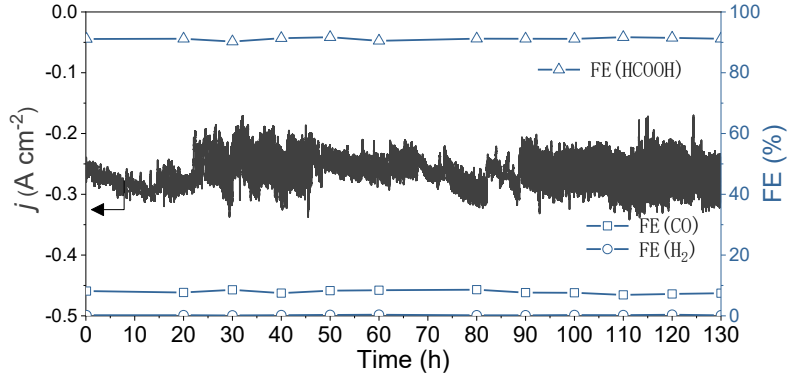


Figure R2. FE of H_2, CO, and HCOOH for stability test using Bi/CCNT in an acidic non-alkali electrolyte (0.05 M H_2SO_4 + 3.0 M $N(CH_3)_4Cl$).

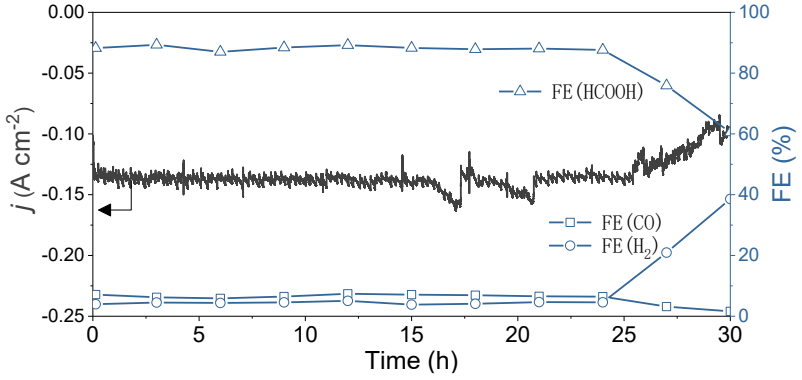


Figure R3. FE of H_2, CO, and HCOOH for stability test using Bi/CNT in an acidic non-alkali electrolyte

(0.05 M H_2SO_4 + 3.0 M $N(CH_3)_4Cl$).

Supplementary Table R1. Comparison of CO_2RR reported in previous works based on the strategy of adding organic cations into electrolytes.

Catalyst	Electrolyte	Organic cation	Product	FE (%)	j (mA cm^{-2})	Stability (h)	Reference
Poly-Cu	0.1 M $KHCO_3$	$C_{18}TA^+$	HCOOH	90	5.8	22.5	Angew. Chem. Int. Ed.[1]
Modified-Cu/PTFE	1.0 M H_3PO_4 + 0.1 M K^+	tolyl-pyr	C_2H_4	31.5	50	5	Angew. Chem. Int. Ed.[2]
Ag-1	0.1 M $KHCO_3$	1-Br_2	CO	90	0.7	24	ACS Catal.[3]
Polycrystalline Cu	0.1 M $KHCO_3$	N-tolyl pyridinium	C_2H_4	40	1	10	ACS Cent. Sci.[4]
Bulk silver	0.5 M $NaHCO_3$	DTAB	CO	95	4	1.67	Appl. Surf. Sci.[5]
Cu foil	0.1 $NaHCO_3$	CTAB	HCOOH	40	1.2	8	ACS Catal.[6]

We have revised **Supplementary Table 5** in our revised Supplementary Information, and also added some description on Page 15 in our revised manuscript, as shown below.

"Importantly, this strategy demonstrates that a metal-cation free electrolyte, namely, $N(CH_3)_4^+$-based electrolyte, assures a decent industrial current density (>200 mA cm^{-2}), a comparable product Faradaic efficiency (FE_{CO}~100%, FE_{HCOOH}~90%, $FE_{C_2H_4}$~50%) and an excellent operation stability (60-160 h) to those observed for alkali-metal-cation-based electrolytes, far exceeding the related limited works on CO_2RR based on (alkyl)ammonium cations as catholytes (Supplementary Table 5)[29,59-62]."

Supplementary Table 5. Comparison of acidic CO_2 reduction reported in literatures based on (alkyl)ammonium-cation electrolytes.

Catalyst	Electrolyte	Product	pH	$FE_{product}$ (%)	$j_{product}$ (mA cm^{-2})	Stability (h)	Reference
Bi/CCNT	0.1 M H^+ + 3.0 M $N(CH_3)_4^+$	HCOOH	Acidic	90.1	378	130	This work
Ag/CCNT		CO		98.2	314	160	
CuO/CCNT		C_2H_4		45.9	238	60	
Au NPs	1.0 M $N(CH_3)_4^+$ (pH=2)	CO	Acidic	85.1	68	0.5	J. Am. Chem. Soc.[33]
CuO NPs	1.0 M $N(CH_3)_4^+$ (pH=14)	C_2H_4	Akaline	33.2	166	10	EES Catal.[34]
Ag NPs	0.1 M H^+ + 1.0 M NH_4^+	CO	Acidic	38.3	38.3	7	ACS Catal.[35]
AuPTFE	0.1 M $N(CH_3CH_2)_4^+$	CO	neutral	78.5	5.1	0.3	J. Am. Chem. Soc.[36]
Bi/C	0.1 M $N(CH_3)_4^+$	HCOOH	neutral	32.2	1.65	2	ACS Catal.[37]

Comment 2.6: Calculating energy efficiency using flow cell data is not valid, which should be done in MEA or other similar cells.

Response: We thank you for your valuable advice. We apologize for the misunderstanding caused by the inappropriate expression of energy efficiency (EE). Actually, in the "Methods" section of main manuscript, the half-cell energy efficiency (or cathodic energy efficiency, CEE) for each product in flow cell is calculated according to these previous reports[7-11]:

$$CEE_{product}(\%) = \frac{\left(1.23V + \left(-E^0_{product}\right)\right) \times FE_{product}}{\left(1.23V + \left(-E_{applied}\right)\right)}$$

where $E^0_{product}$ refers to the thermodynamic potential for the formation of a specific CO_2RR product; $E_{applied}$ is the applied potential vs. RHE obtained from the electrolyser without iR compensation; $FE_{product}$ is the Faradaic efficiency of a specific CO_2RR product at an applied potential. And this calculation method has also been recognized and verified for comparing the energy utilization efficiency in

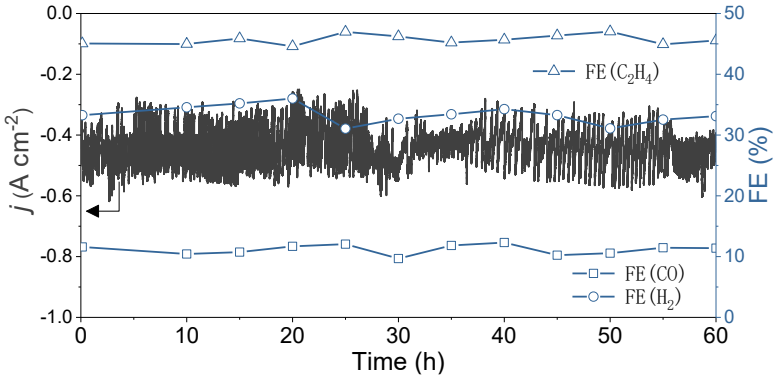
flow cell (*Nat. Synth.* 2025, 4, 53-66; *Angew. Chem. Int. Ed.* 2025, 64, e202504785; *Angew. Chem. Int. Ed.* 2023, 62, e202300226; *Angew. Chem. Int. Ed.* 2024, 63, e202408412; *Appl. Catal. B Environ.* 2025, 361, 124681). We have thoroughly checked and corrected the inappropriate expression of energy efficiency (EE) as cathodic energy efficiency (CEE) in our revised manuscript to avoid causing misleading.

Comment 2.7: For the sake of manuscript completeness, the authors are advised to supplement the stability test of CuO.

Response: We thank you for your constructive comment. Following your suggestion, we further test the operation stability of CuO/CCNT in the acidic electrolyte of 0.05 M H_2SO_4 + 3.0 M $N(CH_3)_4Cl$ to validate the applicability of our CCNT-additive strategy compatible with tetramethylammonium cations toward various metal catalysts. Like bismuth and silver metal catalysts, the CuO/CCNT also exhibits good durability and works steadily under high current density of 450 mA cm^{-2} for 60 h with an average C_2H_4 selectivity of 45% (**Supplementary Fig. 51**).

We have added **Supplementary Fig. 51** in our revised Supplementary Information, and also added following discussion on Page 15 in our revised manuscript, as shown below.

"Moreover, the acidic CO_2RR with CuO/CCNT maintains a total current density of 450 mA cm^{-2} at an $FE_{C_2H_4}$ of ~45% for 60 h in 3.0 M $N(CH_3)_4^+$ (Supplementary Fig. 51)."



Supplementary Figure 51. FE and total current density for stability test using CuO/CCNT in 0.05 M H_2SO_4 + 3.0 M $N(CH_3)_4Cl$.

Comment 2.8: In the rotating disk electrode (RDE) studies, the limiting diffusion currents of CNTs and CCNTs are nearly identical in the diffusion-limiting region. This contradicts the authors' claim that CCNTs reduce the H^+ diffusion coefficient-if CCNTs indeed decreased the H^+ diffusion coefficient, the corresponding limiting diffusion current should be lower.

Response: We thank you so much for your valuable comment regarding RDE studies.

In the RDE test (**Fig. R4**), there are several important information:

(1) In the region of -0.8 to -1.1 V, it mainly contains the proton reduction current. The data suggest that higher densities of cations can reduce the proton reduction current. In addition, the current reaches the plateau much faster for CNT, implying the quick consumption of proton and fast proton transport.

(2) In the region of -1.1 to -1.5 V, there are several differences.

First, CNT reaches the plateau much faster, but also starts the water reduction at lower overpotentials, implying the easy access to both proton and water. This also supports the effect our cationic charges.

Second, when we zoom in the diffusion-limiting region, there are still some subtle differences in the limiting diffusion current density between CNTs and CCNTs **(Fig. R5)**. For CNT and CCNT-0.5, the

difference in the plateau current density is 1.81 mA cm^{-2}, which is less than that of between CNT and CCNT-2.0 (2.57 mA cm^{-2}).

Third, note that the diffusion-limiting current is affected by the diffusion of proton, which contains the proton diffusion in bulk solution and in the interfaces. To further quantify the impact of interface modification on the observed proton diffusion, we further calculate the diffusion-limited current of hydronium reduction according to the Levich equation:

$$j_{plateau} = 0.62nFAD^{\frac{3}{2}}v^{-\frac{1}{6}}c_{0,H^+}\omega^{\frac{1}{2}}$$

where n is the number of electrons transferred in the reaction, F is the Faraday constant (9.65 × 10^4 C mol^{-1}), A is the electrode surface area, D is the diffusion coefficient of hydronium ions, v is the kinematic viscosity of electrolyte, c_{0,H^+} is the bulk concentration of hydronium ions, and ω is the rotation speed of the RDE (rad s^{-1}). Therefore, compared with CCNT, CCNT-2.0 shows a decrease in the observed diffusion coefficient of hydronium ions based on the calculation results of the Levich equation (**Supplementary Table R2**).

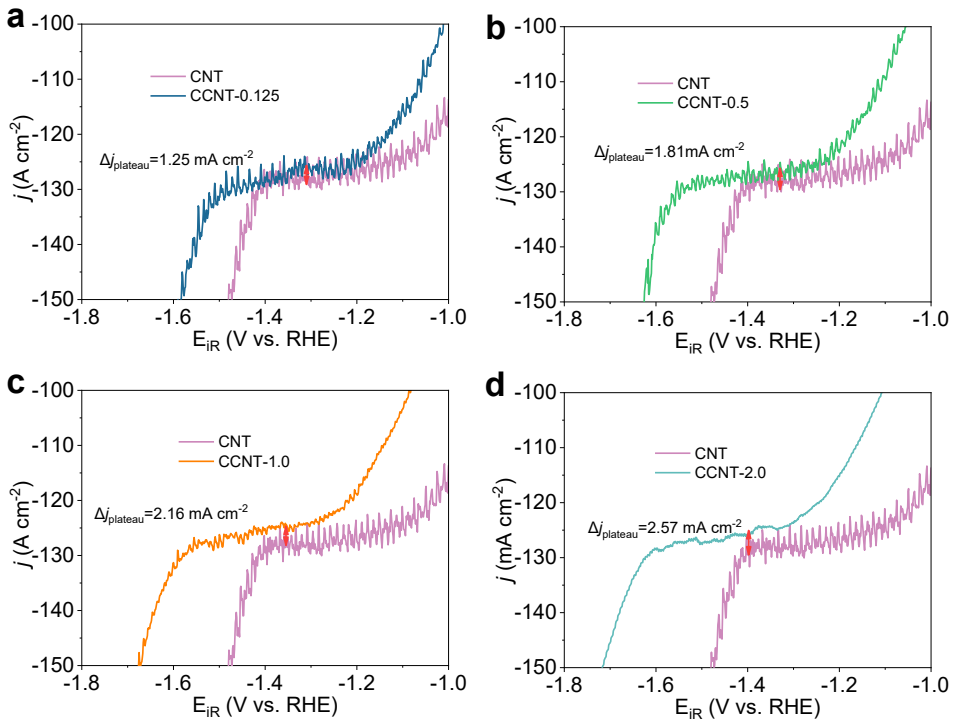


Figure R5. Comparison of RDE voltammetry in the diffusion-limiting region for (a) CNT and CCNT-0.125, (b) CNT and CCNT-0.5, (c) CNT and CCNT-1.0, and (d) CNT and CCNT-2.0.

Supplementary Table R2. RDE results for our CCNT strategy as measured in 0.05 M H_2SO_4 + 0.5 M K_2SO_4.

	$j_{plateau}$ (mA) vs. $\omega^{1/2}$			
Electrode	Slope (mA $s^{-1/2}$)	R^2	$Slope_{CCNT-n}/Slope_{CNT}$	$D_{obs,H^+,CCNT-n}/D_{obs,H^+,CNT}$
CNT	2.5307	0.9991	1.000	1.000
CCNT-0.125	2.4728	0.9994	0.977	0.986
CCNT-0.5	2.4101	0.9993	0.952	0.968
CCNT-1.0	2.3745	0.9993	0.938	0.958
CCNT-2.0	2.3357	0.9994	0.923	0.949

To Reviewer #3

General Comment: This manuscript presents an innovative and versatile strategy that employs cationic carbon nanotubes (CCNTs) as a universal additive to achieve efficient CO_2 reduction reaction (CO_2RR) in strongly acidic media. The cationic modification significantly suppresses the severe hydrogen evolution reaction (HER) typically associated with pristine carbon nanotubes. Furthermore, replacing conventional alkali metal-based electrolytes with an organic cation-based alternative effectively prevents salt deposition, thereby improving long-term stability and energy efficiency without obviously compromising the HCOOH FE. The study is innovative and is well-supported by extensive data.

Response: We thank you so much for the positive and encouraging feedback, and for thoughtfully highlighting the key contributions of our work. We are grateful that the reviewer recognizes that the versatility of CCNT as a universal additive for various mental catalysts to enable efficient CO_2RR in strong acids, the effectiveness of our CCNT strategy compared to pristine CNT to inhibit the competing HER, and the novelty of using organic cation-based electrolytes to improving long-term stability. The following are detailed response to comments.

Comment 3.1: The influence of CO_2 flow rate on HCOOH yield should be determined. If a correlation exists, both the flow rate and the corresponding yield should be incorporated into the economic assessment of HCOOH production.

Response: We sincerely thank you for your kind suggestion about the influence of CO_2 flow rate on HCOOH yield. When the CO_2 flow rate decreases from 50 to 2 sccm at 200 mA cm^{-2}, the Bi/CCNT always maintains an excellent FE_{HCOOH} over 94% (**Fig. 2d**). A high single-pass carbon efficiency (SPCE) of 68.5% is achieved at a CO_2 flow rate of 2 sccm, close to the theoretical maximum SPCE value of 74.78%. However, when the CO_2 flow rate is further decreased to 1.5 sccm, 75.59% of SPCE for HCOOH is achieved, but FE_{HCOOH} decreases significantly to only 75.82%. Then, the partial current density and production rate for HCOOH are obtained immediately under various CO_2 flow rates (**Supplementary Fig. 14**). The HCOOH partial current density drops to 151.6 mA cm^{-2}, corresponding to a production rate of 2.83 mmol h^{-1} cm^{-2} at CO_2 flow rate of 1.5 sccm (lower than ~3.56 mmol h^{-1} cm^{-2} at 2-50 sccm). Therefore, it is found that the CO_2-to-HCOOH process at the flow rate of 2 sccm has the highest economic value by balancing carbon efficiency, product selectivity and production rate, since the economic value of HCOOH is $1000 USD per ton which far exceeds that of CO_2 of $70 USD per ton[12,13].

We have revised the **Fig. 2d** and also added some discussion on Page 8 in our revised manuscript, as shown below.

"However, when further reducing CO_2 flow rate to 1.5 sccm, a remarkable SPCE of 75.59% for HCOOH is achieved, while FE_{HCOOH} decreases significantly to only 75.8%."

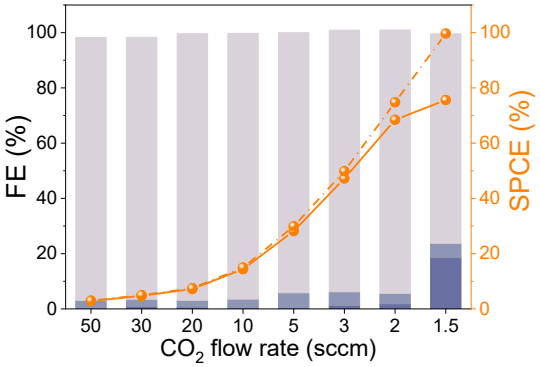
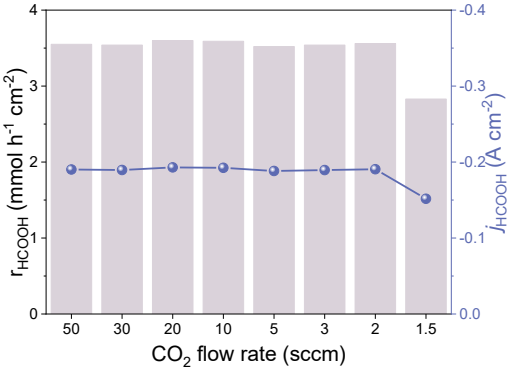


Fig. 2d Single-pass carbon efficiency (SPCE) and FE for Bi/CCNT at various CO_2 gas flow rates under a total current density of -200 mA cm^{-2} (solid line: measured; dashed line: expected).

We have added the **Supplementary Fig. 14** in our revised Supplementary Information, and also added some discussion on Page 8 in our revised manuscript, as shown below.

"Since the economic value of HCOOH is $1000 USD per ton, the CO_2-to-HCOOH process at the flow rate of 2 sccm has the highest economic value by balancing carbon efficiency, selectivity and productivity (Supplementary Fig. 14)."



Supplementary Figure 14. Partial HCOOH current density and HCOOH production rate at different CO_2 gas flow rates under a total current density of -200 mA cm^{-2}.

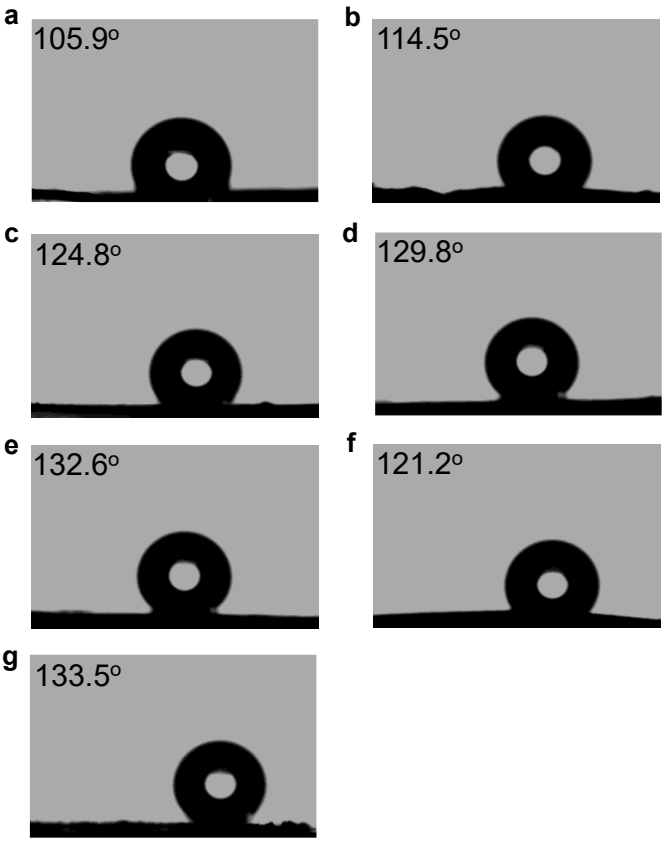
Comment 3.2: The PTFE-coating strategy is selected as a benchmark due to its ability to mitigate flooding. It is suggested to provide the contact angle for both PTFE-coating and CCNT. It would be interesting to investigate whether the hydrophobic environment provided by the long alkyl chains of CCNT contributes to its high performance.

Response: We thank you for your constructive suggestion regarding contact angle. According to your advice, we have measured the water contact angle to evaluate the surface hydrophobicity of PTFE-coating and CCNT-additive samples. As expected, water contact angles demonstrate that all types of CCNT exhibit stronger hydrophobicity than pristine CNT, which is due to the introduction of long alkyl chains (**Supplementary Fig. 57**). It is worth noting that although the PTFE-coating structure has a higher contact angle, the increased impedance and the unavailability of catalytic sites caused by the introduction of PTFE may be the reasons for its poor performance.

We have added the **Supplementary Fig. 57** in our revised Supplementary Information, and also added some

description on this point which are highlighted in red color on Page 16 in our revised manuscript, as shown below.

"We then measured the contact angles to evaluate the surface hydrophobicity (Supplementary Fig. 57). Experimental results demonstrate that all samples exhibit hydrophobic character with water contact angles >90°. As the quantities of cationic groups covalently anchored on CNT increases, the hydrophobicity increases in the order of CCNT-2.0 (132.6°) > CCNT-1.0 (129.8°) > CCNT-0.5 (124.8°) > CCNT-0.125 (114.5°) > CNT (105.9°)."



Supplementary Figure 57. Water contact angle measurements for (a) CNT, (b) CCNT-0.125, (c) CCNT-0.5, (d) CCNT-1.0, (e) CCNT-2.0, (f) CNT/PTFE-mix and (g) CNT/PTFE-layer.

Comment 3.3: The FE values and partial current density curves for the Bi/CCNT-0.5 sample appear to be missing. These data are essential for evaluating the effect of CCNT charge density on acidic CO_2RR performance and should be provided.

Response: We thank you so much for your invaluable comment, which is essential for understanding the phenomena. Based on your suggestion, we have provided the FE values and partial current density curves for the Bi/CCNT-0.5 to better assess the influence of charge density for CCNTs on CO_2RR in strongly acidic media (**Fig. 3e**).

We have added the **Fig. 3e**, and also added the following discussion on Page 10 in our revised manuscript, as shown below.

"For Bi/CCNT-0.5, it achieves a decent selectivity of >94% at a partial current density of 708.5 mA cm^{-2} near -2.01 V_{iR}, and then FE_{HCOOH} slightly decreases to ~85% at -2.07 V_{iR} (Fig. 3e)."

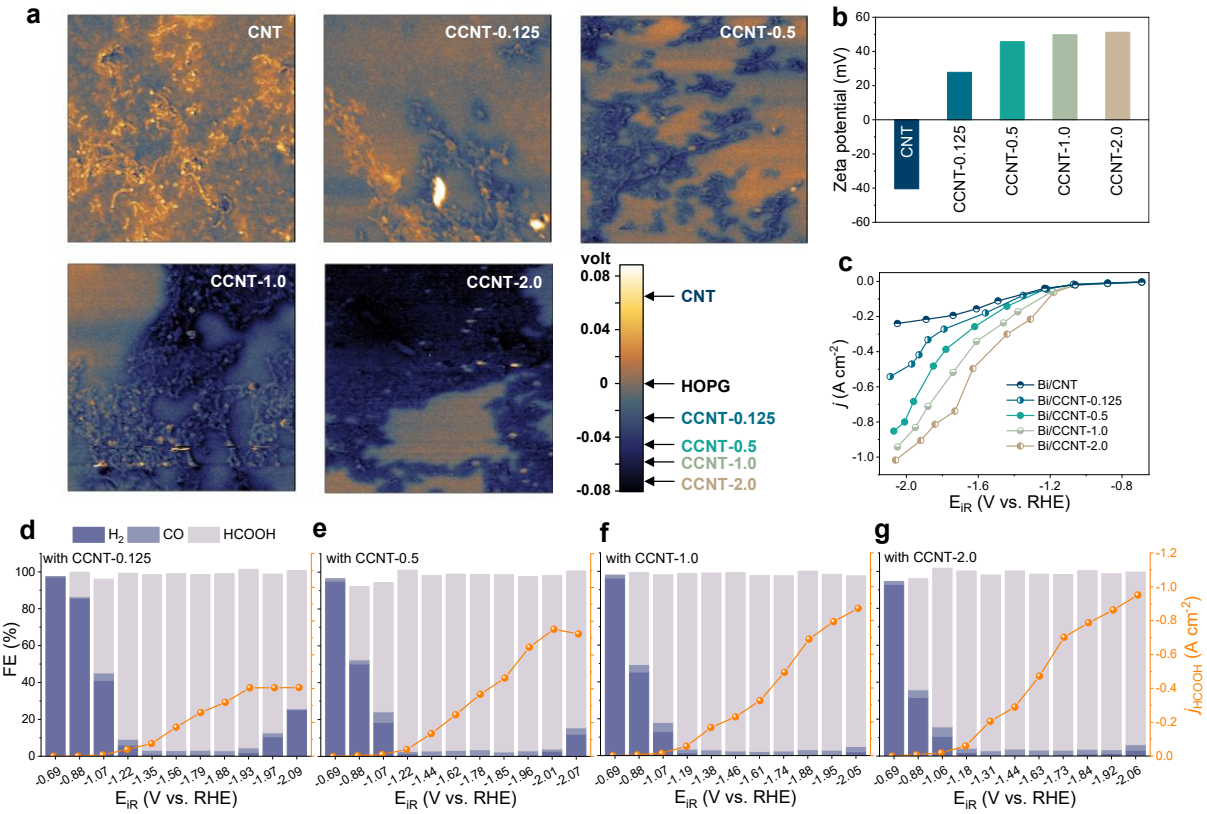


Fig. 3 CNTs bearing cationic groups of varying quantity enabling efficient CO_2RR in acidic medium. **a**, Surface potential scans of pristine CNT and CCNT-n by atomic force microscope with a Kelvin probe (KPFM). **b**, Zeta potential of pristine CNTs, CCNT-n (n=0.125, 0.5, 1.0, 2.0). **c**, Total current density of the Bi/CCNT-n in 0.05 M H_2SO_4 + 3.0 M KCl. **d**, **e**, **f**, **g**, FE values and partial current density curves for (**d**) Bi/CCNT-0.125, (**e**) Bi/CCNT-0.5, (**f**) Bi/CCNT-1.0 and (**g**) Bi/CCNT-2.0.

Comment 3.4: The formula used for calculating the turnover frequency (TOF) should be provided in the manuscript.

Response: We sincerely thank you for your helpful suggestion regarding offering the calculation formula of TOF.

We have added the detailed calculation formula for TOF, which is highlighted in red color on Page 25 in our revised manuscript, as shown below.

"The turnover frequency (TOF) is defined as the number of reduction product generated per electrocatalytic active site per unit time, calculated as follows:

$$TOF_{product}(h^{-1}) = \frac{j_{tot} \times FE_{product}}{2F \times n_{tot}} \times 3600$$

Where j_{tot} denotes the total recorded current (A); $FE_{product}$ denotes the Faradaic efficiency of a CO_2RR product (%); n_{tot} denotes the total loading amount of metal catalysts (mol); F denotes the Faraday constant (96485 C mol^{-1})."

Comment 3.5: With the increase of charge density of CCNTs, the operation potential window with high HCOOH FE is increased. The underlying reason for this correlation should be clarified, as it is important for understanding the mechanism.

Response: We thank you for your insightful suggestion to discuss the effect of CCNTs' charge density on

the operation potential range. More immobilized cationic groups on CNT could extend the applied potential window for stronger HER inhibition. Our mechanistic studies provide insights into how the cation effect and alkyl effect suppress HER and boost CO_2RR production.

Firstly, the positive charges of quaternary ammoniums repel hydroniums via Coulomb repulsion, leading to a decrease in the diffusion coefficient of hydronium ions for CCNT versus CNT, thus decreasing hydronium reduction activity (**Fig. R6**). Additionally, the cationic groups can electrostatically stabilize the negatively charged CO_2^- intermediate, achieving efficient CO_2RR under higher applied potentials[14].

Secondly, establishing cations groups with more long alkyl chains can further deactivate the water reduction activity. Rotating disk electrode voltammetry demonstrates that the water reduction activity decreases in the order of CCNT-2.0 < CCNT-1.0 < CCNT-0.5 < CCNT-0.125 < CNT. CCNT-2.0 with highest quantity of long alkyl chains shows significantly lowest water reduction current density among all tests, confirming its inferior water reduction activity. The long alkyl chains can regulate the interfacial water environment through decreasing water and hydronium availability, thus hindering the competing HER. The unavailability of water is due to the fact that all CCNT samples are hydrophobic with water contact angles >90° (**Fig. R7**). As the amount of alkyl chains become more, the hydrophobicity increases with water contact angles of 130° and 140° for CCNT-1.0 and CCNT-2.0, respectively. Therefore, the hydrophobic and cationic interface microenvironments generated by the quaternary ammonium cations reduce the activity of hydronium and water reduction, thus improving acidic CO_2 electroreduction.

Thirdly, in addition to the interfacial water, the alkyl chain can improve interfacial gas availability. For example, Ohlin and coworkers discovered that the CO solubility increases with the chain length of the alkyl substituent[15]. The CO solubility would increase in the order of $-C_8H_{17}$ (4.20 mM bar^{-1}) > $-C_6H_{13}$ (3.92 mM bar^{-1}) > $-C_4H_9$ (3.60 mM bar^{-1}) > $-C_2H_5$ (3.30 mM bar^{-1}) > $-CH_3$ (3.13 mM bar^{-1}). CO_2 reduction is simultaneously promoted since the alkyl chains provide multiple aerophilic tunnels for CO_2 transportation. The molecular dynamics (MD) simulations also confirm the weakened water/hydronium reduction activity and increased surface CO_2 coverage around the catalyst center.

Combining the above interactions, we achieve more efficient CO_2RR in strong acid (pH ~0.5) with the assistant of CCNT with more charge density.

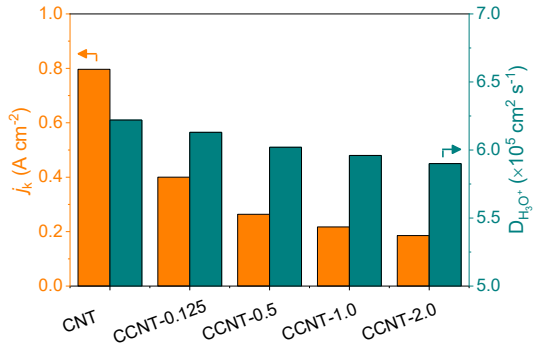


Figure R6. Kinetic current density of HER and diffusion coefficient of hydronium calculated from Koutecký-Levich equations at -1.0 V_{iR}.

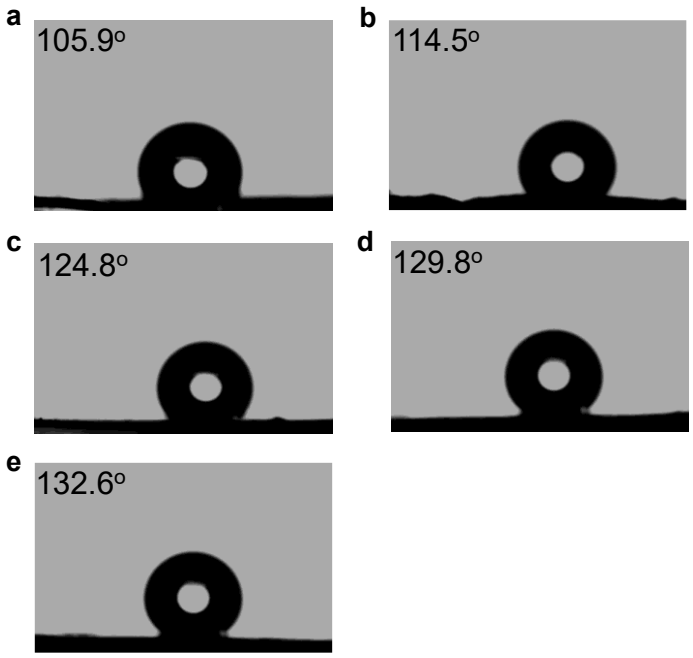


Figure R7. Water contact angle measurements for (a) CNT, (b) CCNT-0.125, (c) CCNT-0.5, (d) CCNT-1.0 and (e) CCNT-2.0.

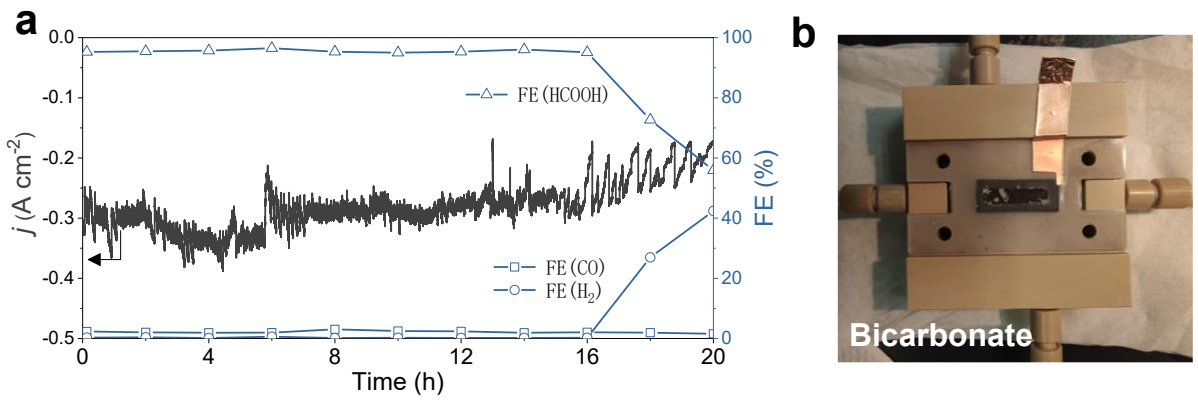
We appreciate your insight and we have added the following discussion on Page 16 in our revised manuscript. "Collectively, the cationic CNT with hydrophobic alky chain effectively hinders competing HER through decreasing hydronium and water availability, and CO_2 reduction is simultaneously promoted since the alkyl chains provide multiple aerophilic tunnels for CO_2 transportation, thus extending the applied potential window for inhibited HER and boosted CO_2RR."

Comment 3.6: The long-term stability of the Bi/CCNT catalyst in the 0.05 M H_2SO_4 + 3 M KCl electrolyte should be supplemented to confirm whether salt deposition occurs.

Response: We sincerely thank you for your constructive comment regarding the long-term stability test. Following your suggestion, we further test the operation stability of Bi/CCNT in the acidic electrolyte of 0.05 M H_2SO_4 + 3.0 M KCl to verify effectiveness of our CCNT strategy compatible with organic cations in inhibiting salt deposition. As expected, the Bi/CCNT initially exhibits good durability and works steadily under high current density of 280 mA cm^{-2} for 16 h with an average HCOOH selectivity of 95%. However, the FE_{HCOOH} decreases from 95% to 56%, and the total current density also decreases to 200 mA cm^{-2} after that because of the severe salt precipitation (**Supplementary Fig. 27**).

We have added the **Supplementary Fig. 27** in our revised Supplementary Information, and also added following description on Page 12 in our revised manuscript, as shown below.

"While for 3.0 M KCl, stability test suggests that a decrease in the total current density and product selectivity for Bi/CCNT occur during the 20-h electrolysis due to the salt deposition (Supplementary Fig. 27)."



Supplementary Figure 27. (a) FE and current density for stability test using Bi/CCNT in 0.05 M H_2SO_4 + 3.0 M KCl, (b) Photo of the back side of gas diffusion electrode after stability test showing salt deposition in the acidic electrolyte of 3.0 M K^+.

Comment 3.7: The effect of the electrolyte change from KCl to $N(CH_3)_4Cl$ on the HCOOH formation pathway and rate-determining step requires further investigation.

Response: We sincerely thank you for your insightful comment. The HCOOH formation pathway goes through CO_2 → *OCHO → *OCHOH → + HCOOH,[16] which differs from the CO formation (CO_2 → *COOH → *CO → + CO). Since Bi in KCl and $N(CH_3)_4Cl$ both produce HCOOH, the formation pathway is unchanged. However, the different interaction between K^+/$N(CH_3)_4^+$ and intermediates might affect the rate-determining step[17]. When comparing the Tafel plot (**Fig. R8**), we found the slopes are very similar between K^+/$N(CH_3)_4^+$, implying the same rate-determining step of proton-concerted electron transfer.[16]

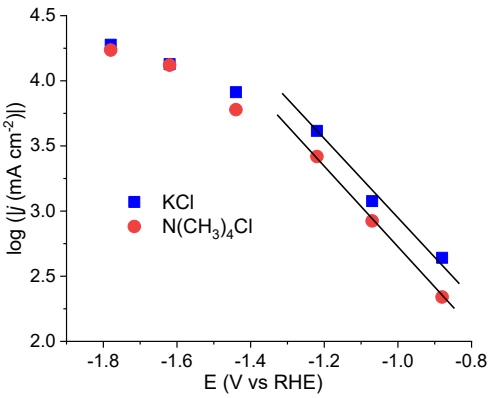


Figure R8. Tafel analysis in KCl and $N(CH_3)_4Cl$.

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Response to Reviewers' comments

Dear reviewers,

Thank you for your precious time to constructive comments on our manuscript titled "**Cationic carbon nanotube modulates surface fields for general acidic CO_2 reduction with aqueous organic cations**" (**Manuscript number: NCOMMS-25-91536A**) for ***Nature Communications***. We sincerely appreciate your comments and suggestions on our work, which are highly valuable for further improvements to our manuscript. According to all the comments, we have made a detailed response and substantial revisions to our revised manuscript. We sincerely hope that our response will fully address your concerns about our work. Thank you for your time and effort.

To facilitate reading, we use blue color for the reviewers' comments, black color for our replies, and red color for our change in manuscript.

To Reviewer #3

General Comment: The authors have addressed all my concerns and I recommend the manuscript for acceptance in its current form.

Response: We sincerely thank you so much for your support of our work. We greatly appreciate the effort and time you have devoted to reviewing our manuscript. We highly appreciate your constructive and valuable comments.

To Reviewer #4

General Comment: In this manuscript, the authors demonstrate that grafting long alkyl chain organic cations onto carbon nanotubes (CNTs) serves as a universal additive capable of enhancing CO_2RR performance of different metal catalysts in acidic media. This approach stands in contrast to previous strategies, which typically involve adding high concentrations of alkali metal cations to the electrolyte or incorporating cationic ionomers into the catalyst layer. It offers a novel pathway to promote acidic CO_2RR. The authors support this enhancement with extensive comparative data and provide a detailed analysis of the underlying mechanism. I believe this work is suitable for publication in Nat. Commun. I have also reviewed the previous referees' comments and the authors' responses. While most concerns have been adequately addressed, a few minor points remain for the authors' consideration.

Response: We sincerely thank you so much for your approval of our work and for taking the time to raise valuable suggestions. All feedback is crucial to our improvement, and we have carefully revised the relevant content in the revised manuscript. We have carefully analyzed the questions you raised and sincerely hope that the revised manuscript will meet your strict standards for publication.

Comment 4.1: Following the grafting of cationic groups, the CNTs are expected to exhibit both electronic and ionic conductivity. Could the authors separately measure the electronic and ionic conductivities of the modified CNTs? It would be important to consider whether the CCNTs function dually as both conductive agents and ionomers within the catalyst layer, rather than acting merely as an H^+ migration suppressor as proposed.

Response: We sincerely thank you very much for raising this insightful comment regarding the dual electronic/ionic nature of CCNTs. Firstly, CNTs can typically reach an exceptionally high intrinsic electronic conductivity on the order of ~10^5 S m^{-1}, enabling highly efficient electron transport networks in electrodes[1, 2]. In the field of electrochemical CO_2 reduction, CNTs have been widely employed as conductive additives to enhance the overall electrical conductivity of the catalyst layer, thereby obtaining larger current densities (**Fig. R1**)[3-7]. It is therefore well established that CNTs, and by extension CCNTs, function effectively as conductive agents within the catalyst layer.

However, it is crucial to clarify that CCNTs do not possess meaningful intrinsic ionic conductivity (**Supplementary Table R1**). The benchmark ion conductor, quaternary ammonium (QA)-type polymers, exhibits an ion conductivity of ~0.1 S cm^{-1}, setting the standard for any ionomer[8]. In contrast, pure CNTs show excellent electronic conductivity of 10^5 S m^{-1}, but their ionic conductivity is negligible. While for QA-grafted conductive carbon nanofiber, a system closely analogous to our CCNTs, the reported ionic conductivity is merely 1.28×10^{-3} S cm^{-1}, which is two orders of magnitude lower that of state-of-the-art QA-type polymers[9]. Even in composite electrodes where functionalized CNTs are mixed with polymers, the measured ionic conductivity remains on the order of 10^{-3} to 10^{-2} S cm^{-1}, still significantly lower than that of QA-type polymers[10-13]. In such composites, the functionalized CNTs serve only to maintain the ionic conductivity of the polymer matrix without significant loss, rather than providing ion conductivity independently. Furthermore, studies have demonstrated that CNTs primarily act as an electronic scaffold, and their presence physically obstructs and disrupts the continuous ion-conducting pathways that a true ionomer would provide[14]. This fundamental performance gap confirms that while CCNTs function effectively as electronic conductive agents, they cannot substitute a dedicated ionomer for ionic transport.

[FIGURE REDACTED]

Figure R1. Linear sweep voltammogram curves at sweep rate of 10 mV s^{-1} for (a) pure catalysts and (b) catalysts/CNTs composites[4].

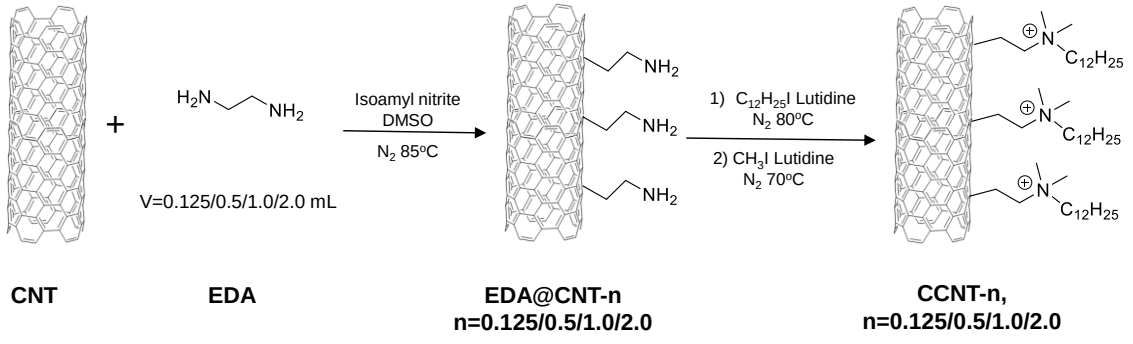
Supplementary Table R1. Comparison of ionic conductivity for various material systems.

Material system	Ionic conductivity (S cm^{-1})	Notes
QA-type polymers	~10^{-1}	Standard for any ionomer[8]
Pure CNTs	Negligible	Electronic conductor only; no intrinsic ionic conductivity
QA-grafted conductive carbon nanofibers (system most analogous to CCNTs)	1.28×10^{-3}	Two orders of magnitude lower than QA-type polymers[9]
Functionalized CNTs/polymers composite electrodes	10^{-3}-10^{-2}	Still significantly lower than QA-type polymers; functionalized CNTs serve only to maintain polymer matrix conductivity[10-13]

Comment 4.2: In Supplementary Figure 1, to prevent any confusion with the volume of ethylenediamine (EDA) used during synthesis, it is recommended that the grafted alkyl chain be explicitly labeled with its molecular formula $C_{12}H_{25}$.

Response: We sincerely thank you for your constructive advice, which is essential for understanding the synthesis process of cationic CNTs. Based on your suggestion, we have thoroughly corrected the inappropriate expression of -C_nH_{2n+1} with its explicit molecular formula -$C_{12}H_{25}$ in our revised Supplementary Information to avoid causing any confusion (**Supplementary Fig. 1**).

We have revised **Supplementary Fig. 1** in our revised Supplementary Information, as shown below.



Supplementary Figure 1. Scheme for the synthesis of CCNT-n (n=0.125, 0.5, 1.0 and 2.0).

To Reviewer #5

General Comment: The authors' efforts in addressing the previous concerns are appreciated, but several technical and mechanistic issues remain unresolved. The manuscript still lacks the rigor required for Nature Communications and is likely better suited for a more specialized journal.

Response: We sincerely thank you so much for your time and insightful suggestions. Your comments have been invaluable in strengthening our manuscript. In this revision, we have carefully addressed all remaining technical and mechanistic concerns to enhance the rigor of our work. We greatly appreciate the constructive review process, which has significantly improved the quality of this study. Below, we provide our detailed point-by-point responses.

Comment 5.1: While the authors have now included *iR*-compensated data in the SI, Figure 2 still presents uncompensated potentials. Since uncompensated data makes it difficult to evaluate and compare intrinsic catalytic activity, the authors should provide a clear explanation for why this was retained for the primary results.

Response: We sincerely thank you for this careful observation. We agree that *iR*-compensated data are essential for evaluating intrinsic catalytic activity and thus have provided these data in the Supplementary Information. However, we still retained uncompensated potentials in the main figure for two reasons.

First, presenting raw and uncompensated data allows readers to explicitly assess the magnitude of ohmic losses in both Bi/CCNT and Bi/CNT/PTFE-mix composites. While the polymer-coating strategy is effective for acidic CO_2RR, the inherently high impedance of PTFE inevitably results in a notable decrease in current density (**Fig. R2**). In contrast, our CCNTs strategy sustains industrially current densities owing to the exceptional electronic conductivity. Therefore, this direct comparison under uncompensated conditions highlights the practical advantage of our approach more intuitively. Second, the *iR*-compensated data show trends identical to those in the main figure (**Fig. R3**), demonstrating that all relative activity differences and overall conclusions are robust and unaffected. In summary, the choice to retain uncompensated data in the main figure ensures comparability with the polymer-coating strategy, while the *iR*-compensated data confirm that none of our conclusions depend on uncompensated resistance artifacts.

According to your valuable suggestion, we have provided a detailed clarification of using uncompensated data for better understanding. The detailed explanation has been added on Page 8 in our revised manuscript, as shown below.

"Uncompensated potentials are presented to facilitate direct comparison with polymer coating strategy, because in practical applications ohmic loss is an important issue."

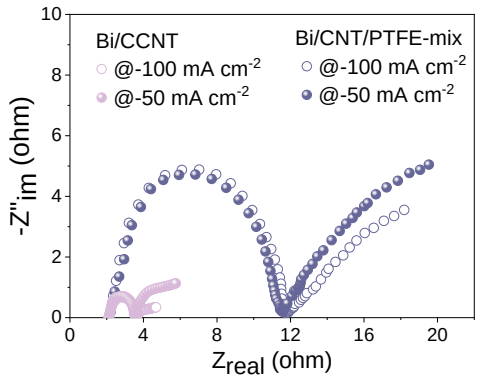


Figure R2. Electrochemical impedance spectroscopy (EIS) measurements of Bi/CCNT and Bi/CNT/PTFE-mix at different current densities.

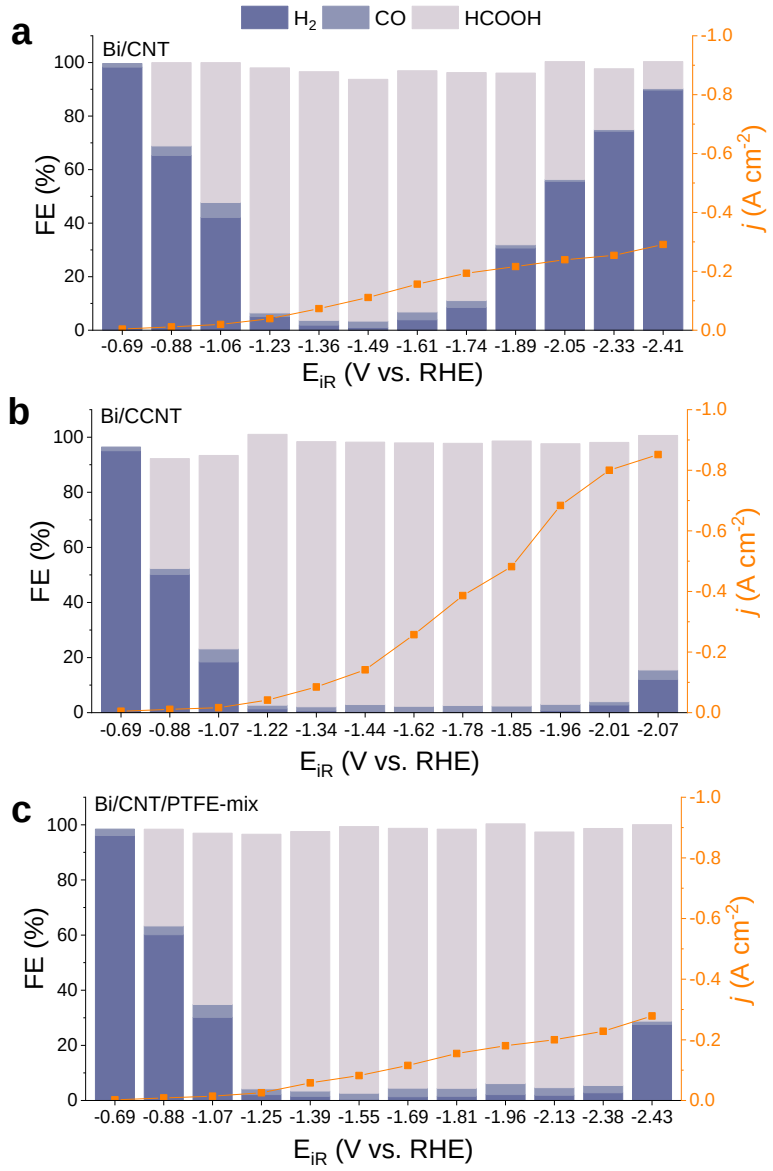


Figure R3. Total current density and Faradaic efficiency (FE) values of CO_2RR products for (a) Bi/CNT, (b) Bi/CCNT and (c) Bi/CNT/PTFE-mix at *iR*-compensated potentials.

Comment 5.2: The authors attributed the poor stability of Bi/CNT in acidic $N(CH_3)_4Cl$ to electrode flooding, yet this raises a fundamental question. Flooding is an inherent property of porous CNTs (J. Am. Chem. Soc. 2024, 146, 16348), how cation modification suddenly mitigates this intrinsic mass transport problem? Since stability is a key claim of this study, the authors should provide specific evidence and explanation for this underlying mechanism.

Response: We sincerely thank you for this insightful question. We fully acknowledge that flooding is indeed an intrinsic challenge for CoPc-NH_2/CNT to reduce CO_2 into methanol (*J. Am. Chem. Soc.* 2024, 146, 16348-16354). We appreciate the opportunity to clarify how cation modification can mitigate this problem.

Our water contact angle measurements reveal that all types of cationic CNTs (CCNTs) exhibit stronger hydrophobicity than pristine CNTs, attributable to the introduction of long alkyl chains (**Fig. R4**). The

enhanced hydrophobicity of CCNTs directly suppresses excessive electrolyte intrusion into the catalyst layer. In unmodified Bi/CNT composites, the insufficient hydrophobicity leads to uncontrolled water flooding, which obstructs gas diffusion pathway for CO_2 and destabilizes the three-phase boundary. By contrast, the grafted long alkyl chains render the CCNTs more hydrophobic, effectively limiting water penetration while preserving the delicate balance of the three-phase interface during prolonged electrolysis.

Notably, in this work (*J. Am. Chem. Soc.* 2024, 146, 16348-16354), the used CNTs underwent two purification steps, air calcination and acid washing, which inevitably lead to a decrease in the hydrophobicity of CNTs and may even render the CNTs hydrophilic. This likely explains why the CoPc-NH_2/CNT electrode in that work is particularly susceptible to flooding.

In summary, the increased hydrophobicity of CCNTs, confirmed by water contact angle data, serves as the primary mechanism mitigating the intrinsic flooding issue.

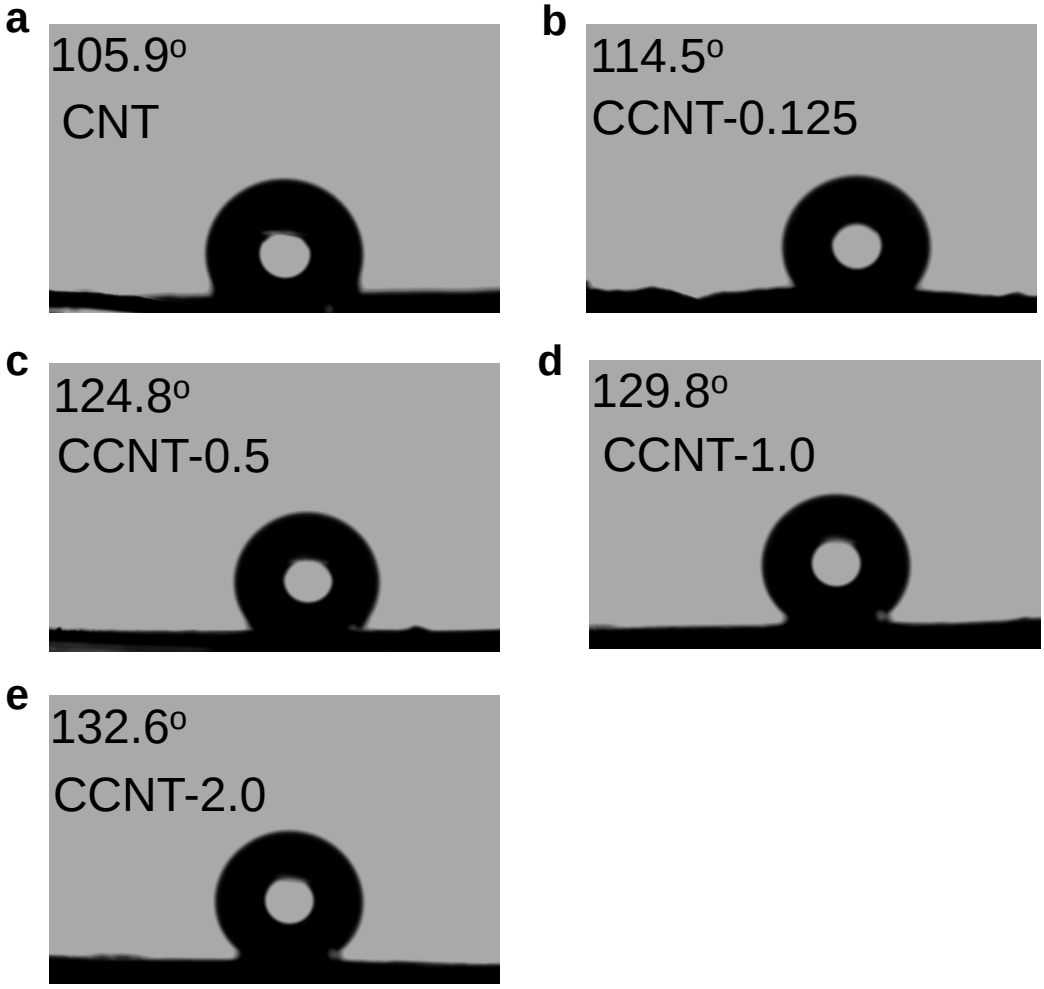


Figure R4. Water contact angle measurements for (a) CNT, (b) CCNT-0.125, (c) CCNT-0.5, (d) CCNT-1.0 and (e) CCNT-2.0.

Comment 5.3: In the RDE studies, the authors observed suppressed HER current density on CCNTs in the kinetic-limited regime, yet attempted to justify this using decreased H^+ diffusion. The interpretation of HER suppression is conceptually inconsistent. Additionally, the negligible difference in diffusion coefficients between CNTs and CCNTs cannot explain the significant HER activity difference, even in the mixed kinetic-mass transport regime. This confusion between fundamental surface kinetics and diffusion processes

undermines the core mechanistic claims of the work.

Response: We sincerely thank you for this insightful comment regarding the RDE study. As presented in our original manuscript, the Levich analysis yields an approximately 5% decrease in the diffusion coefficient of hydronium ions for CCNT-2.0 versus CNT, and the Koutecký-Levich equations:

$$\frac{1}{j_{tot}} = \frac{1}{j_k} + \frac{1}{j_{plateau}}$$

where j_{tot} is the total current density, j_k is the kinetic current density and $j_{plateau}$ is the diffusion limiting current density, reveals a fourfold decrease in the kinetic current density (from 796 mA cm^{-2} for CNT to 186 mA cm^{-2} for CCNT-2.0, **Fig. R5**). These quantitative results, already included in the manuscript, firmly establish that the pronounced difference in the kinetic current density between CNTs and CCNTs leads to the significant HER activity difference. Our data firmly establishes that the activity difference is kinetic in origin. The significantly suppressed kinetic current density points to a surface-level kinetic effect, consistent with hindered access of H_3O^+ to the active sites, for example via electrostatic repulsion or steric blocking by the quaternary ammonium groups with long alkyl chains at the electrode-electrolyte interface.

Note that the diffusion limiting current strongly depends on the interface properties. For molecular modified surface, since it differs at the length of carbon chain (a few angstrom), it is expected that the diffusion limiting current will be close to each other. This is different from the polymer coating method, as reported in *Angew. Chem. Int. Ed.* 62, e202216102 (2023). The diffusion limiting current can have a significant variation due to the much thicker coating (tens to hundreds nanometer) that retards proton transfer in the diffusion layer.

Following your valuable suggestion, we have added a corresponding discussion to ensure that our interpretation is fully consistent with this kinetic origin. We greatly appreciate this comment, which has helped us improve the clarity and rigor of our presentation. The detailed discussion has been added on Page 16 in our revised manuscript, as shown below.

"These quantitative results firmly establish that the difference in HER activity between CNTs and CCNTs arises from a suppressed j_k due to the molecular surface modification, and is not attributable to a mass transport effect in the diffusion layer, as the $j_{plateau}$ does not differ significantly."

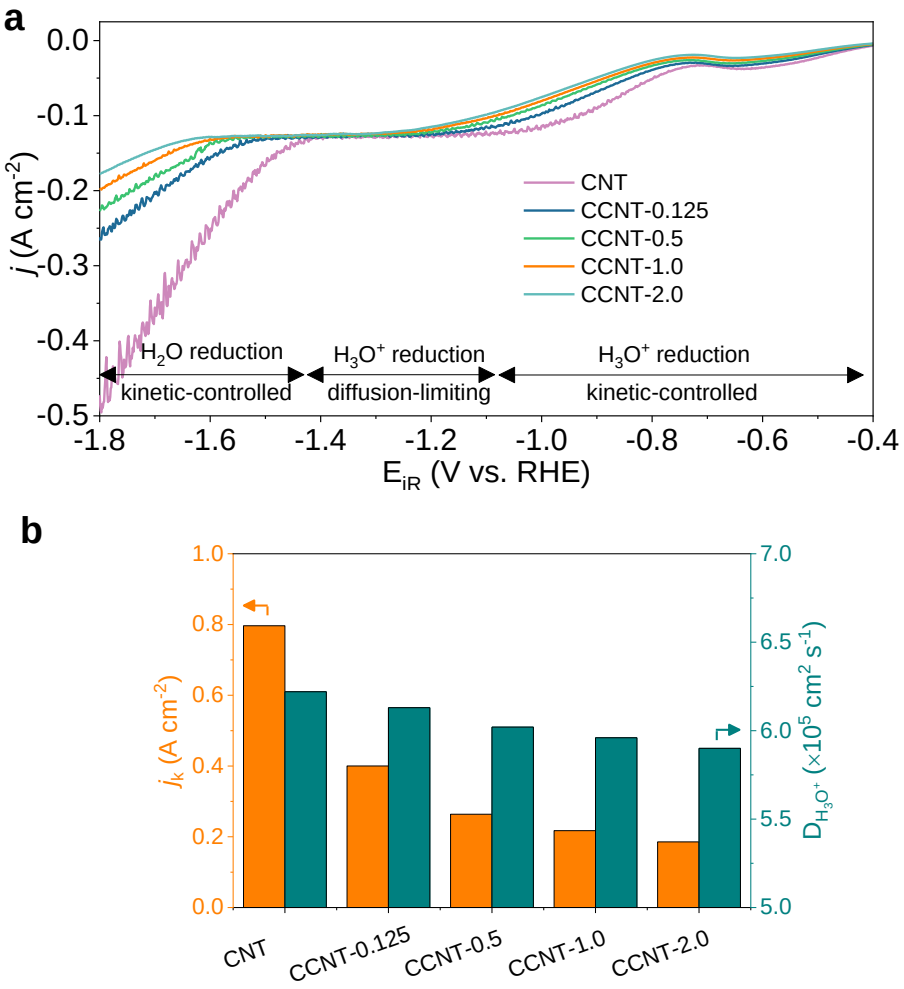


Figure R5. (a) Rotating-disk electrode voltammetry in Ar-saturated 0.05 M H_2SO_4 + 0.5 M K_2SO_4 at 1200 rpm, (b) Kinetic current density of HER and diffusion coefficient of hydronium calculated from Koutecký-Levich equations at -1.0 V_{iR}.

Comment 5.4: The authors proposed an electric field mechanism to explain enhanced CO_2RR and suppressed HER, yet supporting evidence such as detection of the local electric field at electrochemical interface is missing. Importantly, as the CCNTs and metal catalysts are only physically mixed, it is unclear how an electric field localized on CNTs effectively modulates spatially separated metal active sites. Without clarifying this interaction, the proposed mechanism remains speculative.

Response: We sincerely thank you for this incisive and critical comment, which rightly questions the heart of our mechanism proposal, how an electric field generated on CCNTs can effectively modulate spatially separated metal active sites in a physically mixed system. We appreciate this valuable opportunity to clarify this crucial point and strengthen our arguments.

We respectfully clarify that our proposed mechanism operates through a cooperative interfacial modulation effect within the microenvironment between electrolyte and electrode. The CCNTs and metal catalysts are physically mixed in the catalyst layer in nanoscale proximity (**Fig. R6**). Under these conditions, a unified, synergistic interfacial electrostatic microenvironment is created. The CCNTs act as dispersed 'electrostatic modulator', and the metal active sites experience this collectively altered microenvironment.

Crucially, already in our original manuscript, we provide direct experimental support for this cooperative

modulation through zeta potential measurements (**Fig. R7**). The pristine CNTs exhibit a strongly negative zeta potential of -40.4 mV, whereas CCNT-2.0 shows a highly positive value of +51.2 mV, a net shift exceeding 90 mV. The complete series confirms the systematic and tunable cationic nature of the modified CNTs. This dramatic reversal in surface charge demonstrates that the quaternary ammonium groups fundamentally alter the electrostatic character of the solid-liquid interface. In a physically mixed catalyst layer, the metal active sites necessarily reside within an interfacial microenvironment whose ionic composition and potential distribution are strongly influenced by the cationic CCNTs. The electric field is therefore not a signal "transmitted" from one particle to another over distance, but a collective interfacial property to which the CCNTs impart a strong positive electrostatic baseline.

Also, this interpretation is further corroborated by multiple independent lines of evidence.

1) RDE kinetics (**Response 5.3**). The fourfold suppression of kinetic current density for HER on CCNTs confirms that the cationic and hydrophobic surface strongly reduce the abundance of H_3O^+. In the mixed system, this creates a proton-deficient local environment near the metal active sites, suppressing HER while favoring CO_2RR.

2) Systematic selectivity tuning. The product selectivity and current density increase monotonically with the zeta potential of CCNT, while HER is progressively suppressed (**Fig. R8**). This compositional dependence is a hallmark of an interfacial modulating effect and aligns perfectly with the zeta potential trend.

3) Literature precedent. This concept of physically mixed modulator/catalyst has been reported by several studies[15-19]. Seminal work by Strasser et al. (using PTFE to suppress HER on the Ni-N-C catalyst)[17] and Wei et al. (using biopolymer coatings on Cu nanoparticles to achieve 90% C_{2+} FE)[19] both demonstrate that physical additives can effectively re-engineer the local microenvironment of a catalyst.

We believe our experimental data, from interfacial charge (zeta potential) to functional outcome (RDE kinetics) to systematic performance tuning, provides a robust foundation for our proposed cooperative interfacial modulation mechanism. We are grateful to the reviewer for raising this point, which has allowed us to significantly clarify and strengthen our argument.

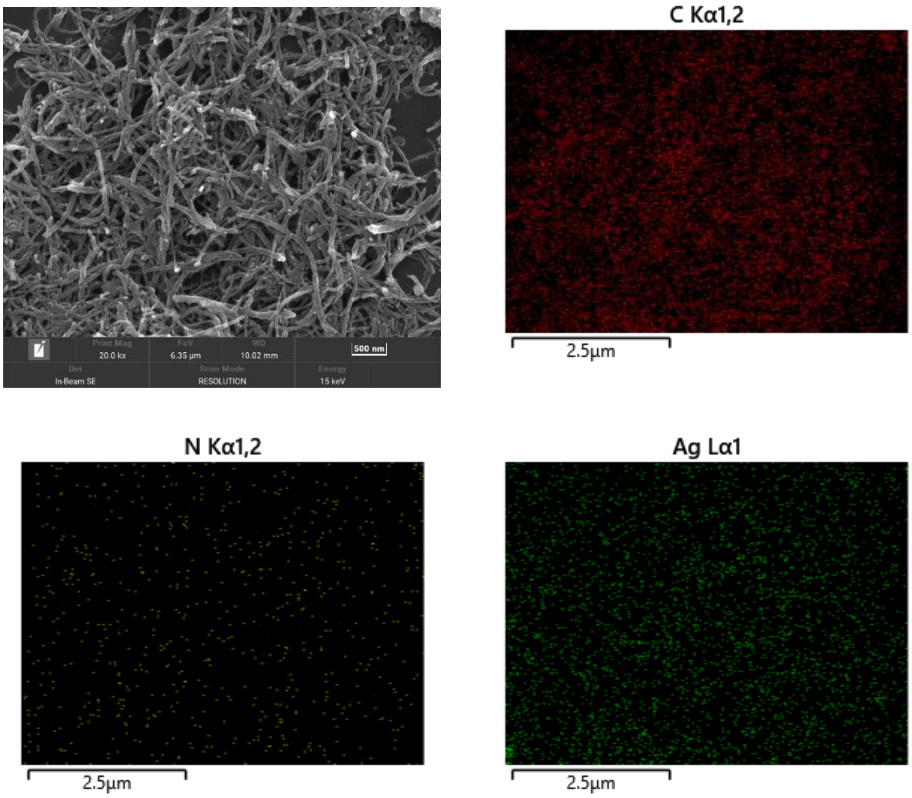


Figure R6. EDS mapping of Ag/CCNT.

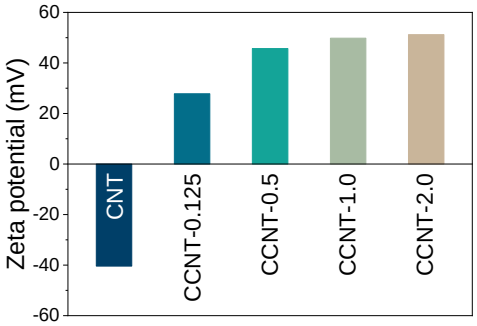


Figure R7. Zeta potential of pristine CNTs, CCNT-n (n=0.125, 0.5, 1.0, 2.0).

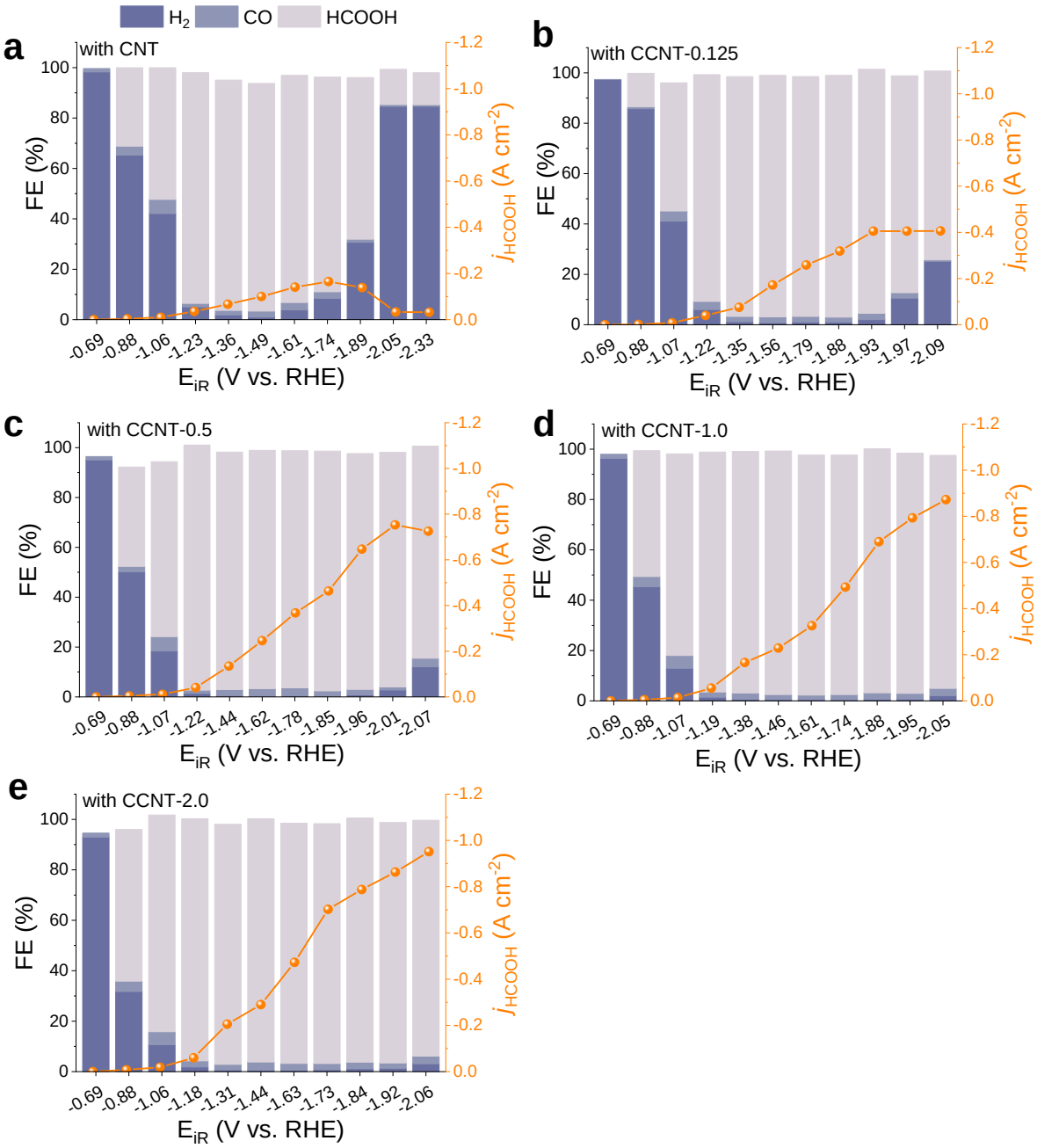


Figure R8. FE values and partial current density curves for (a) Bi/CNT, (b) Bi/CCNT-0.125, (c) Bi/CCNT-0.5, (d) Bi/CCNT-1.0 and (e) Bi/CCNT-2.0.

To Reviewer #6

General Comment: The authors have adequately addressed the concerns regarding the theoretical explanation, and the computational details that separating the roles of DFT (providing accurate electrostatics via ESP charges) and classical MD (capturing long-timescale CO_2 mass transport) have added to the revised manuscript, confirming that the key conclusions are governed by the DFT-derived charges, reducing the sensitivity to the specific choice of force-field parameters, and thus robust enough for the current study.

Response: We sincerely thank you so much for your constructive suggestions, which have helped improve the quality of our manuscript. We are also grateful for your recognition of our efforts and for the valuable time and support provided throughout the review process.

References

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