Promoting CO$_2$ electroreduction on CuO nanowires with a hydrophobic Nafion overlayer†

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Copper-based materials could produce a series of products through the CO$_2$ electroreduction reaction, and are regarded as the most promising catalysts to produce fuels and value-added chemicals using renewable energy sources. However, the competitive hydrogen evolution reaction (HER) is a daunting challenge for the selectivity of carbonaceous products. Here, a hydrophobic electrode surface was constructed by modifying the CuO nanowire electrode with a thick Nafion overlayer, which exhibited enhanced selectivity toward the CO$_2$ RR (especially for CO) and suppressed HER activity. This work highlights the importance of hydrophobicity in the selectivity of CO$_2$ reduction and hints at the additional role of Nafion in powder-based catalyst electrodes.

Introduction

The electrochemical CO$_2$ reduction reaction (CO$_2$ RR) to fuels and value-added chemicals offers a promising approach for renewable energy storage and promotes the closing of the anthropogenic carbon cycle. A key challenge to commercialize this process is developing catalyst electrodes with high efficiency, high selectivity and stability. Among all the metals explored to date, copper (Cu) holds a unique position due to its special electronic properties which enable moderate bonding to the intermediates, leading to up to 16 different products toward aqueous CO$_2$ electro-reduction (12 of them are C$_2+$ species). Thus, various strategies were employed to further enhance the intrinsic catalytic activity of Cu, such as defect engineering (grain boundary, steps, and vacancy), strain modulation, faceting, morphology control, bimetallic catalysts, crystal phase control and molecular modification.

Despite significant efforts in improving the activity, the electrocatalytic performance of Cu in aqueous CO$_2$ electro-reduction remains less than satisfactory. One of the reasons is the low solubility of CO$_2$ in aqueous electrolyte, which impedes the transport of CO$_2$ to active sites while facilitating the competing hydrogen evolution reaction (HER). Therefore, increasing the concentration of CO$_2$ or the accessibility of CO$_2$ around the active sites while suppressing the supply of water (protons) would be a feasible approach to enhance the CO$_2$ RR performance. Previously reported works employed different approaches to enhance the local concentration of CO$_2$ around active sites, such as testing under high pressure, employing organic solvents, and loading catalysts onto the gas diffusion layer (GDL). Additionally, the HER was suppressed by modifying the catalysts with a hydrophobic overlayer or organic molecules. For instance, highly suppressed HER activity and a drastic increase of CO$_2$ RR selectivity were achieved on the Cu nanodendrite modified with a bio-inspired hydrophobic coating, which was assigned to the trapped gaseous CO$_2$ at the triple-phase boundary, making the CO$_2$ mass transport omnidirectional. Furthermore, an aerophilic and hydrophobic Cu nanoarray was constructed by polytetrafluoroethylene (PTFE) modification. As a result, the CO$_2$ adsorption was promoted, while the supply of protons was limited, which led to enhanced selectivity for C$_1$ products. Similarly, hydrophobic PTFE treated Cu nanoneedles (Cu NNs) achieved highly suppressed HER activity and high selectivity for C$_2$ products.

Inspired by previous works, we accidentally found that a Nafion overlayer, a sulfonated fluoropolymer which has been widely used as an organic binder or a proton exchange membrane, could form a uniform overlayer on the CuO nanowire electrode and endow it with hydrophobicity. The obtained hydrophobic electrode (CuO-Nafion) exhibited enhanced CO$_2$ RR selectivity and suppressed HER activity compared to the bare CuO nanowire electrode.

Experimental

CuO-Nafion nanowire electrode preparation and characterization

The CuO nanowire electrode was prepared by anodizing a clean Cu mesh substrate at a current density of 10 mA cm$^{-2}$ in
3 M KOH for 600 s, followed by thermal annealing at 180 °C in air for 60 minutes.26 To prepare the Nafion modified electrode, 40 µL of ethanolic dispersion of Nafion (20, 60, and 180 µL in 1 mL ethanol) was carefully dropcast onto both sides of the CuO nanowire electrode (10 × 10 mm) twice (Fig. 1). Finally, the obtained CuO-Nafion nanowire electrode was dried in a vacuum oven at 60 °C overnight. The as-prepared samples were labelled as CuO-Nafion-x, where x is the volume of Nafion added in the ethanol, and CuO-Nafion-60 was selected as a representative of all the CuO-Nafion-x electrodes. The untreated CuO nanowire was used as a control sample.

Powder X-ray diffraction (XRD) measurements confirm that the crystalline phase of the sample before Nafion modification is CuO26 (PDF#80-0076) mixed with a small amount of Cu2O (PDF#78-2076), which might result from the diffusion of Cu atoms from the substrate into CuO during the annealing process (Fig. 2a).27 After Nafion modification, the crystalline phase and the structure of the sample remain unchanged. The three strong peaks flagged by “♣” correspond to the Cu substrate.28 The electronic states of elements in the CuO-Nafion-60 nanowire and pristine CuO nanowire were analyzed by X-ray photoelectron spectroscopy (XPS, Fig. 2b–f). The Cu valence state in CuO-Nafion-60 is very similar to that in CuO, where the main Cu 2P3/2 peaks and 2P1/2 peaks accompanied by strong satellites can be uniquely ascribed to divalent Cu26 (Fig. 2b). The absence of Cu+, showed in the XRD pattern, might be due to the depth detection limitation of XPS.26 The O 1s spectra of both CuO-Nafion-60 and CuO show two bands in the binding energy region of 532–528 eV, which could be assigned to the O–H bond and O–Cu bond.24 Uniquely, the CuO-Nafion-60 electrode shows a band centered at 535.25 eV, which could be ascribed to the oxgens in –SO3 (Fig. 2c).29 Similar phenomena were observed in the fine spectra of F 1s, S 1s and C 1s, respectively (Fig. 2c–f).29 All the above results demonstrate the successful preparation of the CuO-Nafion electrode.

Scanning electron microscopy (SEM) images (Fig. 3a, b and Fig. S1, S2†) of all the CuO-Nafion electrodes show a similar morphology compared with that of the bare CuO nanowire sample (Fig. S3†). Transmission electron microscopy (TEM) images reveal a continuous and semi-transparent overlayer coating on the surface of the CuO-Nafion-60 nanowire (Fig. 3c and Fig. S4†), demonstrating the uniform coating of Nafion. Elemental mapping analysis from TEM shows that F, S and C, the characteristic elements in Nafion, are homogeneously distributed on the surface of Cu, especially C, further demonstrating the uniform coverage of Nafion on the CuO nanowire (Fig. 3d–j). Thanks to the good wettability of ethanol to CuO, Nafion could distribute along the CuO nanoforest from the top to bottom, demonstrated by the uniform distribution of F, S, and C elements in cross-section elemental mapping analysis from SEM (Fig. S5†). The homogeneous coverage of Nafion over the nanowire surface is critical to the hydrophobicity. Contact angle measurements illustrated that the CuO-Nafion-60 surface is hydrophobic with a contact angle of 145.61° (inset in Fig. 3a, Movie S1†). A similar hydrophobic phenomenon also appeared in the other CuO-Nafion electrodes (Fig. S6†). In contrast, the pristine CuO nanowire is hydrophilic, and the solution permeates the nanoarray readily upon dropping on the surface (Movie S2†).

The electrodes were first activated before the CO2 RR via a pre-reduction process and were further characterized. For convenience, the CuO-Nafion-x and CuO electrodes after pre-reduction were labelled as R-CuO-Nafion-x and R-CuO, respectively. Both the XRD patterns and fine XPS spectra showed that the CuO in CuO-Nafion-60 was reduced to metallic Cu after pre-reduction (Fig. 4a and b).9 The negligible peaks of CuO (Cu2+) in the fine XPS spectra of Cu 2p (Fig. 4b) might be resulted from the inevitable oxidation in air during the electrode transfer process.28 A similar phenomenon also occurred in the bare R-CuO electrode (Fig. S7†). The combined results from the fine spectra of O 1s, F 1s, S 1s and C 1s clearly...
demonstrated the existence of Nafion in the pre-reduced electrode (Fig. 4c–f).

SEM images show that the R-CuO-Nafion-60 and R-CuO electrodes maintained the nanowire morphology, but abundant nanoparticles appeared on the surface of the nanowire, making the surface much rougher than before (Fig. 5a, b and Fig. S8, S9†), which might be resulted from the reduction of the volume of the crystal30 and the formation of grain boundaries (GB) during the electroreduction process according to previous literature reports.7 The intact and uniform coverage of Nafion on R-CuO-Nafion-60 is evidenced by the TEM image, which shows that the nanowire surface is covered by a semi-transparent thin film, demonstrating the retention of the Nafion overlayer after pre-reduction (Fig. 5c). Elemental mapping of TEM reveals the homogeneous distribution of Cu, O, F, S and C, while O, F, S and C prevail at the outside surface (Fig. 5d–j), further demonstrating that the nanowire was covered by a Nafion layer. The appearance of carbonaceous nanoparticles on the nanowire surface of R-CuO-Nafion-60 revealed by the TEM elemental mapping (Fig. 5g–j) was supposedly caused by the partial aggregation of Nafion during pre-reduction, which is similar to a previous report.13 Nevertheless, the uniform coating of Nafion on the R-CuO-Nafion nanowires after pre-reduction is undeniable, which is further proved by SEM cross-section elemental mapping analysis (Fig. S10†), in which the elements of Cu, O, F, S and C are distributed along the nanoforest from the top to bottom. Consistent with the CuO-Nafion-60 sample, the R-CuO-Nafion-60 sample retains good hydrophobicity with a contact angle of 127.11° (inset in Fig. 5a). In comparison, the CuO electrode shows an absolute hydrophilicity from the beginning to the end.

**Results**

**Evaluation of CO₂ electroreduction performance**

The faradaic efficiencies (FEs) of various products were evaluated quantitatively by chronoamperometry measurements (CA) under different potentials coupled with online gas chromatography (GC) and offline high-performance liquid chromatography (HPLC) analysis. Consistent with previous literature reports,24,26 the R-CuO electrode presents an FE of around 40% for H₂ in the whole tested potential range, indicating a high concentration of the Cu–H species located at the surface of R-CuO. With the negative shift of the test potential, the FEs of C₂+ products (C₂H₄, C₂H₅OH, (CH₃)₂CO and n-C₃H₇OH) increase, accompanied by the decrease of CO gradually (from 8.72 to 3.13%), indicating that CO is a key intermediate in the formation of C₂+ products (Fig. 6a and Table S1†). In comparison, the HER on the R-CuO-Nafion-60 electrode was suppressed, with FEs around 30% over the tested potential range, and the FE of carbonaceous products increased to 70%. Interestingly, the FE of CO increased dramatically and peaked at −1.3 V vs. RHE with an FE of 33%. Nevertheless, the FE of the C₂+ products only slightly decreased (Fig. 6b and Table S2†). CuO nanowires coated with different thicknesses of Nafion were prepared to further identify the suppression of HER activity on the hydrophobic surface. As a result, both thinner and thicker Nafion overlayers provide good hydrophobicity to the CuO-Nafion nanowire (Fig. S6†). As for product distribution on (a) the R-CuO nanowire electrode and (b) the R-CuO-Nafion-60 nanowire electrode under different working potentials. (c) FE for H₂ and CO on CuO nanowires modified with different thicknesses of the Nafion overlayer under −1.3 V (left) and −2.0 V vs. RHE (right). 0 means the bare CuO nanowires. (d) Stability test of the R-CuO-Nafion-60 electrode at −1.3 V vs. RHE.
distribution, it is clear that the HER was suppressed on thick Nafion modified electrodes (R-CuO-Nafion-60 and R-CuO-Nafion-180). Interestingly, the HER was enhanced on the thin Nafion modified electrode under both potentials (R-CuO-Nafion-20, Fig. 6c and Fig. S11†). The FE of CO increased monotonically under both potentials, and even reached 43.15% on the R-CuO-Nafion-180 electrode at $-1.3 \, \text{V vs. RHE}$ (Fig. 6c and Fig. S12†), which is comparable to previous CuO nanostructure-based electrodes for CO production (Table S3†). Extended CO2 reduction on the R-CuO-Nafion-60 electrode over 10 h at $-1.3 \, \text{V vs. RHE}$ showed a stable current density around 25 mA cm$^{-2}$, accompanied by a stable production of CO and H2 with FEs around 32% and 27%, respectively (Fig. 6d).

### Discussion

Nafion is widely used as an effective binder in electrode preparation for powder-based electrocatalysts, and is believed to have no influence on the CO2 RR activity and selectivity.$^{9,12,14}$ However, recent Cu electrodes covered with Nafion overlayers showed a high FE of 88% for CH4 production, which was attributed to the stabilization of the CO intermediate by the Nafion overlayer.$^{31}$ In this work, we find that the Nafion overlayer could change the hydrophilicity of the CuO nanowire, which also enhances the CO2 RR performance by suppressing the HER activity on a thick overlayer.

Nafion consists of a hydrophobic PTFE backbone and side chains terminated by strongly acidic hydrophilic sulfonic acid groups (–SO3) (Fig. S13†), and the sulfonic acid groups endow Nafion with proton conductivity.$^{31,32}$ In this work, the R-CuO-Nafion-60 and R-CuO-Nafion-180 electrodes showed suppressed HER activity compared with the R-CuO electrode, indicating that the –SO3 group of Nafion absorbed on CuO nanowires while the hydrophobic PTFE backbone was exposed to the electrolyte, resulting in a highly hydrophobic electrode (Fig. 1 and 7). Therefore, the transport of protons was limited, but the transport of CO2 was not affected. Consequently, the selectivity of carbonaceous products was enhanced compared with that of the bare R-CuO electrode. We also note that most of the Cu surface of R-CuO-Nafion-60 is still electrochemically accessible, demonstrated by nearly the same double-layer capacitance ($C_{dl}$, represents the electrochemical surface area) (Fig. S14†) and linear sweep voltammograms (Fig. S15†) before and after Nafion modification. For the R-CuO-Nafion-20 electrode, both H2 and CO were enhanced compared with those of the bare CuO nanowire electrode, which may be caused by the excessive exposure of –SO3 to the electrolyte in the thin Nafion overlayer rather than being absorbed on CuO nanowires. In this case, proton conductivity was liberated, and the hydrophobic effect played a minor role.

In terms of product distribution, it is obvious that the HER was suppressed, while the CO2 RR was enhanced after thick Nafion modification (R-CuO-Nafion-60 and R-CuO-Nafion-180). In detail, CO was greatly promoted among all the carbonaceous products, accompanied by a slight increase of HCOOH. It is reasonable since the production of CO and HCOOH only involves the transfer of two electrons coupled with two protons.$^{31,14}$ When the supply of protons becomes insufficient due to the hydrophobic Nafion modification, the *CO intermediate formed on the surface of Cu tend to desorb and release as the gaseous CO product rather than undergoing further hydrogenation or C-C coupling. Thus, the CO formation was kinetically enhanced (Fig. 7). The increased production of HCOOH could be explained by a similar pathway; also, it has been reported that a hydrophobic/aerophilic surface is favourable for the desorption of liquid products,$^{24}$ which might give rise to the enhancement of FE for formate to some extent. As for the C2 products, it is not surprising that their FEs decreased more or less after thick Nafion modification. Firstly, the production of C2 products needs more protons (12 for CH3OH and CH3OH, 14 for CH3OH, 16 for (CH3)2CO and 18 for CH3(CH2)OH)$^{3,5}$ When the supply of protons is insufficient, their productivity would decrease theoretically. Secondly, *CO is the upstream intermediate for the production of C2 products,$^{15,18}$ when most of it was released as a gaseous product (CO), the FE for C2 products would decrease consequently.

### Conclusions

In summary, a hydrophobic surface was constructed on the CuO nanowire electrode with a thick Nafion modification. After the hydrophobic treatment, the electrode showed suppressed HER activity and enhanced CO2 RR performance, which was mainly ascribed to the limited proton transfer. Especially for CO production, its FE increased from 8.72% to 43.15% at $-1.3 \, \text{V vs. RHE}$. This work highlights that Nafion could make an electrode hydrophobic, and promote the CO2 RR performance. The hydrophobic surface treatment is a facile but efficient pathway to promote the performance of the CO2 RR.

### Author contributions

M. Wang performed all of the experiments and wrote the manuscript. M. Wang and J. Luo analysed the experimental...
data. L. Wan helped revise the manuscript. J. Luo guided the study and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


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