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# Enhanced electroreduction of CO₂ to ethanol *via* enriched intermediates at high CO₂ pressures†

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Electrochemical conversion of CO₂ into liquid fuels such as ethanol, powered by renewable electricity, is an efficient strategy for CO₂ utilization to produce high value-added products. In this work, we discovered that the primary C₂₊ product could be switched from gaseous ethylene to liquid ethanol by directly increasing the CO₂ pressure when Cu₂O@Cu with a hollow sphere morphology was adopted as the catalyst. The faradaic efficiency (FE) of ethanol reached as high as 36.6% at a low overpotential of −1.0 V *vs.* Ag/AgCl (−0.48 V *vs.* RHE) at 100 bar, which was 4.6 times higher than that of 1 bar. Moreover, faster kinetics and lower overpotential for ethanol formation were obtained at high CO₂ pressures. *In situ* Raman spectroscopy studies at different pressures in combination with density functional theory calculations demonstrated that the *CO surface coverage was increased significantly at increased CO₂ pressure, which is responsible for facilitating ethanol formation during the electrochemical CO₂RR. This study provides a novel and promising strategy for the selective production of ethanol on Cu-based catalysts by facilely adjusting the CO₂ pressure.

## Introduction

Carbon capture and conversion has received considerable attention as a potential means of reducing anthropogenic CO₂ emissions.[1] The electrochemical CO₂ reduction reaction (CO₂RR) into high value-added chemicals and fuels has great potential for closing the carbon cycle and alleviating the energy shortage crisis.[2,3] Tremendous effort has been devoted to developing a series of novel heterogeneous catalysts for the electrochemical conversion of CO₂ into C₁ products (*i.e.*, CO[4–7]

and HCOO⁻ [8,9]) using renewable energy. However, further reduction of these chemicals into more valuable chemicals and fuels (C₂₊ compounds, *i.e.*, ethylene,[10–13] ethanol[14–18] and *n*-propanol[19,20]) is highly desired. Ethylene and ethanol, as vital C₂₊ chemicals with high energy density, share many intermediates in the 12-electron transfer process. Obtaining ethanol from electrochemical CO₂ reduction is an extremely attractive approach owing to its high energy density and economic value. However, there are still numerous challenges that exist in selectively producing ethanol due to the C–C coupling limitation and the presence of the competitive reaction for ethylene.[21,22]

At present, Cu-based materials have been regarded as the most effective catalysts to generate C₂₊ products by the electroreduction of CO₂.[23,24] Many tactics for designing catalysts have been applied to CO₂ (CO) electroreduction to generate C₂₊ products, including oxide-derived copper,[25–27] selective facet exposure,[28–30] morphological control,[31,32] heteroatom doping/ bimetallic strategies,[33–35] vacancy effect,[36] molecular modifications,[15,37,38] introducing compressive strain,[39] and free-copper based catalysts.[40,41] Other experimental parameters including local pH environment,[42] temperature[43] and pressure[44,45] have also been considered, which would greatly affect the selectivity of products in the CO₂RR.

It has been recognized that the low solubility of CO₂ in the aqueous electrolyte at ambient pressure often forms limited

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active carbon species, which results in lower current density and inferior selectivity.[46,47] Thus, adjusting the type of electrolyte is a prevalent approach to improve $CO_2$ solubility such as using ionic liquid-based electrolytes.[48–50] Furthermore, some research groups have reported that increasing the $CO_2$ concentration by increasing $CO_2$ pressure can effectively accelerate mass transfer and thus enhance the current density, along with suppressing the hydrogen evolution reaction (HER) to improve $CO_2$RR selectivity.[51,52] For example, Fontecave *et al.* have reported that an Ag alloyed Zn electrode can drastically increase the partial current density of CO production from $-21$ mA cm$^{-2}$ at 1 bar to $-286$ mA cm$^{-2}$ at 9.5 bar. Meanwhile, $FE_{CO}$ maintained an average of 90% over 40 h and an average of 85% over 100 h at 9.5 bar.[53] Dai *et al.* have reported that square-wave-$Cu_2O$/Cu can reduce $CO_2$ electrochemically to nearly pure formate at 45 bar, while the HER was the dominant reaction at ambient pressure.[46] Typically, $C_1$ chemicals are the primary products in the electrochemical $CO_2$RR at high pressures in previous studies. However, there are very rare studies realizing $CO_2$–ethanol conversion using electrical energy at high pressures especially above the supercritical pressure as far as we know, which highly deserves further exploration.

Herein, a $Cu_2O$@Cu hollow sphere catalyst (denoted as HS-Cu) was prepared successfully and its performance for $CO_2$ electrocatalysis at different $CO_2$ pressures was studied comprehensively. We surprisingly discovered that the product distribution could be regulated remarkably with an increase in the $CO_2$ pressure, accompanied by increasing the current density. In particular, at ambient pressure, a broad distribution of products ($H_2$, CO, $CH_4$, HCOOH, $C_2H_4$, $CH_3CH_2OH$ and *n*-propanol) was observed, and ethylene was the main $C_{2+}$ product. Interestingly, ethylene production was suppressed and the production of ethanol was improved greatly by increasing the $CO_2$ pressure. The FE of ethanol could reach as high as 36.6% at a low overpotential of $-1.0$ V *vs.* Ag/AgCl ($-0.48$ V *vs.* RHE) at 100 bar, which was 4.6 times higher than that of 1 bar. Moreover, *in situ* Raman spectroscopy measurements at different $CO_2$ pressures coupled with density-functional theory (DFT) calculation studies demonstrate that denser *CO surface coverage at a higher $CO_2$ pressure is responsible for the promotion of ethanol formation during the $CO_2$ electrocatalysis process. To the best of our knowledge, this is the first report using a Cu catalyst to mainly produce liquid ethanol from the $CO_2$RR only with the assistance of a high $CO_2$ pressure. The primary $CO_2$RR products could be easily switched from gaseous ethylene at ambient pressure into liquid ethanol at a high $CO_2$ pressure.

# Experimental

## Materials and chemicals

Copper(II) chloride dihydrate ($CuCl_2·2H_2O$, AR), sodium hydroxide (NaOH, AR), D-glucose (AR), potassium bicarbonate (AR), dimethyl sulfoxide (DMSO, AR) and isopropanol

(AR) were produced by Sinopharm Chemical Reagent Co., Ltd. Deuterium oxide ($D_2O$, 99.9 atom% D) was provided by Energy Chemical. Nafion solution (5 wt% in water and isopropanol) was obtained from Meryer (Shanghai) Chemical Technology Co., Ltd. Conductive carbon paper (hydrophobic) was purchased from Suzhou Sinero Technology Co., Ltd. $CO_2$ (99.999%) was provided by Fuzhou Xinhang Industrial Gases Co., Ltd. Unless otherwise noted, deionized water (18 MΩ cm$^{-2}$) was used throughout this work.

## Catalyst preparation

The $Cu_2O$@Cu hollow sphere catalyst was prepared according to the reported literature with some modifications.[54] $CuCl_2·2H_2O$ (0.3410 g) was added to a mixed solution of 20 mL of ethylene glycol and 10 mL of deionized water, and the solution was stirred for 10 min and transferred into a 100 mL two-necked flask immersed in a 60 °C water bath. Whereafter, 10 mL of NaOH (2 g) aqueous solution was added drop by drop. After 5 min, 10 mL of D-glucose (2 g) solution was added rapidly and kept at 60 °C for 30 min. The resulting product was centrifuged, and rinsed with distilled water several times. Finally, the $Cu_2O$@Cu hollow sphere catalyst was obtained by drying it in a vacuum oven at 70 °C for 12 h.

## Characterization of materials

Powder XRD was recorded using a Rigaku SmartLab-SE powder X-ray diffractometer with Cu Kα radiation ($λ = 1.5418$ Å) at room temperature. SEM images were acquired using a field emission scanning electron microscope from ZEISS Sigma. The morphology of the products was measured using an FEI Tecnai F30 transmission electron microscope at an acceleration voltage of 300 kV. XPS measurements were implemented with a Thermo Escalab 250Xi spectrometer using a photon energy of 461 eV at an energy resolution of 0.1 eV. $^1H$ NMR spectra were operated using a Bruker AVANCE III 500 MHz nuclear magnetic resonance spectrometer. *In situ* Raman measurements were conducted with a Renishaw invia instrument using a 633 nm excitation laser and signals were recorded using 20 s integration in a home-made high pressure *in situ* Raman cell setup with a three-electrode, the laser power was 0.4 mW, and the objective (Nikon, ×10, NA 0.25) was used for exciting and collecting the Raman signals.

## Preparation of the working electrode

The as-prepared $Cu_2O$@Cu hollow sphere catalyst (10 mg) was dispersed in 1980 μL of isopropanol and 20 μL of Nafion solution (5 wt% in water and isopropanol), followed by ultra-sonication for 1 h at room temperature. Then 200 μL of catalyst ink was drop-coated onto hydrophobic carbon paper (geometric area: 1 × 1 cm$^2$), the catalyst loading was about 1 mg cm$^{-2}$, and the electrode was dried in a vacuum oven at 70 °C for 12 h. HS-Cu was then obtained by *in situ* electroreduction of the $Cu_2O$@Cu hollow sphere catalyst.

# Results and discussion

The HS-Cu catalyst was first synthesized through a simple wet-chemical method. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the $Cu_2O@Cu$ catalyst exhibited a hollow sphere morphology (Fig. 1a and b). High-resolution TEM (HR-TEM) images (Fig. 1c) revealed that the two different sets of lattice fringes in $Cu_2O@Cu$ correspond to the (111) facet of $Cu_2O$ and the (111) facet of Cu, respectively. The X-ray diffraction (XRD) pattern (Fig. 1d) showed three peaks located at 43.4°, 50.5° and 74.1°, corresponding to the diffraction from the Cu(111), (200) and (220) facets, respectively. Furthermore, the peak at 36.6° could be assigned to the diffraction from the $Cu_2O(111)$ facet, which was consistent with the HR-TEM characterization results. Two peaks at 953.8 eV and 933.9 eV were observed in the Cu 2p X-ray photoelectron spectroscopy (XPS) spectra (Fig. 1e), corresponding to $Cu^{2+}$, which could be caused by the rapid and unavoidable surface oxidation of $Cu^+/Cu^0$ when exposed to the air.[55,56] Auger electron spectroscopy (AES) of Cu LMM showed two peaks located at 574.1 eV and 569.2 eV, corresponding to $Cu^+$ and $Cu^0$, respectively (Fig. 1f). Taken together, the HS-Cu catalyst containing $Cu^+$ and $Cu^0$ was synthesized successfully.

HS-Cu was then obtained by *in situ* electroreduction of the $Cu_2O@Cu$ hollow sphere catalyst *via* five runs of linear sweep voltammetry (LSV) with a scan speed of 20 mV s$^{-1}$ over a potential range from −0.3 V to −2.1 V *vs.* Ag/AgCl. The XRD pattern of HS-Cu displayed only metallic Cu facets (Cu(111),

Cu(200) and Cu(220)) as shown in Fig. S1.† Whereafter, the $CO_2$RR performance over HS-Cu at ambient and high pressure was inspected carefully. For the electrochemical measurement at ambient and high $CO_2$ pressures, the $CO_2$ electroreduction reaction was performed in a high-pressure electrolytic cell with a two-compartment PEEK lining separated by a proton exchange membrane to prevent the crossover of liquid products (Fig. 2a and Fig. S2†). The concentration of active $CO_2$ (aq.) and $H_2CO_3$ species in the electrolyte increased with an increase in $CO_2$ pressure (Fig. S3†).[44] The detailed calculation of the concentrations of carbon species and protons in 0.1 M $KHCO_3$ at various $CO_2$ partial pressures is shown in the experimental section of the ESI.†

The $CO_2$RR product distribution at ambient and high pressures (100 bar) is shown in Fig. 2b and c. A linear sweep voltammetry (LSV) test was conducted with a sweep rate of 20 mV s$^{-1}$ at different $CO_2$ pressures. It should be noted that the LSV curves emerged with a decreasing trend of the overpotential and an increase in current density (Fig. 2d and Fig. S4†), suggesting the immense impact of the different $CO_2$ pressures in the $CO_2$RR. Product analysis at a low overpotential of 1 bar revealed that the reaction was dominant by the competitive HER (ranging from −1.2 V *vs.* Ag/AgCl to −1.6 V *vs.* Ag/AgCl, $FE_{H_2} > 60\%$) (Fig. 2b and Fig. S5†). Though the HER was suppressed at a high overpotential (ranging from −1.7 V *vs.* Ag/AgCl to −2.1 V *vs.* Ag/AgCl, $FE_{H_2} < 40\%$), a wide $CO_2$RR product distribution was observed. It could be seen that CO was the dominant $C_1$ product ($FE_{CO} = 25.7\%$ at −1.8 V *vs.* Ag/AgCl) and ethylene was the main $C_{2+}$ product ($FE_{ethylene} = 27.8\%$ at −2.1
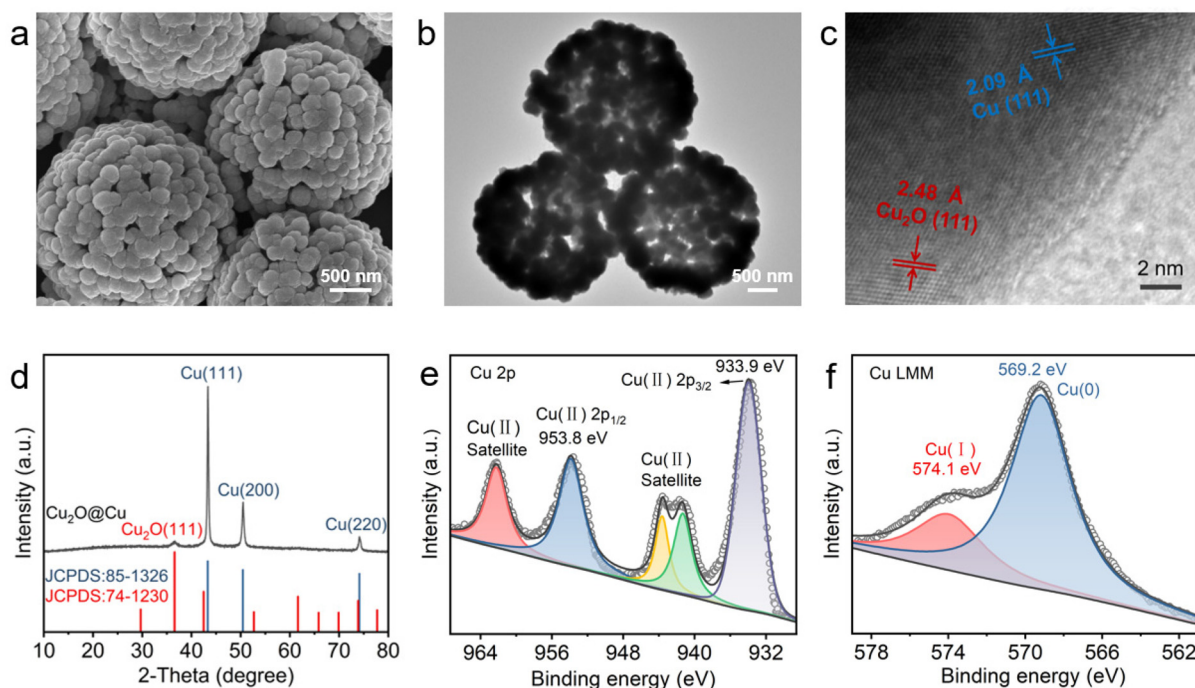


**Fig. 1** Characterization of the as-prepared HS-Cu catalyst. (a) SEM image, (b and c) HRTEM image, (d) XRD pattern, (e and f) XPS Cu 2p and Cu LMM Auger electron spectra of $Cu_2O@Cu$.

**Fig. 2** $CO_2RR$ performance at different $CO_2$ pressures. (a) Schematic description of the high-pressure electrolytic cell. (b) Faradaic efficiencies of different products on the HS-Cu electrode at 1 bar and various potentials for one hour test. (c) Faradaic efficiencies of different products on the HS-Cu electrode at 100 bar and various potentials. (d) LSV of HS-Cu in 0.1 M $KHCO_3$ aqueous solution at different $CO_2$ pressures. (e) Correlation of $FE_{ethanol}$ and $CO_2$ pressure. (f) A comparison of the potential-dependent $FE_{CO}$, $FE_{ethylene}$ and $FE_{ethanol}$ at 1 bar and 100 bar $CO_2$ pressure. (g) Tafel slopes for the ethanol partial current density ($j_{ethanol}$) at 1 and 100 bar. (h) Stability test of the HS-Cu catalyst on a glassy carbon electrode at 100 bar $CO_2$ pressures at a potential of −1.0 V vs. Ag/AgCl (non-iR corrected. The red and purple balls represent the corresponding FEs of ethanol and formate, respectively).

V vs. Ag/AgCl). In addition, the maximum $FE_{ethanol}$ was only 7.9% at −2.1 V vs. Ag/AgCl.

However, the product selectivity of the $CO_2RR$ at different high pressures (25 bar, 50 bar, 75 bar and 100 bar) showed a significant difference. In particular, analysis of the liquid products illustrated that the selectivity of ethanol was obviously improved with increasing $CO_2$ pressure. The $FE_{ethanol}$ values at 25 bar, 50 bar and 75 bar were 11.8%, 22.8% and 35.8%, respectively (Fig. S6–S8†). Remarkably, a $FE_{ethanol}$ of 36.6% was achieved at a higher $CO_2$ pressure of 100 bar, which was 4.6 times higher than that obtained at 1 bar. Also, only −1.0 V vs. Ag/AgCl (−0.48 V vs. RHE) was required for the cathodic reduction, which is a low reduction overpotential for the $CO_2RR$ to ethanol (Fig. 2c). To reveal the variation tendency of $FE_{ethanol}$ influenced by different high $CO_2$ pressures, the correlation between $FE_{ethanol}$ and $CO_2$ pressure was studied (Fig. 2e). The FE of ethanol was rapidly enhanced upon increasing the $CO_2$ pressure from 1 bar to 75 bar. When the pressure continued to rise to 100 bar, the $FE_{ethanol}$ reached a plateau. This indi-

cates that the $FE_{ethanol}$ is mainly affected by the $CO_2$ pressure up to supercritical $CO_2$ conditions. Surprisingly, a significant decrease in $FE_{ethylene}$ was observed accordingly. A very low $FE_{ethylene}$ of 3.5% was attained at 25 bar and no ethylene was detected at 50 bar, 75 bar and 100 bar as shown in Fig. 2c and Fig. S6–S8.† These results manifest that the ethylene product, as the competitive product of ethanol, was restrained by suppressing at the same potentials at 100 bar, which we surmise is due to the higher $CO_2$ solubility at the high pressure (Fig. 2c and Fig. S5†).[46,52,53] For $C_1$ products, as displayed in Fig. 2c and Fig. S5–S8,† $FE_{CO}$ was decreased and $FE_{HCOOH}$ was improved at a high $CO_2$ pressure. Moreover, $FE_{CO}$, $FE_{ethylene}$ and $FE_{ethanol}$ in the potential range of −0.8 to −2.0 V vs. Ag/AgCl at 1 bar and 100 bar are presented in Fig. 2f, which revealed a super-low ethanol overpotential (<−0.8 V vs. Ag/AgCl (<−0.3 V vs. RHE)) at 100 bar in contrast to that at 1 bar (−1.6 V vs. Ag/AgCl).[20] The $FE_{ethanol}$ was increased accompanied by the decrease of $FE_{CO}$ at 100 bar, which strongly implies that CO is a vital intermediate for the $CO_2RR$ to ethanol.

To investigate whether the product distribution is caused by $CO_2$ pressure directly or pH changes at high $CO_2$ pressure, the $CO_2RR$ experiments at 1 bar used 0.1 M $KHCO_3$ + $H_2SO_4$ aqueous solutions of pH ~ 5.0 as the electrolyte was operated. As shown in Fig. S10,† a similar product distribution was obtained in the $CO_2RR$ at 1 bar in different local pH environments, which indicates that the $FE_{C_{2+}}$ switching with the increase of $CO_2$ pressure is due to the $CO_2$ pressure inherently. For the CORR of the HS-Cu catalyst, a similar trend for $FE_{ethylene}$ has been observed in the CORR at different CO pressures shown in Fig. S11,† which indicated that $FE_{ethylene}$ was decreased with the CO concentration increase. There is no noticeable change in $FE_{ethanol}$ at 1 bar and 3 bar, which is probably due to the other $C_{2+}$ competitive products.

In order to compare the reaction kinetics of the $CO_2RR$ at ambient and high pressures, we obtained Tafel slopes for the $CO_2RR$ current density attributed to ethanol production ($j_{ethanol}$). The slopes were found to be 208 mV dec$^{-1}$ and 805 mV dec$^{-1}$ for 100 bar and 1 bar, respectively (Fig. 2g). The decreased Tafel slope value with increased $CO_2$ pressure suggested that a faster reaction kinetics could be achieved at a higher $CO_2$ pressure.[44] In addition, the continuous $CO_2RR$ at 100 bar was performed at −1.0 V vs. Ag/AgCl for 12 h to illuminate the long-term stability of the HS-Cu. As displayed in Fig. 2h, there were no obvious changes in both the current density and FE of the ethanol and formate, illustrating the excellent stability of the prepared HS-Cu catalyst at a high $CO_2$ pressure.[52] Furthermore, XRD, XPS and SEM of the electrode after the $CO_2RR$ at 100 bar were characterized. Only characteristic peaks of bare Cu could be observed from the XRD pattern (Fig. S12†), but a minor signal of the $Cu^+$ peak was detected from XPS analysis (Fig. S13†), which could be ascribed to the reoxidation of $Cu^0$ after exposure to air during the sample transfer process. The SEM image showed that the sample still exhibited the hollow sphere morphology (Fig. S14†), which further indicated the good stability of the catalyst.

To gain insight into the reaction mechanism on HS-Cu for the $CO_2RR$ at different $CO_2$ pressures, in situ Raman measurement was conducted at various applied potentials in a custom-made high pressure in situ Raman cell (Fig. S15†). As shown in Fig. 3 and Fig. S16,† the spectra at different potentials were collected to uncover the reaction intermediates at different $CO_2$ pressures. The C≡O stretching vibration of adsorbed *CO at ca. 2091 cm$^{-1}$ and the C–H stretching vibration of adsorbed $CH_3$ at ca. 2861 and 2930 cm$^{-1}$ were clearly observed at negative applied potentials from −0.8 V to −1.3 V vs. Ag/AgCl at 80 bar (Fig. 3a), which could be assigned to the key intermediates for producing ethanol.[57–59] Moreover, the peaks at ca. 278 cm$^{-1}$ and 352 cm$^{-1}$ assigned to the Cu–CO stretching vibration modes could be unambiguously detected. In addition, a broad peak emerging at ca. 2091 cm$^{-1}$ corresponds to the *CO vibrational mode. With the applied potential being increased to −1.3 V vs. Ag/AgCl, the peak intensity increased continuously, which indicates that the *CO coverage on the catalyst was improved (Fig. 3a).[60] Furthermore, in situ Raman spectra at different $CO_2$ pressures were compared at a controlled potential (−1.0 V vs. Ag/AgCl). Due to the weak adsorption of *CO on the catalyst surface at ambient pressure, no obvious peak could be observed at different potentials at 1 bar $CO_2$ pressure. The elevated peak intensity of the Cu–CO and *CO stretching vibrations with the increased $CO_2$ pressure from 1 bar to 80 bar is due to the effective enrichment of the adsorbed *CO intermediates on the surface of the catalyst under the high-pressure conditions (Fig. 3b). In situ Raman data collected at various applied potentials and $CO_2$ pressures thus directly and clearly demonstrates that the high $CO_2$ pressure contributes to improving the *CO coverage on the catalyst,[60,61] which effectively promotes C–C coupling and enhances ethanol selectivity. Besides, the characteristic $Cu_2O$ peaks at around 520 cm$^{-1}$ and 620 cm$^{-1}$ disappeared with the overpotential from −0.1 to −1.3 V vs. Ag/AgCl, further indicating that only Cu(0) existed stably during the $CO_2RR$ at high pressure (Fig. S16†).
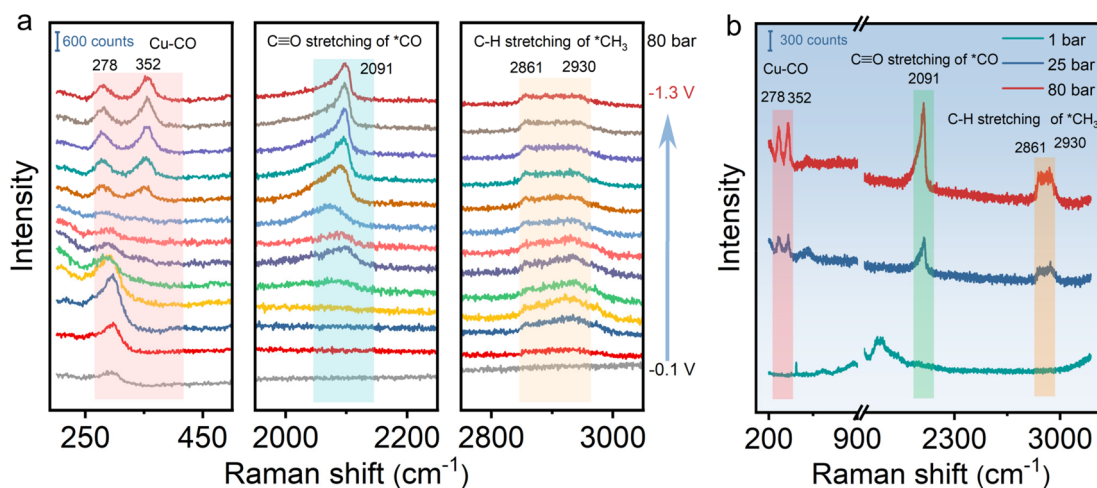


**Fig. 3** *In situ* Raman spectra of HS-Cu obtained (a) in the potential range of −0.1 to −1.3 V vs. Ag/AgCl during the $CO_2RR$ at 80 bar $CO_2$ pressure, (b) at different $CO_2$ pressures during the $CO_2RR$ at a controlled potential of −1.0 V vs. Ag/AgCl.
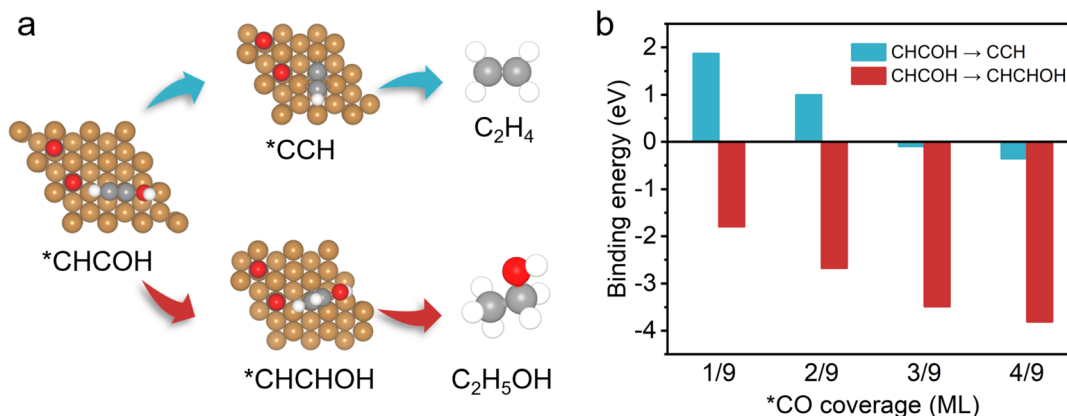
**Fig. 4** DFT calculation results on the effects of *CO coverage. (a) Key reaction pathways for the $CO_2RR$ to ethylene and ethanol on the Cu(111) surface. Yellow, copper; grey, carbon; red, oxygen; and white, hydrogen. (b) Binding energies of *CCH (cyan) and *CHCHOH (red) intermediates at different *CO coverages on the Cu(111) surface.

On the basis of the observed pressure-dependent activity for $CO_2$ conversion to ethanol, DFT calculations were further conducted to gain a more in-depth understanding of the underlying relationship between the production pathways of ethylene, ethanol and the local *CO concentration on the catalyst surface (Fig. 4 and S17†). Previous reports proposed that the formation of the intermediate *CHCOH is a decisive step in generating $C_{2+}$ products during the process of the $CO_2RR$ on the Cu(111) surface model systems.[60,62] The *CHCOH intermediate is further hydrogenated to form *CCH and *CHCHOH, which are the critical intermediates for ethylene and ethanol formation, respectively (Fig. 4a). We first calculated the binding energy of *CHCHOH and *CCH intermediates (Fig. 4b). We found that the binding energy decreases more for the formation of *CHCHOH (ethanol path) compared with that of *CCH (ethylene path) in the presence of *CO. With the increase of *CO coverage from 1/9–4/9 ML, the binding energy of *CHCHOH intermediates also reduces continuously, which indicates that more heat is released during the formation of *CHCHOH intermediates. Therefore, we discovered that higher *CO coverage on the catalyst surface effectively facilitates the selective formation of ethanol rather than ethylene. Besides, it is reasonable to calculate the required free energy for generating the intermediates *CCH and *CHCHOH to evaluate the possible reaction paths (Fig. S18†). The free energy of *CHCHOH decreases more than that of *CCH with *CO coverage reaching from 1/9 to 4/9. This phenomenon, which allows for high *CO coverage on the catalyst surface, is beneficial for generating *CHCHOH, thus promoting the production of ethanol. The good agreement with experimental results and the DFT calculations suggests that the selectivity for $C_{2+}$ products in the $CO_2RR$ could be effectively controlled by modulating the *CO coverage on the surface of Cu-based catalysts.

Furthermore, we have also conducted techno-economic analysis (TEA) of the electrocatalytic $CO_2$ conversion to ethanol at high pressures. From the technology and its impact on society, the process of electrochemical $CO_2$ reduction to produce ethanol is the green pathway for $CO_2$ conversion relevant to carbon reduction/utilization. Meanwhile, the high-pressure strategy does not obviously depend on the pressurization/$CO_2$ supply cost but mainly on the electrolysis energy cost (as displayed in the ESI† in detail).

## Conclusions

In summary, different $CO_2$ pressures from 1 to 100 bar were facilely introduced into an electrochemical $CO_2RR$ system to regulate the product selectivity, and it was interesting to find that the main $C_{2+}$ products could be switched from ethylene at ambient pressure to ethanol under high pressure conditions over the HS-Cu catalyst. In our work, the $FE_{ethanol}$ could reach as high as 36.6% at 100 bar $CO_2$ pressure, which is 4.6 times higher than that of 1 bar accompanied by faster kinetics and lower overpotential for ethanol formation. *In situ* Raman spectra at different pressures prove that higher *CO coverage on the surface of the HS-Cu catalyst could be detected at higher $CO_2$ pressures. DFT calculations further confirmed that higher *CO coverage at a high $CO_2$ pressure on the Cu surface effectively facilitates the selective formation of ethanol rather than ethylene. This work provides a facile strategy for regulating $CO_2$ conversion into ethanol by using renewable electricity with the assistance of high $CO_2$ pressure. In particular, to further enhance the $FE_{ethanol}$, the $CO_2RR$ performance of other Cu-based catalysts which have already been demonstrated with good $FE_{ethylene}$ or $FE_{ethanol}$ under ambient conditions will be evaluated with the assistance of high $CO_2$ pressures in the near future. Moreover, we believe that the interesting observation under a high pressure $CO_2$ regulation system reported here could also be extended to plenty of other novel catalysts for the efficient conversion of $CO_2$ to high value-added chemicals and fuels.

## Author contributions

R. X. Q., L. P., S. L. Y., and J. L. proposed the project, designed the experiments, and wrote the manuscript. R. X. Q. performed the whole experiment. J. J., and Y. Z. G. conducted the DFT calculations. J. R. L., J. Z., D. T. S., Z. Y. L., and C. L. performed the analysis of experimental data. R. Q. L., S. Y., and B. R. conducted a part of the characterization studies. Z. P. L., T. W. X., G. K. X., L. X. C., and Y. Z. H. participated in the discussions. L. P., S. L. Y., J. L., and B. X. H. supervised the whole project.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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