Ultrasound-boosted selectivity of CO in CO\textsubscript{2} electrochemical reduction

Yang Yang\textsuperscript{a,b}, Yiqing Feng\textsuperscript{a}, Kejian Li\textsuperscript{a}, Saira Ajmal\textsuperscript{a}, Hanyun Cheng\textsuperscript{a}, Kedong Gong\textsuperscript{a}, Liwu Zhang\textsuperscript{a,c,*}

\textsuperscript{a} Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, PR China
\textsuperscript{b} School of Life Science, Huaibei Normal University, Huaibei 235000, PR China
\textsuperscript{c} Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, PR China

A R T I C L E   I N F O

Keywords:
Electrochemical CO\textsubscript{2} reduction
CO
Ultrasound
Cu electrode
In-situ Raman

A B S T R A C T

Among the possible products of CO\textsubscript{2} electrochemical reduction, CO plays a unique and vital role, which can be an ideal feedstock for further reduction to C\textsubscript{2} products, and also the important component of syngas that can be used as feedstock for value-added chemicals and fuels. However, it is still a challenge to tune the CO selectivity on Cu electrode. Here we newly construct an ultrasound-assisted electrochemical method for CO\textsubscript{2} reduction, which can tune the selectivity of CO\textsubscript{2} to CO from less than 10\% to \textgreater80\% at \textminus1.18 V versus (vs.) reversible hydrogen electrode (RHE). The partial current density of CO production is significantly improved by 15 times. By in-situ Raman study, the dominating factor for the improved CO production is attributed to the accelerated desorption of \textsuperscript{4}CO intermediate. This work provides a facile method to tune the product selectivity in CO\textsubscript{2} electrochemical reduction.

1. Introduction

Over the past decade, the concentration of greenhouse gas CO\textsubscript{2} in atmosphere is increased annually, which has caused serious environmental problems, such as global warming, rising sea levels, melting of polar ice etc. In order to reduce the atmospheric CO\textsubscript{2} concentration and realize energy conversion, electrochemical CO\textsubscript{2} reduction (ECR) has become one of the most attractive approaches to realize the sustainable carbon cycle utilization and energy storage as it can use renewable electricity [1,2]. Among the possible products, CO plays a unique and vital role, which can be an ideal feedstock for further reduction to C\textsubscript{2} products [3,4], but also the important component of syngas that can be used as feedstock for value-added chemicals by downstream thermochemical reactions [5]. It is reported that nanostructured noble metal Au [6,7] and Ag [8] prefer to selectively reduce CO\textsubscript{2} to CO. Although these catalysts perform well, alternative earth-abundant and low-cost catalysts are required.

Cu as one of the earth-abundant elements and showing ability to produce C\textsubscript{2} products have attracted great attention. Cu based catalysts can transfer CO\textsubscript{2} to various carbon-based products (including CO, HCOOH, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{2}CH\textsubscript{2}OH etc.), however, it is difficult to control the selectivity for one specific product. As a result, researchers have tried a variety of approaches to solve the issue, including reactor design, catalyst design, and electrolyte design. Up to now, most research has focused on material designing, such as controlling the particle sizes [9], introducing the grain boundaries [10,11], designing the exposed facets [12–14], constructing the heterojunctions [1,15–18] etc. The Faradaic efficiency of CO on high dense Cu nanowire reached 60\%, which is the highest one ever reported for pure Cu electrode [19]. Sn coated onto the 3D hierarchical Cu have significantly improved the CO Faradaic efficiency to 98.6\% at \textminus0.45 V, while the fabrication process of 3D hierarchical Cu-Sn catalyst is very complex, which need about five steps [20]. Some other well-constructed bimetal such as Cu-Sn [21–23], Cu-In [24,25], Cu-Pd [26–28] etc. also showed high CO selectivity. Unfortunately, these catalysts usually suffer from one or more of the following drawbacks, including high cost, toxicity, poor stability, low activity, complex preparation process etc. Hence, finding a facile method to tune and reach high CO selectivity is still a big challenge.

It has been reported that the \textsuperscript{4}CO desorption is a co-determinant of the formation rate of CO [29]. In addition, the gas bubbles formed at the electrode will block the catalytic surface and decrease the efficiency of electrochemical processes [30]. Therefore, finding some methods to
accelerate CO desorption and mass transport could be a solution for higher CO selectivity. Raising the rotation rate can improve the mass transport and prevent the bubbles accumulation on the surface of electrode [31]. This strategy showed higher turnover frequency of CO₂ but it also results in undesired higher H₂ evolution activity. Therefore, a method to accelerate CO desorption while not enhancing the H₂ selectivity is greatly desired. The Pollet group has done some pioneering work on applying ultrasound to facilitate electrocatalysis [32–40]. They found that ultrasound can remove the hydrogen bubbles from the electrode surface resulting in high current density of hydrogen evolution reaction (HER) in mild acid electrolyte [37]. Recently, they found that introducing molecular hydrogen can increase the yields of hydrocarbons under ultrasonic conditions [40]. However, the effect of ultrasound on CO₂ reduction and its mechanism is still not well understood.

Here we introduce a facile method to greatly improve Faradaic efficiency of CO product on Cu electrode by ultrasound-assisted electrochemistry. In this work, the impact of ultrasound on the activity of Cu (electrochemically polished commercial Cu foil), Cu-Ag (Ag-decorated polished Cu foil) and Cu-R-Ag (Ag-decorated Cu foil, which was first processed in CO₂ atmosphere) were investigated. The reduction products were analysed and compared. The influence of temperature, solubility, mass transport brought by ultrasound were discussed. The detailed reaction mechanism was further studied by in-situ Raman.

2. Experiment

2.1. Materials

All the chemicals were analytical reagent without further purification. Formic acid and Acetic acid standard were purchased from Sigma Aldrich. NaHCO₃ (for HPLC, >99.8%) and Na₂CO₃ (metals basis, 99.999%) were purchased from Aladdin. The other reagents were purchased from Sinopharm Chemical Reagent Co., China. Deionized (DI) water was used throughout the whole experiment.

2.2. Fabrication of electrodes

Cu: The commercial Cu foil (99.9%) were firstly polished with 7000 mesh sandpaper to remove the surface pollutants. Then, the mechanical polished Cu was electro-polished in H₂PO₄ solution (85%) for 5 min at 4 V vs. Cu foil counter electrode. Finally, the polished Cu was rinsed with deionized water for 3 times and dried with hair dryer quickly, the prepared polycrystalline Cu was named as Cu.

Cu-Ag: In detail, the 0.1 mmol/L silver nitrate (AgNO₃), 0.4 mmol/L sodium citrate (C₆H₅Na₃O₇·2H₂O) and 0.1 mol/L sodium nitrate (NaNO₃) solution are contained in the electrolyte. The polished Cu was used as working electrode, Pt wire as the counter electrode and saturated calomel electrode (SCE) as reference electrode. All the experiments were carried out at room temperature (25 ± 2 °C). Electrodeposition of Ag on Cu substrate involves two steps. First, the nucleation step was performed at −1.0 V (vs. SCE) for 100 s. Then, the growth step was performed at −0.5 V (vs. SCE) for 30 min. The obtained sample was named as Cu-Ag.

Cu-R-Ag: The electrochemically polished Cu was firstly used as cathode for CO₂ reduction in H-Cell at −1.68 V vs. RHE for 30 min. The detailed reaction conditions can be obtained in section 2.4. After reaction, the electrode was rinsed with deionized water for 3 times and dried with hair dryer quickly. Then the freshly prepared electrode was used as the substrate for Ag deposition. The electrodeposition process was the same as preparing Cu-Ag. The obtained electrode was named as Cu-R-Ag.

2.3. Characterisation

The X-ray diffraction (XRD) patterns were measured by a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. The general morphologies and energy dispersive X-ray spectroscopy (EDS) of the samples were examined by field emission scanning electron microscopy (FEI, Nova Nano SEM 450) instrument and TESCAN VEGA3. The X-ray photoelectron spectroscopy spectrum were measured by the Thermo ESCALAB 250XI. The in-situ Raman spectra was measured on the XploRA confocal spectrometer (Jobin Yvon, Horiba Gr, France) with a charge coupled device (CCD) detector. The Raman scattering was excited by external-cavity diode (785 nm, with 50% energy) coupled with a 10 × Olympus microscope objective. A holographic notch filter was equipped to filter the excitation line and a holographic grating (1200 gr/mm) was used. A CCD with 1024 × 256 pixels was used to collect the spectra in a resolution of 1.2 cm⁻¹, with 2 accumulation at 2 s acquisition time.

The frequency and power of ultrasonic cleaner (Shanghai kudos ultrasonic instrument Co., Ltd) used for CO₂ reduction is 35 kHz and 180 W, respectively. The capacity of the tank is 6 L. The tank size (L × W × H) and external size (L × W × H) is 300 mm × 150 mm × 330 mm × 180 mm × 290 mm, respectively. To study the influence of ultrasonic frequency, a 40 kHz ultrasonic instrument was used. For in-situ Raman measurement, an ultrasonic cleaner with smaller size (0.8 L) and lower power (50 W) was employed. If there is no special explanation, the ultrasonic instruments used in this paper are 35 kHz and 180 W.

2.4. Catalytic activity evaluation

All electrochemical measurements were carried out on an IVIUM electrochemical workstation in a conventional three-electrode system. A platinum plate and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The distance between cathode and anode is about 9 cm. All voltages used in this work were without compensation. The anode and cathode compartment of electrochemical cell were separated by a Nafion 117 membrane. Before the measurement, CO₂ was bubbled into 50 mL electrolyte of 0.1 mol/L KHCO₃ solution for at least 30 min to reach the saturation. The gas products were analyzed by gas chromatography (SHIMADZU, GC-2014) equipped with TDX-1 and HT-POLT Al₂O₃/S columns. A thermal conductivity detector (TCD) was used to detect and quantify H₂, a flame ionization detector (FID) with methanizer was used to analyze and quantify CO by TDX-1 column, and another FID was used for quantifying CH₃, C₂H₄ and other alkane contents with a HT-POLT Al₂O₃/S column. Ar (99.999%) was used as carrier gas. Liquid products were analyzed by ionic chromatography (IC, Metrohm, 883 Basic IC Plus with Metrosp A SUPP 5–250 column). To quantify the HCOO⁻, the solution was diluted 10 times with ultrapure water, then analyzed by IC. The other liquid products were quantified by ¹H nuclear magnetic resonance (NMR, AVANCE III HD, 500 MHz, Bruker) spectrum. The liquid production (0.7 mL) was mixed with 0.2 mL D₂O and 0.1 mL dimethyl sulfoxide (DMSO, 100 ppm) as the internal standard for a one-dimensional ¹H NMR spectrum test.

3. Results and discussion

3.1. Catalyst characterisation

The morphology of Cu, Cu-Ag and Cu-R-Ag are investigated by scanning electron microscopy (SEM). Fig. 1a shows the SEM image of electrochemically polished Cu. Particles were observed on Cu surface, which could be attributed to the migration of Cu upon bias. More particles can be observed on Cu-R (Cu electrode after CO₂ reduction reaction) compared with electrochemically polished Cu, as shown in Fig. 1b. Yang’s group has investigated the structural transformation process of the Cu nanoparticles under CO₂ electro-reducing conditions. [41] The ex-situ characterization revealed that the Cu nanoparticles were easily oxidized to single-crystal CuO. Hence, the observed particles can be
attributed to the recrystallized Cu$_2$O. [41]. Therefore, particles were observed more clearly on Cu-Ag (Fig. 1c) and Cu-R-Ag (Fig. 1d) electrodes, as electro-polished Cu and Cu-R foils were used as the substrate for further electrochemical deposition of Ag. Fig. S1 show the energy dispersive X-ray (EDX) elemental maps of Cu-R-Ag, indicating that Ag is evenly distributed on the Cu surface. The Ag and O content on Cu-R-Ag electrode (calculated from EDX spectra) was 2.21 at% and 4.87 at%, respectively.

The crystal structure and surface chemical state are characterized by X-ray diffraction (XRD) and X-Ray photoelectron spectroscopy (XPS), respectively. The XRD patterns (Fig. 2a) show that only cubic phase Cu was observed in three typical samples, no obvious signal of Ag was detected indicating the amount of Ag on Cu is low. The Ag 3d XPS data of Cu-Ag and Cu-R-Ag are shown in Fig. 2b. The binding energy between Ag 3d$_{5/2}$ and 3d$_{3/2}$ is 6.0 eV indicating that metallic Ag$^0$ is formed on Cu surface [42,43]. The Cu 2p XPS spectra of Cu-Ag and Cu-R-Ag show the presence of oxides on the surface (shown in Fig. S2).

Fig. 3 shows the liner voltammetry sweeps (scan rate: 10 mV s$^{-1}$) on the Cu, Cu-Ag and Cu-R-Ag electrodes under different conditions. The current density in CO$_2$-saturated KHCO$_3$ electrolyte is significantly higher than that in N$_2$-saturated KHCO$_3$ electrolyte for all tested catalysts. Additionally, the current densities of all electrodes under ultrasonic condition were higher than that without ultrasonic, indicating the reaction rate is improved by ultrasound.

The roughness factor (RF) of electrodes were measured by the double layer capacitance measurement [44,45]. The steady state cyclic voltammetry (CV) curves and corresponding capacitive scans of Cu, Cu-Ag and Cu-R-Ag are displayed in Fig. S3. The linear relationship between current and scan rate demonstrates a negligible ion transport resistance. The RF of the electrodes were calculated from the corresponding capacitance values. Here, the RF of Cu is employed as unit. The calculated RF of Cu-Ag and Cu-R-Ag is about 0.71 and 1.01, respectively.

Fig. 1. SEM images of (a) Cu, (b) Cu-R, (c) Cu-Ag and (d) Cu-R-Ag electrode.

Fig. 2. (a) XRD patterns of Cu, Cu-Ag and Cu-R-Ag; (b) Ag 3d XPS spectra of Cu-Ag and Cu-R-Ag.
3.2. Evaluation of CO\textsubscript{2} reduction activity

Fig. S4 and Fig. 4a show the Faradaic efficiency of products (without ultrasonic treatment) on Cu and Cu-R-Ag electrode, respectively. The Faradaic efficiency of CO over Cu, Cu-Ag and Cu-R-Ag electrodes under ultrasonic treatment are displayed in Fig. 4b. As shown in Fig. S4 and Fig. 4, the Faradaic efficiency of CO on Cu electrode and Cu-R-Ag electrode can be improved from about 0.5% to 23% and 8.3% to 81% at –1.18 V, respectively, with the ultrasonic assistance. At –1.28 V, the Faradaic efficiency of CO can also be significantly improved on both Cu (10 times) and Cu-R-Ag (~8 times) electrodes under ultrasonic condition. It is observed that the Cu-R-Ag electrodes show high Faradaic efficiency of CO (>60%) at a wide potential range with the assistance of ultrasound. Except CO, the main product is H\textsubscript{2} on Cu, Cu-Ag and Cu-R-Ag under ultrasonic treatment, as shown in Fig. S5. The Faradaic efficiency of hydrocarbons on Cu-R-Ag with ultrasonic (Fig. S5c) are smaller than that of Cu-R-Ag without ultrasonic treatment (Fig. 4a). The above results indicate that ultrasonic treatment can manipulate the CO selectivity and tune the ratio of CO/H\textsubscript{2}, facilitating syngas production and inhibiting the hydrocarbons formation. The corresponding current densities of Cu, Cu-Ag and Cu-R-Ag electrode are shown in Fig. S6, S7 and S8, respectively. At –1.18 V, the total current density of Cu-R-Ag can be improved from 5.5 to 8.1 mA/cm\textsuperscript{2}, meanwhile the partial current density of CO is improved from 0.46 to 6.6 mA/cm\textsuperscript{2} under ultrasonic treatment. Fig. S6 and S8 show that the ultrasonic treatment can improve the current density at all tested potentials for both Cu and Cu-R-Ag electrodes. Additionally, the CO\textsubscript{2} reduction reaction of Cu-R-Ag was performed under ultrasound with frequency of 40 kHz (shown in Fig. S9), the catalyst still shows high CO selectivity (74%). The ultrasound effect on the CO\textsubscript{2} electrochemical reduction is confirmed at a different frequency.

It have been reported that the Faradaic efficiency of products and reaction rate also can be affected by the temperature, pressure, gas solubility etc. [46]. Under ultrasonic condition, it is noted that the temperature of the reaction solution increases gradually with the increase of ultrasonic time (after 30 min, from about 25°C to about 38°C). In addition, part of the dissolved gas products may be released from the electrolyte under ultrasonic treatment. Lastly, the mass transport of the reactant can be improved by ultrasound.

Therefore, we designed a series of control experiments to study the dominating factor for the improved CO production. The results of the control experiments are shown in Fig. 5. Due to the minimal solubility of H\textsubscript{2} and the weak adsorption ability, the Faradaic efficiency of H\textsubscript{2} was not significantly affected by ultrasonic treatment. For the Faraday efficiency of CO, we can see that the Faraday efficiency is about 5.6% under room temperature without ultrasonic treatment; When the reaction temperature was increased to the range of 35 – 40°C, the Faraday efficiency of CO is about 25%; After the reaction (in the range of 35 – 40°C), the dissolved gas was released by ultrasonic treatment, and the Faraday efficiency of CO is about 34%, which is still far below the value (73.5 ± 3%) when the reaction was carried out with the assistance of ultrasound. These results suggest that the increased temperature and dissolved gas product releasing can improve the Faraday efficiency of CO, but not the dominating factor.

Another assumption is that the same effect can be achieved by stirring. The Faradaic efficiency of both H\textsubscript{2} and CO are increased when the experiment was carried out under stirring (500 r/min). At –1.38 V, the Faradaic efficiency of H\textsubscript{2} and CO is improved to about 35% and 44%.
respectively. Similar results also can be observed at \(-1.18\) and \(-1.28\) V as shown in Fig. S10. This could attribute to the enhanced mass transport and suppressed bubble accumulation. It was consistent with literature as shown in Fig. S10. This could attribute to the enhanced mass transport and suppressed bubble accumulation. It was consistent with literature as shown in Fig. S10.

Fig. 5. (a) Faradaic efficiency of CO product on Cu-R-Ag catalyst under various conditions.

In summary, experimental results showed that ultrasonic assistance can significantly improve the Faradaic efficiency (80%) and production rate (by 15 times) of CO at wide potential range. A serious of control experiments further demonstrated that the CO Faradaic efficiency enhancement was not dominated by risen temperature, dissolved gas product or the enhanced mass transport. The in-situ Raman spectra showed that the ultrasound can accelerate the desorption rate of \(*CO\) intermediate and suppress the further reduction of \(*CO\) intermediate to hydrocarbon products, resulting in the high CO selectivity. The manipulating of CO production by a facile method of ultrasound assistance facilitates syngas production from CO\(_2\), or further reduction to C\(_2\) products from CO. Because of the microgravity environment in space, this may be a useful strategy for artificial photosynthesis in future space exploration as ultrasound can accelerate the desorption of bubbles that formed at the catalytic surface.

4. Conclusions

The corresponding Raman spectra of Cu-R-Ag at \(-1.18\) V and \(-0.78\) V are shown in Fig. 6 and Fig. S13, respectively. The bands around 280, 360 and 2055 cm\(^{-1}\) are related to CO (*CO) \([29,47]\). The two low-frequency bands (Cu-CO vibrations) at 280 and 360 cm\(^{-1}\) are attributed to the frustrated rotational mode of CO and Cu-CO stretch vibration, respectively \([47]\). The high-frequency band around 2055 cm\(^{-1}\) is considered as the intramolecular C=O stretching vibration \([29,47]\), which can desorb from the surface to form gaseous CO. The Raman spectrum collected in the first minute (without ultrasonic treatment) shows higher Cu-CO and lower C=O intensity. However, when the ultrasonic device was turned on, an obvious decrease in the Cu-CO intensity and an increase of C=O intensity is observed, suggesting the conversion of Cu-CO to intramolecular C=O. With time going, both the Cu-CO and C=O peaks were gradually declined, which is due to the desorption of gaseous CO from the surface of electrode under ultrasonic treatment. Therefore, it is proposed that without ultrasound, the Cu-CO intermediate would be further reduced to hydrocarbons on Cu sites, while with the ultrasonic treatment, the conversion of Cu-CO intermediate to intramolecular C=O and further desorption of the *CO intermediate is improved, resulting in improved CO production. Similar in-situ Raman results can also be observed at \(-0.78\) V, which are shown in Fig. S13.

Declaration of Competing Interest

The authors declare no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21976030 and 22006020), Natural Science Foundation of Shanghai (19ZR1471200), Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation, China (STGEF).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2021.105623.

References

[1] T.T.H. Hoang, S. Verma, S. Ma, T.T. Fister, J. Timoshenko, A.I. Frenkel, P.J. A. Kenis, A.A. Gewirth, Nanoporous Copper-Silver Alloys by Additive-Controlled Electrodeposition for the Selective Electroreduction of CO\(_2\) to Ethylene and Ethanol, J. Am. Chem. Soc. 140 (17) (2018) 5791-5797.
