Accepted Article

Title: Self-Cleaning Catalyst Electrodes for Stabilized CO2 Reduction to Hydrocarbons

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CO₂ Reduction

Self-Cleaning Catalyst Electrodes for Stabilized CO₂ Reduction to Hydrocarbons

Zhe Weng, Xing Zhang, Yuesheng Wu, Shengjuan Huo, Jianbing Jiang, Wen Liu, Guanjie He, Yongye Liang,* Hailiang Wang*

Abstract: *Utilizing clean and renewable energy for electrochemical conversion of CO₂ to fuels and chemical products is a promising pathway towards zero emissions. While Cu metal catalysts have received substantial attention due to their distinct capabilities to catalyze CO₂ electroreduction to hydrocarbons, they still suffer from fast deactivation. Developing a Cu electrocatalyst with long-term catalytic durability for CO₂ reduction remains a big challenge. In this work, we report a surface-restructuring strategy for realizing self-cleaning Cu catalyst electrodes with unprecedented catalytic stability toward CO₂ reduction. Under the working conditions, the Pd atoms pre-deposited on Cu surface induce continuous morphological and compositional restructuring of the Cu surface, which constantly refreshes the catalyst surface and thus maintains the catalytic properties for CO₂ reduction to hydrocarbons. Our Pd-decorated Cu electrode can catalyze CO₂ reduction with relatively stable selectivity and current density for up to 16 h, representing one of the best catalytic durability performances among all Cu electrocatalysts for effective CO₂ conversion to hydrocarbons. The generality of this approach of utilizing foreign metal atoms to induce surface restructuring toward stabilizing Cu catalyst electrodes for CO₂ reduction is further demonstrated by replacing Pd with Rh.*

The rise in CO₂ emissions caused by burning fossil fuels poses considerable risks to the environment and climate as well as all living creatures on the earth.[1] Utilizing clean and renewable energy for electrochemical conversion of CO₂ to fuels and chemical products is considered a promising pathway toward zero emissions.[1a, 2] Many electrocatalysts including solid-state materials and molecular complexes have been extensively investigated for CO₂ reduction

reactions.[2a, 3] Among all the materials studied, Cu metal has received substantial attention due to its distinct ability to generate reasonable amounts of hydrocarbon products,[4] which requires addition of multiple electrons and protons to a CO₂ molecule and C-C bond formation. In the past several decades, a number of strategies have been developed to increase the activity and selectivity of Cu catalysts including shape control,[5] alloying,[6] surface modification[7] and oxidative treatment.[8] However, fast deactivation remains as a major problem for metallic Cu catalysts.[5f, 9]

While there have been numerous reports on observation of fast decay in CO₂ reduction to hydrocarbons and simultaneous rapid dominance by H₂ evolution for Cu electrodes,[9-10] the deactivation mechanism is still under debate. One perspective is that the deactivation is caused by cathodic deposition of metal ion impurities in the electrolyte.[10a] It has been suggested that the metal ion impurities can be removed by purifying the electrolyte solution via pre-electrolysis[10a] or metal ion complexation,[9b] which is able to maintain the product selectivity for up to 2 h. Nevertheless, other studies find that pre-treatment of electrolyte has little improvement in suppressing Cu catalyst deactivation.[10b, 10d, 11] Instead, surface analysis reveals that accumulation of carbonaceous species may be the main reason for catalyst poisoning.[9a, 9c, 10b-d] Possible approaches to tackle this problem include controlling reaction pathways of electrochemical CO₂ reduction to avoid decomposition of reaction intermediates and thus carbon accumulation on Cu surface, or applying a periodic carbon-removing method to clean the catalyst surface. The former has been demonstrated by altering local pH to lower selectivity for methane,[9a, 12] although challenges still remain because the mechanisms of CO₂ electroreduction on Cu are not yet well understood. The latter has been practically enabled by applying oxidative pulses but requires considerable modification and intervention on the reactor level.[10c, 10d] Developing a Cu electrocatalyst with long-term catalytic durability for CO₂ reduction remains a big challenge.

Here we report the discovery of a general strategy for creating self-cleaning Cu electrocatalysts with substantially improved stability for CO₂ reduction. We first verify that plain Cu surface deactivates quickly under the working conditions. The Faradaic efficiency (FE) for CO₂ reduction to hydrocarbons (methane and ethylene) decreases from 56% to 13% within 2 h, while that for H₂ evolution increases from 30% to 80%. The deactivation process is accompanied with increasing coverage of carbonaceous species on the catalyst surface. We then find that the selectivity for CO₂ reduction can be stabilized by pre-decorating the Cu surface with Pd atoms. Our Pd-decorated Cu electrode retains FE (H₂) below 40% and FE (CH₄+C₂H₄) above 50% during 4 h of continuous electrolysis, achieving one of the most durable Cu-metal-based electrocatalysts with high efficiency for CO₂ conversion to hydrocarbons. Under the working conditions, the Pd decoration induces morphological and compositional restructuring of the catalyst surface to form nanoparticles with Cu-rich surface, which refreshes the Cu surface and thus maintains stable electrocatalytic CO₂ reduction. We further find that other noble metals such as Rh can

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perform similar functionalities as Pd. This work presents foreign-metal-induced surface restructuring as an effective approach to stabilizing Cu for electrocatalytic CO_2 reduction.
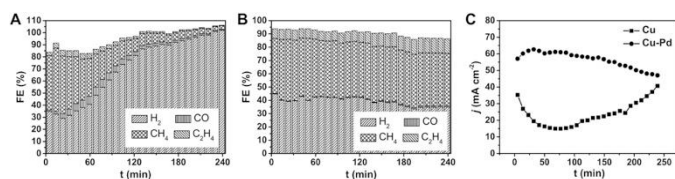

Figure 1. Distributions of gas products as the CO_2 reduction electrocatalysis proceeds on (A) Cu electrode and (B) Pd-decorated Cu electrode, and (C) their time-dependent total current densities at –0.96 V vs RHE in CO_2-saturated 0.5 M $KHCO_3$.

Pre-cleaned Cu mesh electrodes were first examined for electrocatalytic CO_2 reduction in pre-purified 0.5 M aqueous $KHCO_3$ electrolyte under a constant electrode potential of –0.96 V vs the reversible hydrogen electrode (RHE). While the gas products were measured by an on-line gas chromatograph (GC) with an interval of 9 min during electrolysis, the products in the liquid phase were analyzed by ^1H nuclear magnetic resonance (NMR) spectroscopy after the entire electrolysis (Figure S1). Since the liquid products can only be quantified in a time-averaged format and the electrodes exhibit highest hydrocarbon selectivity at –0.96 V vs RHE (Figure S2), our discussion of catalyst deactivation will be based on gas products generated at –0.96 V. The initial gas products generated on the Cu electrode are CH_4, CO, C_2H_4 and H_2 (Figure 1A). All the gaseous CO_2 reduction products account for a total FE of ~50%, among which CH_4 is the dominant product. The initial FE for H_2 evolution is ~30%. Similar to the previous studies,[9c, 10b-d, 11] we observe fast deactivation for the Cu electrode. The CH_4 yield starts to drop rapidly while the FE for H_2 drastically increases after 24 min. After 2 h, FE (CH_4) and FE (C_2H_4) have decreased to 11% and 2% respectively, while FE (H_2) has increased to 80%. The Cu catalyst loses almost all of its catalytic activity for CO_2 reduction after 4 h, with the H_2 evolution reaction consuming ~100% of the current density. Figure 1C shows the evolution of current density as the electrolysis proceeds. The decrease in current density during the first hour is ascribed to loss of electrochemical active surface area (Figure S3 and Table S1). After that, the current density starts to increase depite that the surface area continues to decrease, likely due to increased catalytic activity for H_2 evolution.
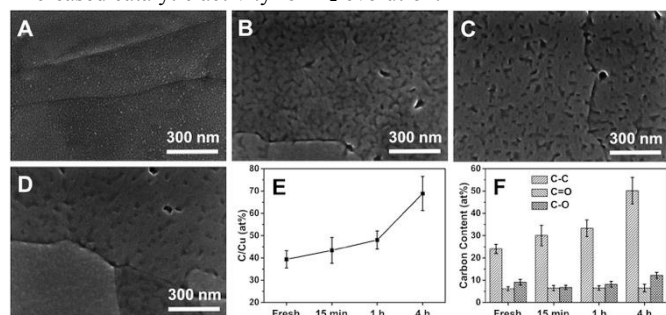

Figure 2. SEM images of (A) a fresh Cu electrode and Cu electrodes having performed electrocatalysis for (B) 15 min, (C) 1 h and (D) 4 h. (E) Surface C/Cu atomic ratios and (F) further breakdown of the C content for the fresh and used Cu electrodes.

We employ scanning electron microscopy (SEM) to image the surface morphology of the Cu electrodes after they experience different amounts of time of electrolysis (Figure 2A-D, S4). The fresh Cu electrode has a relatively smooth surface with an average particle size of ~10 nm (Figures 2A, S4A). After performing electrocatalysis

for 15 min, the surface exhibits larger particle sizes together with cavities (Figures 2B, S4B), which is caused by restructuring under the electrochemical conditions. The surface coalescing continues as the electrolysis proceeds (Figure 2C, D, and S4C, D). X-ray photoelectron spectroscopy (XPS) analysis detects no signal of metal elements other than Cu on the surface of the used Cu electrodes (Figure S5), indicating that the observed deactivation is not a direct result of metal impurity deposition. The corresponding Cu 2p and C 1s core-level XPS spectra are plotted in Figure S6. The Cu 2p spectra all exhibit the $2p_{1/2}$ and $2p_{3/2}$ components at 952.5 and 932.7 eV, respectively, characteristic of metallic Cu surfaces. It is noted that the surface C/Cu ratio of the electrode increases as the electrolysis proceeds (Figure 2E). Deconvolution of the C 1s spectra (Figure S7) reveals that C–C is the major component of the spectrum an responsible for the observed increase in C/Cu ratio over time (Figur 2F). This excludes possible contributions from adsorbed HCO_3^- c CO_2 species, and alludes to deposited carbonaceous specie containing C–C bonds as a major cause of the drastic decay of CO reduction and rise of H_2 evolution, agreeing well with the previou studies.[9c, 10b-d, 11] Since the carbonaceous species is formed on the C surface during the CO_2 electroreduction process and particularly i the pathway of CO_2 conversion to CH_4,[9a, 9c] the deposition rat should be roughly proportional to the catalytic current density an thus the deactivation cannot be mitigated by simply increasing th electrochemically active surface area of the electrode.

In pursuit of modifying the catalytic properties of Cu, w deposited Pd on Cu mesh electrodes via a galvanic replacemer reaction (see SI for experimental details). While the Pd decoratio does not alter the initial product distribution (Figure 1B), it turns ou to be highly effective in suppressing growth of H_2 evolution. The FI (H_2) for the Pd-decorated Cu electrode remains below 40% during th first 4 h of electrolysis (Figure 1B). FE (CH_4) slightly decreases fron 46% to 40%, while FE (C_2H_4) slightly increases from 7% to 11% Even after performing electrocatalysis for 16 h, the Pd-decorated C electrode can keep more than 50 % of the current density devoted t CO_2 reduction (Figure S8). These results reflect that catalyti deactivation of Cu for electrochemical CO_2 reduction can b effectively mitigated by surface Pd decoration. We note that th distribution of the CO_2 reduction products slightly changes as th
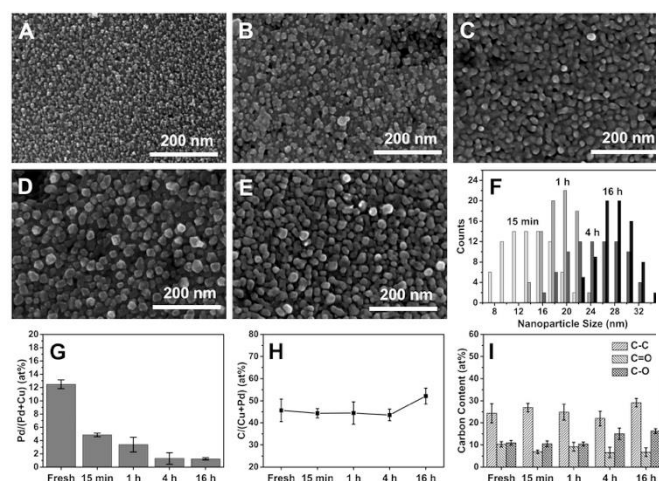

Figure 3. SEM images of (A) a fresh Pd-decorated Cu electrode and Pd-decorated Cu electrodes having performed electrocatalysis for (B) 15 min, (C) 1 h, (D) 4 h and (E) 16 h. (F) Size distributions of the nanoparticles formed on the used Pd-decorated Cu electrodes. (G) Surface Pd/(Cu+Pd) atomic ratios, (H) surface C/(Cu+Pd) atomic ratios and (I) further breakdown of the C content for the fresh and used Pd-decorated Cu electrodes.

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electrolysis proceeds (Figure 1B), although the total FE for CO_2 reduction keeps stable. Compared with the plain Cu electrode, the Pd-decorated Cu electrode shows a much higher initial current density of 57 mA cm^{-2}, which decreases by only 18% during the 4 h of electrolysis (Figure 1C). Taken together, these represent one of the most stable catalytic performances among all reported Cu metal electrocatalysts with high efficiency for CO_2 conversion to hydrocarbons (Table S2). Note that similar electrocatalytic results can also be obtained using polycrystalline Cu foil in place of Cu mesh (Figure S9).

SEM images of the fresh and used Pd-decorated Cu electrodes are shown in Figures 3A-E and S10. Compared with the fresh plain Cu electrode, the fresh Pd-decorated Cu electrode manifests a rougher surface with voids (Figure 3A, S10A), which is a result of the galvanic etching and deposition processes and agrees with the observed higher initial current density (Figure 1C) and larger surface roughness factor (Table S1). Energy dispersive X-ray spectroscopy (EDS) mapping shows that Pd is uniformly distributed as a thin layer on the Cu surface (Figure S11). No X-ray diffraction (XRD) signals other than those associated with Cu metal are detected (Figure S12), indicating that the deposited Pd is likely in the form of small clusters or even single atoms. Interestingly, the Pd-decorated Cu electrode exhibits obviously different surface morphological evolution than the plain Cu electrode during electrolysis. After 15 min of electrolysis, nanoparticles with an average size of ~15 nm have appeared on the electrode surface (Figure 3B, F). As the electrolysis proceeds, the size of the nanoparticles continues to grow and their shape becomes more and more spherical (Figure 3C-F). Only the Cu metal phase is detected by XRD for the Pd-decorated Cu electrode after 16 h of electrolysis (Figure S12), indicating that the formed nanoparticles are metallic Cu.

Surface composition and chemical states of the fresh and used Pd-decorated Cu electrodes were analyzed by XPS (Figure S13). The fresh Pd-decorated Cu electrode contains ~12% of Pd on its surface and the percentage decreases as the electrolysis proceeds (Figure 3G), implying a restructuring process resulting in Cu enrichment. After 4 h of electrolysis, the Pd-decorated Cu electrode contains only ~3% of Pd atoms on its surface. The XPS depth profile reveals that a maximum Pd concentration exists several nanometers underneath the surface (Figure S14B), in contrast to the fresh Pd-decorated Cu electrode for which the maximum Pd concentration is found on the surface (Figure S14A). The C 1s core-level XPS spectra show that the C concentration on the electrode surface remains almost unchanged during the first 4h of electrolysis (Figure 3H, I). Only a minor increase in surface C concentration is observed after the electrode performing electrocatalysis for 16 h. The evolution of surface C concentration correlates very well with the progression of the electrode's catalytic selectivity for CO_2 reduction, suggesting that the Pd decoration on Cu and the consequent surface restructuring limit accumulation of carbonaceous species on the electrode surface and thus stabilize electrocatalytic CO_2 reduction.
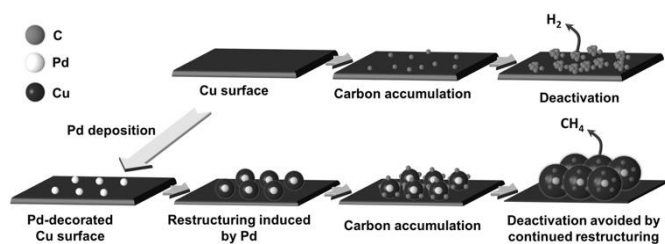
Taking the results together, we can conclude that deactivation of Cu electrode for electrochemical CO_2 reduction is strongly correlated with and likely due to accumulation of carbonaceous species on the catalyst surface (Figure 4). By decorating Cu surface with Pd, we can induce morphological and compositional restructuring and thus impart the catalyst electrode self-cleaning capability against carbon accumulation, which effectively stabilizes the catalytic selectivity for CO_2 reduction. We speculate that the surface restructuring starts from the Pd atoms acting as nucleating agents for Cu deposition. Under the working conditions, there is a dynamic equilibrium between Cu ions in the solution and the solid Cu electrode. In the presence of surface Pd species, Cu ions will preferentially deposit on the Pd sites due to their stronger affinity with Pd.[13] After the initial nucleation, Cu ions will continue to preferentially deposit on smaller or irregularly shaped nanoparticles as a result of their high surface energy, leading to nanoparticle growth and re-shaping toward a more spherical morphology. During this process, the electrode keeps refreshing its surface and thus prevents deactivation by incorporating or desorbing the surface carbonaceous species (Figure 4). Since the Pd-decorated Cu electrode possesses almost the same catalytic selectivity as the Cu electrode and the surface is nearly free of Pd after electrocatalysis, it can be confirmed that Pd does not directly participate in the CO_2 reduction catalysis but only triggers the reconstruction and refreshing of the Cu surface. This restructuring-induced self-cleaning mechanism fundamentally distinguishes from those reported for Cu-Pd bimetallic catalysts where Pd directly participates in catalysis and often alters product selectivity.[6c-f, 14]

It is worth noting that this Pd decoration approach can effectively suppress deactivation of Cu electrodes even in electrolyte without pre-purification (Figure S15). Further, we demonstrate that this approach of utilizing foreign metal atoms to induce surface restructuring is a general strategy for stabilizing the electrocatalytic properties of Cu electrodes for CO_2 reduction. For example, similar surface restructuring and catalytic selectivity stabilization can be observed for Rh-decorated Cu electrodes (Figure S16).

In summary, we have developed a general strategy for achieving stable electrocatalysts for CO_2 reduction to hydrocarbons by decorating Cu electrode surface with foreign noble atoms. Under the working conditions, the foreign atoms induce continuous restructuring of the Cu surface and thus render a self-cleaning catalyst electrode showing unprecedented long-term catalytic stability. This strategy will open up new opportunities for design and development of robust catalysts for a wide range of electrochemical applications.

Figure 4. Schematic illustration of Pd-induced surface restructuring that can avoids the accumulation of carbonaceous species on Cu surface.

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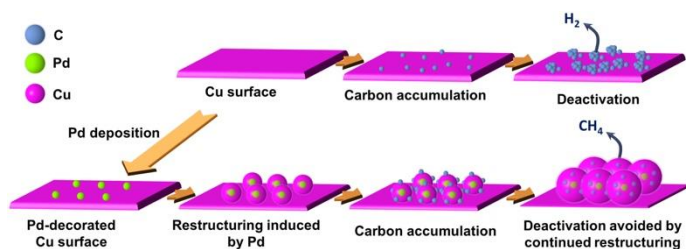
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