Selective electroreduction of carbon dioxide to methanol on copper selenide nanocatalysts

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Production of methanol from electrochemical reduction of carbon dioxide is very attractive. However, achieving high Faradaic efficiency with high current density using facile prepared catalysts remains to be a challenge. Herein we report that copper selenide nanocatalysts have outstanding performance for electrochemical reduction of carbon dioxide to methanol, and the current density can be as high as 41.5 mA cm\(^{-2}\) with a Faradaic efficiency of 77.6% at a low overpotential of 285 mV. The copper and selenium in the catalysts cooperate very well for the formation of methanol. The current density is higher than those reported up to date with very high Faradaic efficiency for producing methanol. As far as we know, this is the first work for electrochemical reduction of carbon dioxide using copper selenide as the catalyst.
Electrocatalytic reduction of carbon dioxide (CO₂) is a potential strategy to transform the intermittent sources of energy into high-energy chemicals, which can potentially reduce our dependence on fossil fuels and alleviate atmospheric pollution⁹–¹³. Among the products formed upon electrochemical CO₂ reduction, hydrocarbons, and alcohols with high energy density, like methanol, are compatible with existing infrastructures and can substitute for fossil fuels⁵–⁷. It is known that the electrocatalytic reduction of CO₂ to methanol requires intricate six-electron/proton coupling steps and sluggish kinetics⁸–¹¹. Therefore, the reaction usually suffers from low current density, poor selectivity and the large overpotential⁹,¹₂–¹⁴. As a result, rational design of highly active and robust electrocatalysts that could generate high current density and high selectivity is critical for large-scale application.

Metal and metal-based catalysts have been used for electro-reduction of CO₂ to CO, hydrocarbons and alcohols⁵,¹⁵,¹⁶. To date, some electrocatalysts, such as precious metal and copper-based catalysts, have been shown to be promising for electroreduction of CO₂ to methanol⁹–¹²,¹⁴,¹⁷–²². Among these materials, Cu has been reported as the promising electrocatalyst that is active and selective for CO₂ reduction to hydrocarbons and alcohols. However, the activity and selectivity of bulk Cu for producing methanol are usually low¹⁴,¹⁸–²⁰. Metallic Pd or Pt, Pd–Cu and Mo complexes have all also been employed as catalysts for electrochemical synthesis of methanol¹⁰,¹²,¹⁹,²¹,²². In addition, Ru/Ti bimetallic oxide is another promising catalyst for production of methanol²³. It was reported that Mo–Bi bimetallic chalcogenide (MoSe₂/Bi₂Se₃) could be used as electrocatalyst to promote the reaction²⁴. Nevertheless, achieving high current density and Faradaic efficiency (FE) simultaneously for conversion of CO₂ to methanol remains to be a challenge, and only a few catalysts reported up to date could reach relatively high current density and selectivity, as shown in Supplementary Table 1. Therefore, designing efficient catalysts to enhance the activity and FE, and reduce the overpotential is very interesting from both scientific and practical viewpoints.

In recent years, nanoscale transition metal oxides (TMOs) and chalcogenides (TMGs) have attracted considerable attention, which have great potential of application in photo-electric devices, lithium-ion batteries, gas sensors, and electrocatalysis²⁴,²⁵. Metal and metal-based oxides, such as copper oxides, have shown to be promising catalysts for CO₂ electroreduction¹¹–¹³. Among these materials, Cu has been reported as the promising electrocatalyst that is active and selective for CO₂ reduction to hydrocarbons and alcohols. However, the activity and selectivity of bulk Cu for producing methanol are usually low¹⁴,¹⁸–²⁰. Metallic Pd or Pt, Pd–Cu and Mo complexes have also been employed as catalysts for electrochemical synthesis of methanol¹⁰,¹²,¹⁹,²¹,²². In addition, Ru/Ti bimetallic oxide is another promising catalyst for production of methanol²³. It was reported that Mo–Bi bimetallic chalcogenide (MoSe₂/Bi₂Se₃) could be used as electrocatalyst to promote the reaction²⁴. Nevertheless, achieving high current density and Faradaic efficiency (FE) simultaneously for conversion of CO₂ to methanol remains to be a challenge, and only a few catalysts reported up to date could reach relatively high current density and selectivity, as shown in Supplementary Table 1. Therefore, designing efficient catalysts to enhance the activity and FE, and reduce the overpotential is very interesting from both scientific and practical viewpoints.

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Herein, we report a facile solvothermal synthesis of Cuₓ−ySe(y) nanocatalysts in diethylenetriamine (DETA, Supplementary Fig. 1 for the structure) and H₂O binary solution, where y represents the volume ratio of DETA and water (V$_{\text{DETA}}$/V$_{\text{H}_2\text{O}}$), and the value of x is in the range of 0.3 to 0.4, depending on the atom ratio of Cu and Se in the catalysts. The properties of the catalysts, such as size and morphology, are solvent-dependent. The catalysts synthesized in the mixed solvent with V$_{\text{DETA}}$/V$_{\text{H}_2\text{O}}$ of 1:3 can convert CO₂ into methanol with a current density of 41.5 mA cm⁻² at FE of 77.6%. The current density is higher than those reported up to date with very high methanol selectivity (Supplementary Table 1).

**Results**

**Synthesis and characterization of Cuₓ−ySe(y) nanocatalysts.** The Cuₓ−ySe(y) nanocatalysts were synthesized by solvent coordination molecular template method³⁴,³⁵, which is shown schematically in Supplementary Fig. 1. In the synthesis of the catalysts, the positively charged ammonium ions coordinated with Se to incorporate into the neighboring Cuₓ−ySe(y) nanoparticles. The protonated amine molecules then act as a template, resulting in the new morphology of the Cuₓ−ySe(y) nanocatalyst³⁴,³⁵.

It is clearly shown that the V$_{\text{DETA}}$/V$_{\text{H}_2\text{O}}$ affected the morphology of the Cuₓ−ySe(y) nanocatalysts considerably (Supplementary Fig. 2). The nanoparticles tended to be granular with increasing content of water in the solvent. In addition, the Cu₁ₓ₂Se₁(3/1) nanoparticles synthesized at the V$_{\text{DETA}}$/V$_{\text{H}_2\text{O}}$ of 1/3 had the smallest size. The detailed characterization results of Cu₁ₓ₂Se₁(3/1) nanocatalysts are shown in Fig. 1. The images of scanning electron microscopy (SEM) (Fig. 1a) and transmission electron microscopy (TEM) (Fig. 1b) reveal that the size of the Cu₁ₓ₂Se₁(3/1) nanoparticles was ~50 nm, which is consistent with the results obtained from dynamic light scattering (DLS, inset of Fig. 1a). Elemental distribution mappings (inset images of Fig. 1b) analysis further indicated the uniform distribution of Cu (yellow) and Se (blue) atoms in the catalysts. Thermogravimetry (TG) curve is shown in Supplementary Fig. 3. The weight loss of DETA (if incorporated into the nanoparticles) should occur at 280–580°C³⁶. It can be seen from the figure that there was no weight loss in the temperature range, indicating that there was no DETA in the catalysts. The high-resolution TEM (HR-TEM) image demonstrated the high crystallinity of nanoparticles (Fig. 1c). Furthermore, X-ray photoelectron spectroscopy (XPS) identified the valence states of Cu and Se in the nanocatalysts. The binding energies of Cu 2p₃/2 and Cu 2p₁/2 at 933.5 and 953.9 eV respectively, and there was a peak at 916.9 eV in the Cu LMM spectrum (Fig. 1e), indicating the existence of Cu(I)³⁷–³⁹. In addition, the binding energies of Cu 2p₃/2 and Cu 2p₁/2 at 933.5 and 953.9 eV (Fig. 1d) along with the satellite lines can be assigned to Cu(II)⁴⁰. The double peaks at 55.3 and 54.6 eV (Fig. 1f) in the XPS spectrum were the typical Se 3d binding energy for lattice Se³⁷–³⁹. The atomic ratio of Cu(I) to Cu(II) in the nanocrystal determined by XPS was 3.41. Meanwhile, the atomic ratio of Cu to Se determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) was 1.64, which is consistent with the value determined by XPS (1.63). In terms of the molecular formula, nonstoichiometric Cuₓ−ySe(y) could be considered as a mixture of stoichiometric CuₓSe and CuₓSe and thus the molecular formula can be estimated as Cuₓ₁₀Se₁(3/1). Similarly, the molecular formula of the nanocatalysts prepared in the solvents at other V$_{\text{DETA}}$/V$_{\text{H}_2\text{O}}$ ratios were Cu₁ₓ₂Se₁(0/1), Cu₁ₓ₂Se₁(1/5), Cu₁ₓ₂Se₁(1/1), Cu₁ₓ₂Se₁(3/1), and Cu₁ₓ₂Se₁(1/0) (Supplementary Table 2), and the HRTEM images and XPS spectra are shown in Supplementary Figs. 4–8. The diffraction peaks of the Cu₁ₓ₂Se₁(3/1) nanocatalysts (Fig. 1g) can be assigned to (111), (200), (220), (311), (400), and (331) planes of cubic Cuₓ−ySe (JCPDS No. 06–0680)³⁷,⁴², which is in agreement with the HR-TEM result (Fig. 1c). Meanwhile, the difference of
XRD patterns of the catalysts synthesized at various V_DETA/V_H2O ratios was not noticeable (Supplementary Fig. 9). The results showed that the crystal structures of different samples were not changed with the V_DETA/V_H2O ratio notably. However, the size and morphology depended strongly on the composition of the solvents, which influenced the performances of CO2 electroreduction.

Electrocatalytic performance of CO2 reduction over Cu2−xSe(y) nanocatalysts. The linear sweep voltammetry (LSV) study was conducted to investigate the performances of the Cu2−xSe(y) nanocatalysts under the same conditions in [Bmim]PF6 (30 wt %)/CH3CN/H2O (5 wt%) ternary electrolyte, and the results are shown in Fig. 2a. The results indicate that Cu1.63Se(1/3) exhibited a more positive onset potential of −1.815 V vs. Ag/Ag+ than other Cu2−xSe(y) nanocatalysts, suggesting that Cu1.63Se(1/3) was favorable to the binding of CO2. In addition, the current density over Cu1.63Se(1/3) reached a high value of about 40 mA cm−2 at −2.1 V vs. Ag/Ag+, which exhibits higher activity than other Cu2−xSe(y) nanocatalysts. The much higher current density of the CO2-saturated than the N2-saturated on the Cu1.63Se(1/3) (around −2.1 V vs. Ag/Ag+) indicates the reduction of CO2.

Constant-potential electrolysis of CO2 over different catalysts was performed in a typical H-type cell. Liquid-phase and gas-phase products were quantified by nuclear magnetic resonance spectroscopy (1H NMR) and gas chromatography (GC), respectively. The current density and FE are displayed in Fig. 2b, c. It can be found that all Cu2−xSe(y) nanocatalysts basically yielded a certain amount of methanol, HCOOH, CO, and H2 with a combined FE of around 100%, and no other product was detected (Supplementary Fig. 10). The Cu1.63Se(1/3) electrode had better performance than other Cu2−xSe(y) nanocatalysts. The maximum FE occurred at −2.1 V vs. Ag/Ag+, and it could reach 77.6% with a current density of 41.5 mA cm−2 (Fig. 2b, c). The equilibrium (thermodynamic) potential for CH3OH was −1.815 V vs. Ag/Ag+, which was obtained by extrapolation of partial current density vs. potential curve to zero partial current density (Supplementary Fig. 11)43–45. Therefore, the overpotential for CO2 electroreduction to methanol was 285 mV at −2.1 V vs. Ag/Ag+. This catalyst exhibits the highest current density with very high FE for producing methanol, as can be known in Supplementary Table 1. The cell voltage is an important factor for practical application, which depends mainly on the performances of the electrocatalysts. In this study, we calculated the cell voltage using the reported method46,47, and the cell voltage of our system was 2.67 V, which is in the range of reported values (2.2–3.7 V, Supplementary Table 3). In Supplementary Fig. 12, the FE for methanol production increased with the cell voltage to reach the maximum value of 77.6% at 2.67 V. We also calculated the energy efficiency (EE) for methanol production at different cell voltages using the reported method48, and the results are given in Supplementary Fig. 12. The EE exhibited a similar tendency to the FE of methanol with variation of the cell voltage. Furthermore, the highest EE was 61.7% at the optimized cell voltage of 2.67 V.

We also carried out the experiment using 13CO2 to replace CO2 in the electrolysis over Cu1.63Se(1/3). The 1H NMR spectra of the product indicated that only 13CH3OH was produced (Supplementary Fig. 13), confirming that the product methanol originated from CO2. Meanwhile, the electrolyte after different electrolysis times was also tested by IR8,49 in Supplementary Fig. 14, which can further confirm formation of methanol. In addition, FE and current density did not vary during 25 h of operation (Supplementary Fig. 15), which indicated exhibit long-term stability in the electrolysis. The composition and structure of the catalyst did not change after the reaction as characterized by XPS and XRD analysis (Supplementary Figs. 16 and 17), indicating the excellent stability of the Cu1.63Se(1/3).

The particle size and morphology of the materials can affect the number of exposed active sites. From Fig. 2d and Supplementary Fig. 1, we can see that the size of the catalysts synthesized at V_DETA/V_H2O = 1/3 was smallest and the current density and FE were larger. More active sites were exposed with more unsaturated Se atoms on the smaller particles may be one of the main reasons for high current density and FE29,30.
**Discussion**

The Tafel plots in Supplementary Fig. 18 and Supplementary Table 2 show the variation of overpotential with partial current density for methanol production over these catalysts. The resulting Tafel plots of various Cu$_{2-x}$Se(y) electrodes are linear in the overpotential (η) range from 0.035 to 0.285 V. The Tafel slope of Cu$_{1.63}$Se(1/3) was smaller than other Cu$_{2-x}$Se(y) nanocatalysts, which leads to faster increment of CO$_2$ reduction rate with increasing overpotential$^{[26,30]}$. Combining with efficient and stable electrocatalytic CO$_2$ conversion to methanol, the Cu$_{1.63}$Se(1/3) nanocatalysts can be a promising catalyst in practical applications.

The excellent activity of Cu$_{2-x}$Se(y) electrodes may also result partially from large electrochemical active surface area. According to the Randles–Sevic equation, the current density at −1.85 V (vs. Ag/Ag$^+$) plotted against the square root of scan rate is shown in Supplementary Fig. 19. The double-layer capacitances ($C_{dl}$) of various catalysts were then calculated and illustrated in Supplementary Table 2. The obvious difference in $C_{dl}$ values (ranging from 0.00906 to 0.0183 F cm$^{-2}$) suggests that the Cu$_{1.63}$Se(1/3) had the largest electrochemistry surface area, which is beneficial to the reaction.

Electrochemical impedance spectroscopy (EIS) also revealed an easier electron transfer process on the electrode interface. The Nyquist plot was conducted by running the experiment at an open circuit potential (Supplementary Fig. 20), and the equivalent circuit R(G(R(Q(RW)))) (Supplementary Fig. 21) is then used to fit the impedance data. The simulated results of charge transfer resistance ($R_{ct}$) are given in Supplementary Table 2. The results confirm that the charge transfer could easily occur on the Cu$_{1.63}$Se(1/3) electrode. It ensures a faster electron transfer to CO$_2$ for stabilizing reduced CO$_2$ intermediate that is vital for electroreduction CO$_2$. All the above results indicate that the particle sizes and morphologies of the catalysts played an important role for electroreduction CO$_2$.

We also used [Bmim]PF$_6$/CH$_3$CN/H$_2$O with different compositions as supporting electrolytes to perform the reaction over Cu$_{1.63}$Se(1/3). Compared with aqueous electrolyte, combination of organic solvents and ionic liquids as electrolytes has obvious advantages. For example, they can accelerate catalytic performance of CO$_2$ reduction by increasing the adsorption rate of CO$_2$,$^{[51,52]}$ and they provide more opportunity to produce various valuable products.$^{[12,33,34]}$ Meanwhile, the ionic liquids (ILs) with imidazolium cation and fluorine-containing anions can be the efficient supporting electrolytes for CO$_2$ reduction.$^{[33,34]}$ From Supplementary Tables 4 and 5, we can find that the [Bmim]PF$_6$ (30 wt%)/CH$_3$CN/H$_2$O (5 wt%) ternary electrolyte was most efficient for CO$_2$ for the reaction, and the current density could reach 41.5 mA cm$^{-2}$ with a Faradic efficiency of 77.6%. To further understand the role of anions in the ILs, other ILs were also used, including [Bmim]PF$_6$, [Bmim]BF$_4$, [Bmim]TF$_2$N, [Bmim]OAc, [Bmim]NO$_3$, and [Bmim]ClO$_4$ and acetoniitrile systems for comparison (Supplementary Figs. 22 and 23). It can be observed that the anions of the ILs also influenced the
electrochemical reaction significantly (Supplementary Fig. 23), which resulted partially from the difference of the interaction between CO2 and the anions of the ILs55. [Bmim]PF6 exhibited higher current density and Faradaic efficiency for methanol among all the ILs used. The separation of the reaction mixture is crucial for practical application. Although this is out of the scope of this work, we would like to discuss this very briefly. For this system, the boiling point of [Bmim]PF6 is much higher than that of CH3OH, CH3CN and H2O, and the IL in the system can be separated via distillation. Meanwhile, the method to separate ternary mixture consisting of CH3OH, CH3CN and H2O has been reported56.

It is very interesting to investigate the reasons for the outstanding performance of the Cu1.63Se(1/3) electrocatalyst in the electrocatalytic reduction of CO2 to methanol. Therefore, we carried out a series of control experiments to investigate the crucial role of Se in the catalysts. CO2 electroreduction with Cu, CuO, Cu2O, CuS, CuSe, and Cu2Se as catalysts were studied. Both current density and FE for methanol over Se-free catalysts were obvious lower (Fig. 3 and Supplementary Fig. 24). The results suggest that the Cu and Se in the catalysts cooperated very well for the formation of methanol. In other words, the capacity of electroreduction of CO2 to methanol was enhanced when O or S atom was replaced by Se atom in the catalysts. Moreover, when commercial CuSe or Cu2Se was utilized as the catalysts, both current density and FE were much lower than that over Cu1.63Se(1/3). The catalytic performance was also evaluated using the electrochemical active surface areas (ECSA) determined by reported method57. Results in Supplementary Fig. 25 and Supplementary Table 6 show that the formation rate of methanol over Cu1.63Se(1/3) was intrinsically higher than that on the other catalysts. Thus, on the basis of above results, we can deduce that Se in the catalysts is crucial for efficient CO2 reduction to methanol.

We also carried out extended X-ray absorption fine structure spectroscopy (EXAFS) experiments to study Cu K-edge, which can disclose the local atomic arrangements of the catalysts. The Cu K-edge $\chi(\kappa)$ oscillation curve for Cu1.63Se(1/3) was obviously different from that for CuSe and Cu2Se (Supplementary Fig. 26). It can be seen that the coordination number in Cu1.63Se(1/3) is smaller than that in CuSe and Cu2Se (Supplementary Figs. 27–30 and Supplementary Table 7). Thus, there existed unsaturated Se atom in the Cu1.63Se(1/3), which may enhance the performance for CO2 electroreduction.

To understand the reaction pathway for the formation of methanol, some control experiments were conducted in the presence of the possible reaction intermediates, such as formic acid, CO and formaldehyde (Supplementary Table 8). From the production rates of methanol, it can be seen that CO and formaldehyde clearly promoted the formation of methanol and thus they are possible intermediates in the formation of methanol. On the basis of the results above, we propose a possible reaction pathway over Cu2–xSe(y) nanocatalysts (Fig. 4a). In the initial stage of the reduction, the electrolyte containing ionic liquids can enhance the concentration of CO2 in electrolyte and transport of CO2 to the catalyst surface to improve further transform of CO2 into adsorbed CO2$^+$. The adsorbed CO2$^+$ could bind with the active sites on the surface of catalysts and accelerate the formation of adsorbed-CO species, which was a crucial intermediate for facilitating methanol production as reported20,58. Furthermore, the appropriate Cu active sites over the catalysts can enhance the initial intermediate of absorbed-CO to accept electrons and protons to form adsorbed-CHO and then reduced to methanol.

The density functional theory (DFT) calculations were also conducted on the multiple elementary reaction steps, and the results are shown in Fig. 4b and Supplementary Figs. 31–33. Comparing with other two catalysts (Cu2Se and CuSe), the formation of intermediate (*COOH) on the Cu1.63Se(1/3) surfaces can reach a stable configuration with lower free energy via two neighboring Cu atoms through Cu-C and Cu-O bonds. The *COOH intermediate binds with the active sites on the surface of catalysts and accelerate the formation of adsorbed *CO species59. The Cu1.63Se(1/3) catalyst also has a moderate binding energy for *CO among the three catalysts, which is beneficial for CO2 transformation to more reduced products that require more than a two-electron reduction20,58. Based on the Brønsted–Evans–Polanyi (BEP) relationship60,61, the reaction barrier has a linear relationship to the reaction energy, and it can also be seen that the step of *CO reduction to *CHO was an endothermic and likely rate-limiting step since the highest energy potential (0.56 eV) is needed in this step. Compared with CuSe and Cu2Se, the free energy of *CHO over Cu1.63Se(1/3) catalyst is more negative, which may be mainly originated from the moderately strong binding energy for *CO intermediate. In addition, the C-Cu bond (Supplementary Fig. 34) between Cu1.63Se(1/3)-CHO is 1.926 Å, which is shorter than those of Cu2Se-CHO (2.188 Å) and CuSeCHO (2.002 Å), indicating that *CHO is easier to adsorb on the surface of the catalyst to accept electrons and protons to form *OCH2 and *OCH3, and then is reduced to methanol. These results illustrate that the structure distortion of Cu1.63Se(1/3) was beneficial for CO2 electroreduction to methanol.

In summary, a series of Cu2–xSe(y) nanocatalysts were synthesized for selective electroreduction of CO2 to methanol. The Cu and Se in the catalysts had excellent cooperative effect for catalyzing the reaction. The size and morphology were crucial for the performance of the catalysts, which could be controlled by the $V_{\text{DETA}}/V_{\text{H2O}}$ ratios. The Cu1.63Se(1/3) nanocatalysts yielded outstanding current density of 41.5 mA cm$^{-2}$ with FE of 77.6% at $-2.1$ V vs. Ag/Ag$^+$. Moreover, the catalyst was also very stable in the catalytic system. Despite the catalytic system is far from industrial production, it is still very interesting that Cu1.63Se(1/3) nanocatalysts can yield highest current density up to date at very high Faradaic efficiency. We believe that some other transition metal selenides can be designed as efficient electrocatalysts for CO2 reduction.

**Methods**

**Materials.** CuCl2·2H2O, sulfuric acid (95–98%), ethanol, acetone and acetonitrile (CH3CN) were obtained from Sinopharm Chem. Reagent Co. Ltd. Na2SeO3, diethylenetriamine (DETA), Cu, CuO, Cu2O, CuS, CuSe, Cu2Se.
Fig. 4 Mechanism study of CO$_2$ reduction to methanol. a Proposed mechanism on Cu$_{2-x}$Se(y) electrode; b free energy diagrams on Cu$_{0.63}$Se(1/3) electrode.

Electrochemical study. All the electrochemical experiments were conducted on the electrochemical workstation (CHI 6081E, Shanghai CH Instruments Co., China). Linear sweep voltammetry (LSV) scans were conducted in a single compartment cell with a three electrodes configuration, including a working electrode, a counter electrode (Pt gauzes), and a reference electrode (Ag/AgCl with saturated KCl). The electrolytes were bubbled with CO$_2$ or N$_2$ at 5 wt% at an open circuit potential (OCP) with an amplitude of 5 mV from 10$^{-2}$ to 10$^3$ Hz. The data obtained from the EIS measurements were fitted using the software of Zview (Version 3.1, Scribner Associates, USA).

CO$_2$ reduction electrolysis. The electrolysis experiments were measured at 25 ℃ in a commonly used H-type cell, including a working cathode (Cu$_{2-x}$Se(y)/CP), a counter anode (platinum gauzes), and a reference electrode (Ag/Ag$^+$/Ag$^+$ with 0.1 M TBAP-CH$_3$CN). In the experiments, NaFon-117 membrane was used as proton exchange membrane to separate the cathode and anode compartments. 0.5 M HSO$_4$ aqueous solution and [Bmim][PF$_6$]-CH$_3$CN$_2$H$_2$O served as anodic and cathodic electrolytes, respectively. In each experiment, the amount of anodic and cathodic electrolytes was 30 mL. Before starting the electrolysis experiment, the electrolytes were bubbled with CO$_2$ for 30 min under stirring and the electrolysis was carried out under a steady stream of CO$_2$ (10 sccm).

Physicochemical characterization. The microstructures of the catalysts were characterized by scanning electron microscope (SEM, HUTCHICH S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100F) equipped with energy dispersive spectrometer (EDS). Dynamic light scattering (DLS) measurements in water with a volume ratio of VDETA/VH$_2$O = 1/3 (0.3 mL, 3/1, 1/1, 1/5 and 0/1). After stirring for half an hour at room temperature, the blue solution was then transferred into a Teflon-lined autoclave. Subsequently, the sealed Teflon-lined autoclave was maintained at 180 ℃ for 15 h and then naturally cooled to room temperature. The resulting precipitates were obtained via the method of centrifugation and washed with distilled water and absolute ethanol five times, followed by drying at 80 ℃ overnight in a vacuum oven.

Tafel analysis. The partial current densities for products under different potentials were measured, and the equilibrium potential was obtained by extrapolation method. The overpotential was obtained from the difference between the equilibrium potential and the catalytic potential. Multiple electrolysis experiments were performed at each potential to obtain the current density versus overpotential data in the H-type electrolysis cell as described above. Tafel plots were constructed from these data.

Synthetic procedures for Cu$_{2-x}$Se(y) nanocatalysts. The Cu$_{2-x}$Se(y) nanocatalysts were prepared according to the procedures reported by other researchers. In a typical procedure, 1 mmol Cu$_2$ZnL$_2$O$_4$, 1 mmol Na$_2$SeO$_3$, and 2 mL hydroxylamine were added into a mixed solvent (80 mL) including DETA and deionized water with a volume ratio of VDETA/VH$_2$O = 1/3 (0.3 mL, 3/1, 1/1, 1/5 and 0/1). After stirring for half an hour at room temperature, the blue solution was then transferred into a Teflon-lined autoclave. Subsequently, the sealed Teflon-lined autoclave was maintained at 180 ℃ for 15 h and then naturally cooled to room temperature. The resulting precipitates were obtained via the method of centrifugation and washed with distilled water and absolute ethanol five times, followed by drying at 80 ℃ overnight in a vacuum oven.
The shift $\Phi$ of the $\eta$ can be determined using Eq. (1):

$$\eta = E - \Phi^{\text{CO}_2-\text{methanol}}$$  \hspace{1cm} (1)

Here, the $\Phi^{\text{CO}_2-\text{methanol}}$ refers to the equilibrium potential for CO$_2$ transformation to CH$_3$OH, which can be obtained by extrapolation methods$^{34-35}$. Taking the Cu$_{1.63}$Se(1/3) electrode as an example, stepped potential electrolysis experiments between $-1.8$ and $-2.0$ V were carried out and the electrolysis products were collected and characterized. The current densities for CH$_3$OH at each potential are shown in Supplementary Fig. 11, and the potential at $U_{\text{CH}_3\text{OH}} = 0$ by extrapolation method is the equilibrium potential. Therefore, the overpotential can be obtained. The method to calculate the overpotential over other electrodes was similar.

**The calculation of cell voltage.** In this study, we calculated the cell voltage using the method reported$^{46,47}$. It is mainly from the half reaction potentials for water oxidation, CO$_2$ reduction and the ohmic drop ($\eta$) from electrolyte resistance ($R_i$). The $R_i$ stands for solution resistance which was determined by electrochemical impedance spectroscopy (EIS) at frequencies ranging from 10$^{-2}$ to 10$^2$ Hz and the $I$ represents for amps of current. Therefore, we calculated $E_{\text{cell}}$ by Eq. (2).

$$E_{\text{cell}}(\text{vs. RHE}) = R_i \times I \text{amps of average current}$$  \hspace{1cm} (2)

The cell efficiency. A characteristic cell energy efficiency (EE) of reduction CO$_2$ to methanol was obtained by Eq. (4)$^{48}$. EE is the fraction of the actual reaction energy of the cell to the theoretical energy, which is given by Eq. (5).

$$EE = \frac{\text{FE}(\%)}{\text{applied cell voltage}}$$  \hspace{1cm} (4)

In the equation, $\Delta\Phi$ represents the difference between the standard half reaction potentials for water oxidation (1.23 V vs. RHE) and reduction CO$_2$ to methanol ($-0.89$ V vs. RHE).

**Extended X-ray absorption fine structure (EXAFS) experimental details.** The homogeneously mixed samples (20 mg) and graphite (100 mg) sample were pressed into circular slices with a diameter of 10 mm which was used for further EXAFS measurement under ambient condition. The EXAFS measurements were carried out on the beamline 1W1B station of Beijing Synchrotron Radiation Facility, P.R. China (BSRF). A water-cooled Si (111) double-crystal monochromator (DCM) was utilized to monochromatize the X-ray beam and the detuning was done by 10% to remove harmonics. The electron storage ring of BSRF was operated at 2.5 GeV with a maximum current of 250 mA. The EXAFS data of Cu K-edge was obtained in the energy range from $-200$ to 1000 eV in transmission mode. The EXAFS oscillations were then extracted according to standard procedures via the ATHENA module implemented in the IFEFFIT software packages. With a Fourier transform k-space range of 2.2–12.8 Å$^{-1}$, the quantitative curve-fittings were conducted in the k-space according to the module ARTEMIS of IFEFFIT software packages. The phase shift $\Phi(k)$ and backscattering amplitude $f(k)$ were calculated by FEFF 8.0 code.

**Computational method.** The free energies of CO$_2$ reduction states were performed using Vienna Ab-initio Simulation Package (VASP)$^{49}$, taking advantage of the density functional theory (DFT) and the Projected Augmented Wave (PAW) method$^{50}$. The revised Perdew–Burke–Ernzerhof (RPBE) functional was used to describe the exchange and correlation effects$^{51}$. For all the geometry optimizations, the cutoff energy was set to be 450 eV. The (110) surface was chosen to represent the catalysis surface of CuSe; while the (220) surface was modeled to simulate the sites on Cu$_{1.63}$Se(1/3) and Cu$_2$Se. The Monkhorst-Pack grid$^{52}$ of $2 \times 2 \times 1$, $3 \times 4 \times 1$, and $3 \times 4 \times 1$ were used to carry out the surface calculations on CuSe, Cu$_{1.63}$Se(1/3), and Cu$_2$Se, respectively.

The reduction of CO$_2$ to CH$_3$OH could occur via a pathway involving six elementary steps$^{53}$ by Eqs. (5–10):

- $\text{CO}_2 + (H^+ + e^{-}) + * \rightarrow \text{COOH}$
- $\text{COOH} + (H^+ + e^{-}) \rightarrow \text{CO} + \text{H}_2\text{O}$
- $\text{CO} + (H^+ + e^{-}) \rightarrow \text{CHO}$
- $\text{CHO} + (H^+ + e^{-}) \rightarrow \text{OCH}_2$
- $\text{OCH}_2 + (H^+ + e^{-}) \rightarrow \text{OCH}_3$
- $\text{OCH}_3 + (H^+ + e^{-}) \rightarrow \text{CH}_3\text{OH} + *$

where * denotes the active sites on the catalyst surface. Based on the above mechanism, the free energies of the corresponding intermediate states are important to identify the activity of a given material in catalyzing CO$_2$ reduction. The computational hydrogen electrode (CHE) model$^{54}$ proposed by Norskov et al. was used to calculate the free energies of CO$_2$ reduction intermediates, based on which the free energy of an adsorbed species is defined as Eq. (11):

$$\Delta G_{\text{ads}} = \Delta G_{\text{ads}} + \Delta G_{\text{P}2\text{E}} - T\Delta S_{\text{ads}} + \int C_{\text{p}2\text{D}}dT$$  \hspace{1cm} (11)

where $\Delta G_{\text{ads}}$ is the electronic adsorption energy, $\Delta G_{\text{P}2\text{E}}$ stands for the zero point energy difference between adsorbed and gaseous species, $T\Delta S_{\text{ads}}$ denotes the corresponding entropy difference between these two states, and $C_{\text{p}2\text{D}}DT$ is the enthalpy correction. The electronic binding energy is referenced as graphene for each C atom, $\frac{1}{2}$ H$_2$ for each H atom, and (H$_2$O – H$_2$) for each O atom, plus the energy of the clean slab. The corrections of zero point energy, entropy, and enthalpy of adsorbable can be found in Supplementary Table 9.

**Code availability.** All code supporting the findings of this study are available from the corresponding author on request.

**Data availability.** Data for Figs. 1 to 4, Supplementary Figures 1 to 34 and Supplementary Tables 1 to 9 can be found in the Source Data file.

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Author contributions
D.X.Y., Q.G.Z., and B.X.H. proposed the project, designed the experiments, and wrote the manuscript; D.X.Y. performed the whole experiments; C.J.C., H.Z.L., Z.M.L., Z.J.Z., X.Y.Z., and S.J.L. performed the analysis of experimental data; B.X.H. and Q.G.Z. supervised the whole project.

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