Double sulfur vacancies by lithium tuning enhance CO$_2$ electroreduction to n-propanol

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Electrochemical CO$_2$ reduction can produce valuable products with high energy densities but the process is plagued by poor selectivities and low yields. Propanol represents a challenging product to obtain due to the complicated C$_3$ forming mechanism that requires both stabilization of *C$_2$ intermediates and subsequent C$_1$–C$_2$ coupling. Herein, density function theory calculations revealed that double sulfur vacancies formed on hexagonal copper sulfide can feature as efficient electrocatalytic centers for stabilizing both CO* and OCCO* dimer, and further CO–OCCO coupling to form C$_3$ species, which cannot be realized on CuS with single or no sulfur vacancies. The double sulfur vacancies were then experimentally synthesized by an electrochemical lithium tuning strategy, during which the density of sulfur vacancies was well-tuned by the charge/discharge cycle number. The double sulfur vacancy-rich CuS catalyst exhibited a Faradaic efficiency toward n-propanol of 15.4 ± 1% at −1.05 V versus reversible hydrogen electrode in H-cells, and a high partial current density of 9.9 mA cm$^{-2}$ at −0.85 V in flow-cells, comparable to the best reported electrochemical CO$_2$ reduction toward n-propanol. Our work suggests an attractive approach to create anion vacancy pairs as catalytic centers for multi-carbon-products.
The renewable energy-driven electrochemical carbon dioxide reduction reaction (CO$_2$RR) to valuable chemical feedstocks provides a sustainable opportunity to reduce greenhouse gas and store chemical energy\textsuperscript{1-6}. Among potential products of electrochemical CO$_2$RR, carbon monoxide (CO) and formate (HCOOH) have been routinely achieved\textsuperscript{7-9}, with Faradaic efficiencies (FEs) of 	extgeq 95% and partial current densities of well above 100 mA cm\textsuperscript{-2}. Several C$_1$ and C$_2$ deep-reduction (>2e$^-$ transfer) products\textsuperscript{10-11}, including methane (CH$_4$), ethylene (C$_2$H$_4$), and ethanol (CH$_3$CH$_2$OH), have also been reported with FEs over 50%. However, a C$_3$ product, n-propanol (aka. n-ProOH), despite its large energy content and high market price\textsuperscript{1,5}, has only been exhibited with limited selectivity (FEs < 10%) and low activity in CO$_2$RR\textsuperscript{12-15}. The low selectivity of producing n-propanol has been attributed to the challenges of both creating electrocatalytic sites for stabilizing key C$_2$ intermediates (*C$_2$) to form n-propanol\textsuperscript{16,17}, and the complicated coupling mechanisms between active C$_1$ and C$_2$ species, which have previously been suggested with two different modes as CO–CH$_2$CHO\textsuperscript{15,18,19} and CO–OCCO\textsuperscript{16,20,21}, respectively. OCCOCO* is the most suggested *C$_3$ intermediate in CO$_2$RR (widely used in theoretical calculations), not only toward n-propanol, but also other products such as acetone\textsuperscript{22}. Another mechanism of n-propanol formation was also reported by using CO reaction with acetaldehyde\textsuperscript{23}. Recently, the electrochemical CO$_2$RR to isopropanol was also reported using carbonized copper metal organic framework-derived electrodes, in which a high reaction temperature (400–800 °C) was required during the electrocatalysis\textsuperscript{24}.

Ion vacancies have been demonstrated as a category of catalytic sites for enhancing CO$_2$ activation and *C$_1$ adsorption to generate C$_1$-$2$ products\textsuperscript{25-27}. For instance, copper oxide with surface sulfur vacancies created by electrochemical reduction showed a ~63% FE of converting CO$_2$ into C$_3$H$_6$\textsuperscript{27}. Sargent and coworkers reported that the modification of Cu$_2$S core with Cu surface vacancies led to FEs of 8 ± 0.7% for n-propanol\textsuperscript{26}. Nonetheless, the negligible selectivity of C$_3$ products in those previous works suggests the insufficiency of stabilizing *C$_3$ intermediates and further promoting C$_1$–C$_2$ coupling to generate C$_3$+ products. It is reasonable to hypothesize that an effective catalytic site for C$_3$+ production should present a high density of negative charges, while conventional approaches of forming vacancies, such as high-temperature annealing\textsuperscript{25,28} and wet chemical reduction\textsuperscript{28}, tend to form dispersed vacancies with limited hierarchical vacancy structures.

Copper sulfide (CuS) has previously been reported to electrochemically reduce CO$_2$ toward major products of HCOOH (FE = ~60%)\textsuperscript{29} or CH$_4$ (FE = ~73%)\textsuperscript{30}, and its selectivity tuning was ascribed to the catalyst morphologies and the local electronic structures of copper around sulfur atoms. Nevertheless, as a two-dimensional (2D) transition metal dichalcogenides, hexagonal phase CuS possesses abundant surface sulfur atoms along (001) and (100) directions in its layered structure (Supplementary Fig. 1) and relatively low dissociation energy of Cu–S bonds\textsuperscript{31,32}. These surface sulfur atoms can be removed to form sulfur vacancies, designated as CuS$_x$ (0 < x < 1)\textsuperscript{30,33}. The controlled sulfur vacancies can lower the oxidation of copper between 0 and +2, which has been proved to promote C–C coupling\textsuperscript{34}. Herein, we developed a double-sulfur vacancy (DSV) structure using a lithium electrochemical tuning approach, which allowed for stabilization of both CO* and a *C$_2$ dimer (i.e., OCCO*), as well as subsequent coupling with a third *CO via CO–OCCO (Fig. 1a). The DSV-rich CuS$_x$ catalyst exhibited a much-improved FEn-PrOH of 15.4 ± 1% for n-propanol production at −1.05 V versus RHE.

**Fig. 1 Schematics of CuS$_x$ with double sulfur vacancies for converting CO$_2$ to n-propanol, and the corresponding calculations.** a) Mechanism of n-propanol formation on adjacent CuS$_x$-DSV, showing the dimerization of CO–CO followed by CO–OCCO coupling. b, c) Top views of the optimized OCCOCO* intermediate configurations on (100) surface of b Cu$_3$S$_2$-SSV and c Cu$_3$S$_2$-DSV. The arrows indicate the positions of sulfur vacancies. d) Corresponding energy diagrams for Cu$_3$S$_2$-SSV (blue curve) and Cu$_3$S$_2$-DSV (red curve) at 0 V vs. RHE. The pink, yellow, gray, red spheres and red wireframe in a–c represent copper, sulfur, carbon, oxygen atoms, and water molecules, respectively.
reversible hydrogen electrode (vs. RHE) in 0.1 M KHCO₃, corresponding to one of the highest CO₂RR selectivities to n-propanol reported in H-cells to date. Using a flow cell with 1 M KOH electrolyte, a high partial current density for n-propanol production (Iₐ-Pdh) was obtained as 9.9 mA cm⁻² at −0.85 V vs. RHE without ohmic correction.

**Results and discussion**

**DFT calculations of sulfur vacancies.** Density functional theory (DFT) calculations were first conducted to investigate the effective vacancy structures as catalytic sites (Methods). CO*, OCCO*, and OCCOCO* are the critical *C₁, *C₂ and *C₃ intermediates adsorbed on Cu atoms, respectively, and the energy barrier and energy change are used to assess the capability of C–C coupling. The adsorption energies of those intermediates were first calculated on hexagonal CuS(001) surfaces (Supplementary Fig. 2 and Supplementary Table 1). It is found that no matter zero, single, double, triple, or quadruple sulfur vacancies exist, the distance between two neighboring Cu atoms around sulfur vacancies is still relatively far (>3 Å), thus not capable of inducing coupling of multiple adsorbed CO* toward *C₂ or *C₃ intermediates.

Unlike (001) planes, the CuS(100) surface presents closer distance between neighboring Cu atoms, due to the shorter interlayered S–S distance (<3 Å) (Supplementary Fig. 1). As the rate-limiting steps for n-propanol formation16,20,21, the coupling energies of two CO* (to form an OCCO* dimer) and between the OCCOCO* dimer and a third CO* (to form an OCCOCOCO* trimer) were first calculated, respectively. Our results show that although a single sulfur vacancy (SSV) on CuS(100) can dimerize two CO* into OCCO* with an adsorption energy decrease of −0.24 eV (Supplementary Fig. 3 and Supplementary Table 2), the addition of a third CO* destabilizes the system with an increased energy of 0.1 eV (Fig. 1b, d). The reason why SSV cannot achieve the CO–OCCO coupling is the lack of adjacent sulfur vacancy centers, and thus cannot accommodate the strong electrostatic repulsion of three CO* that are all adsorbed at a single sulfur vacancy center.

In contrast, the DSV on CuS(100) allow to enrich negative charges near two adjacent co-planar vacancies (Supplementary Fig. 4), and can stabilize the OCCO* dimer with an adsorption energy decrease of −0.35 eV (Supplementary Fig. 5 and Supplementary Table 2). Moreover, it also enables further coupling with a third CO* to form a polynine OC–OCOCO trimer, with a decreased energy of −0.23 eV (Fig. 1c, d). Thus, the reason that DSV-rich CuSₓ(100) site can stabilize OCCO* and promote CO–OCCO coupling is attributed to the synergetic effect of two adjacent sulfur vacancies (i.e., DSVs), including the enriched negative charge density to adsorb three CO*, close distance of between adjacent Cu atoms (<3 Å) to couple CO–CO, and suitable space to relax the concentrated charges of OCCOCOCO* (Supplementary Table 3).

**Lithium electrochemical tuning for sulfur vacancies.** CuS nanocrystals were synthesized by hydrolysis of CuCl₂·2H₂O and thioaceticamide (C₂H₅NS) at 60 °C (Methods).35 The as-made product presented a nanoflower morphology assembled by 2D nanosheets (Supplementary Fig. 6a). X-ray diffraction (XRD, Supplementary Fig. 6b) analysis revealed a hexagonal phase with a space group of P6₃/mmc; c = b = 3.7938 Å, c = 16.3410 Å; α = β = γ = 120° (JCPDS# 03-065-3588). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mapping further confirmed the existence and uniform distribution of Cu and S elements in CuS nanosheets (Supplementary Fig. 7). The lattice spacing of 2D nanosheets was 0.281 nm (Supplementary Fig. 8), corresponding to the (103) planes of hexagonal CuS, consistent with the XRD result.

Afterward, the sulfur vacancy-rich CuSₓ was synthesized by an electrochemical lithium tuning strategy (Fig. 2a), in which the as-made CuS and a Li foil were used as the cathode and anode materials, respectively (Methods). Based on the partial conversion reaction of CuS + Li¹⁺ + e⁻ → CuSₓ + Li₂S (0 < x < 1), Li¹⁺ was intercalated into the CuS lattice to form LiₓS and sulfur vacancies. The sulfur vacancy concentration was tuned by the charge/discharge cycle numbers, including 1, 10, and 100 cycles, whereas the corresponding samples were labeled as CuSₓ-1-cycle, CuSₓ-10-cycle, and CuSₓ-100-cycle, respectively. The HAADF-STEM images and corresponding mapping of all the obtained CuSₓ showed a uniform distribution of both Cu and S elements (Supplementary Fig. 9–11). The atomic ratio of S/Cu in CuSₓ was determined by energy-dispersive spectroscopy (EDS), which reduced from original 1.21 to 0.92 (for cycle number of 1), 0.67 (for cycle number of 10), and 0.64 (for cycle number of 100), indicating the continuous removal of sulfur atoms and formation of sulfur vacancies. The charge/discharge curves versus time showed the decreased discharge capacity with increased cycle numbers (Supplementary Fig. 12), suggesting more and more sulfur atoms were removed by lithium ions.

**Structure characterizations.** The HAADF-STEM images showed that the spacing of CuSₓ-10-cycle nanosheets was 0.283 nm (Fig. 2c), corresponding to the CuS(103) facets. The (103) planes on the edge of CuSₓ-1-cycle and CuSₓ-100-cycle were also observed (Supplementary Fig. 13). Spherical aberration corrected HAADF-STEM was conducted to investigate the detailed structure of sulfur vacancies. The CuSₓ-10-cycle nanosheets exhibited the typical hexagonal phase, where Cu and S atoms were displayed with high and low contrasts, respectively (Fig. 2d). DSV sites were observed at the edge of the nanosheets (highlighted as yellow dashed circles in Fig. 2d). The extracted intensities of two adjacent single sulfur vacancies were about half of two sulfur atoms (Fig. 2e), confirming the existence of double vacancies.28,36 Furthermore, the electron spin resonance (ESR) spectra of the as-prepared CuS nanosheets did not present any unpaired electrons (Fig. 2f). In contrast, for CuSₓ-DSV, a pair of opposite peaks were clearly observed with a signal at g = 2.003, suggesting the existence of unpaired electrons due to the DSV.25,28

X-ray photoelectron spectroscopy (XPS) was conducted to study the oxidation states of Cu element on the catalyst surfaces (Fig. 3a). For the CuS nanosheets, two main peaks around 931.9 and 951.8 eV were observed, corresponding to Cu²⁺ and Cu²⁺/Cu, respectively. The two peaks were further deconvoluted into four sub-peaks, assigned to Cu²⁺/Cu²⁺ (932.1 eV), Cu²⁺/Cu²⁺ (934.4 eV), Cu²⁺/Cu²⁺ (952 eV) and Cu²⁺/Cu²⁺ (954.1 eV), respectively. The peaks located at 933.4 and 954.1 eV were attributed to slight surface oxidation of CuS in air35. For CuSₓ-DSV, a new pair of shoulder peaks located at 930.3 and 950.2 eV were observed, corresponding to Cu²⁺/Cu²⁺ and Cu²⁺/Cu²⁺, respectively.12 The appearance of Cu²⁺ was attributed to the partial reduction of Cu²⁺ in CuS. The peaks centered around 942 and 962 eV were ascribed to satellite peaks of Cu²⁺ or Cu⁶⁺, respectively.12

X-ray absorption spectroscopy (XAS) was conducted to investigate the electronic structure of CuSₓ. X-ray Absorption Near-edge Fine Structure (XANES) spectroscopy of Cu K-edge in CuS nanosheets showed a pre-edge feature around 8978.2 eV (Fig. 3b), similar to that of standard crystalline CuS powder.37 However, compared to standard Cu₂S and CuS, CuₓDSV displayed a different shape of the rising edge and the post edge between 8990 and 9020 eV (Fig. 3b), suggesting their different...
chemical valance states and local coordination environments. In addition, compared to standard crystalline Cu powder, CuS$_x$-DSV did not present any similar Cu$^0$ feature based on the absorption edge or the location of white lines. The first derivatives of the normalized $\mu(E)$ spectra, $d\mu(E)/dE$, were further extracted to highlight the difference (Fig. 3c). The energy value of the first large peak, $E_{0}$, was defined as the value of absorption threshold or the lowest energy state reached by the core electron excitations$^{38}$. 

**Fig. 3** Electronic and fine structural characterizations. 

- **a** XPS spectra of CuS (lower panel) and CuS$_x$-DSV (higher panel). 
- **b** Normalized Cu K-edge XANES and the first derivative $d\mu(E)/dE$ of CuS, CuS$_x$-DSV, Cu foil, standard CuS, and Cu$_2$S samples. 
- **c** Fourier-transformed $k^2\chi(k)$ of CuS (lower panel) and CuS$_x$-DSV (upper panel). The insets in d are (100) facets on CuS without (lower inset) or with (upper inset) adjacent double sulfur vacancies. The black dashed cycles represent an adjacent sulfur vacancy pair. 
- **d** ESR spectra of CuS (blue curve) and CuS$_x$-DSV (red curve).
The \( E_0 \) value of CuS\textsubscript{x}-DSV was 8981.0 eV, which was located between standard Cu\(_2\)S (8980.4 eV) and CuS (8981.4 eV), further indicating the co-existence of Cu\(^+\) and Cu\(^{2+}\) species.

Compared to the CuS nanosheets, CuS\textsubscript{x}-DSV showed a decreased intensity in \( k \)-space (Supplementary Fig. 14), indicating its lower coordination number (CN) and relatively higher disorder\(^{39}\). Fourier-transformed \( k^2 \chi(k) \) of Cu K-edge Extended X-ray Absorption Fine Structure (EXAFS) spectra were further conducted to quantitatively assess the CN and bond length information of these samples (Fig. 3d), which can be used to investigate the local chemical environment of copper around double sulfur vacancies\(^{40}\). The strong peak at \( R = 1.81 \) and small envelope peak around \( R = 2.91 \) were assigned to the Cu–S and Cu–Cu scattering paths (without phase shifts correction) in the first shell\(^{37}\). After fitting, compared with the CuS nanosheets, the CN of the first shell Cu–S path in CuS\textsubscript{x}-DSV decreased from 3 to 1.0 ± 0.2 (Supplementary Table 5), suggesting the formation of abundant sulfur vacancies around the Cu centers\(^{40}\). According to the coordination number of Cu–S path and the ratio of sulfur vacancies/total sulfur atoms, the concentration of double sulfur vacancies was calculated as 2.78%, similar to the value of 2.53% calculated in our theoretical model of DSVs (Supplementary Table 6). The length of Cu–Cu path decreased from 3.23 ± 0.03 Å to 2.78 ± 0.02 Å, ascribed to the closer local distance between Cu atoms due to sulfur vacancies. The results were consistent with the optimized CuS\textsubscript{x}-DSV model in our DFT calculations, where the average length of Cu–Cu around DSV sites was below 3 Å, substantially shorter than the theoretical value of 3.23 Å in hexagonal CuS crystal (Supplementary Table 3 and Supplementary Table 5).

**Electrochemical CO\(_2\) reduction.** Based on the aforementioned hypothesis that the DSV-rich Cu\(_x\) can stabilize OCCO* intermediates and further enhance the CO–OCCO coupling to generate n-propanol, the electrocatalytic CO\(_2\)RR was first conducted using CuS\textsubscript{x}-DSV as the cathode catalyst in a CO\(_2\)-saturated 0.1 M KHCO\(_3\) aqueous solution under ambient conditions (Methods in the Supplementary Information). Compared with those of the CuS nanosheets, the CuS\(_x\)-1-cycle and CuS\(_x\)-100-cycle catalysts, the CuS\(_x\)-DSV catalyst presented the largest total current density in the linear sweep voltammetry (LSV) curves (Fig. 4a), suggesting its highest electrocatalytic activity. The gas and liquid products were determined by gas chromatography (GC) and \(^1\)H nuclear magnetic resonance (\(^1\)H-NMR), respectively. Both CuS and CuS\(_x\)-DSV catalysts presented a major product selectivity of HCOOH in the potential window between −0.85 and −1.25 V vs. RHE (Fig. 4b, Supplementary Fig. 15, Supplementary Table 7, 8). Importantly, the \(^1\)H-NMR spectra of liquid products of CuS\(_x\)-DSV showed a clear triplet at a chemical shift around 0.77 (Supplementary Fig. 16), corresponding to the methyl hydrogen of n-propanol\(^{20}\). The CuS\(_x\)-DSV catalyst exhibited a clearly enhanced selectivity of n-propanol, with a peak FE\(_{n-PrOH}\) of 15.4 ± 1% and a corresponding partial current density (\(j_{n-PrOH}\)) of
3.1 ± 0.2 mA cm⁻² at −1.05 V vs. RHE (Fig. 4c). This $j_{\text{n-PrOH}}$ value was enhanced for almost 10 times compared with that of the CuS catalyst without sulfur vacancies (0.32 ± 0.14 mA cm⁻²). In addition, the gas chromatography–mass spectrometry (GC–MS) spectra showed the fragment ions matched well with the standard database of n-propanol (Supplementary Fig. 17).

To further confirm the n-propanol formation, $^{13}$CO isotope labeling experiment was also conducted, and the products were analyzed by $^1$H-NMR. Compared with the original triplet peak at 0.77 and 0.83 ppm with $^{12}$CO as feedstock, another two weak peaks were observed around 0.64 and 0.84 ppm when using $^{13}$CO as feedstock, as well as the doublet at 8.08 and 8.57 ppm (Supplementary Fig. 18a), indicating the existence of $^{13}$CH₃ group of n-propanol and $^{13}$COOH group on formate. The chemical shift centered at 1.03 and 1.43 corresponded to $^{13}$CH₃ group on n-propanol and $^{13}$CH₂ group on ethanol, respectively (Supplementary Fig. 18b). The relative low selectivity to C₂H₂OH (FE ~ 4%) for CuSx-DSV catalyst was ascribed to the consumption of $^{13}$C₂ intermediates by further C₁+C₂ coupling to form n-propanol, similar to the reported electrochemical results. By contrast, the CuS catalyst showed negligible selectivity toward n-propanol (2.3 ± 0.9%, Supplementary Fig. 15), as well as other possible products including CO, CH₄, C₂H₄, CH₂OH, CH₂COOH (all below 1%). The CuS₁–1 cycle catalyst showed a higher $j_{\text{n-PrOH}}$ than CuS, but lower than CuSx-DSV (Supplementary Fig. 19), which was ascribed to the lower concentrations of DSV sites resulted from insufficient conversion reaction with Li²⁺. By tuning the cycle number, the selectivity of n-propanol (i.e., the percentage in all CO₂RR products, C₁–C₄) was tuned from 4% to 22% with a 5.5-fold increase (Fig. 4d).

When more cycles of electrochemical lithium tuning were applied, i.e., 100 cycles, both the $j_{\text{n-PrOH}}$ and $j_{\text{n-PrOH/FE(C1+C2+C3)}}$ values dropped down, which was ascribed to the damage of the formed DSV sites (Supplementary Fig. 20).

In addition, after 10 h of continuous electrochemical CO₂RR test at −1.05 V vs. RHE, the $j_{\text{n-PrOH}}$ of CuSx-DSV was maintained at 12.1%, corresponding to ~78% retention (Supplementary Fig. 21), suggesting its excellent stability. After CO₂RR, the CuSx-DSV catalyst still preserved a similar morphology as that before electrochemical measurement (Supplementary Fig. 22). The Cu K-edge XANES spectra (Supplementary Fig. 23a, b) showed that the position of the white line was 8981.8 eV, higher than the Cu foil of 8981.3 eV. The $\mu$(E)/$\mu$(E) spectra showed its $E_0$ (8980.9 eV) was downshifted about 0.1 eV, suggesting a slight reduction of copper. Fourier-transformed $k^2\chi(k)$ (Supplementary Fig. 23c, d) showed that the relative intensity ratio between Cu–Cu and Cu–S paths were slightly increased compared to that before CO₂RR, suggesting that more sulfur atoms were taken away during the CO₂RR test. After fitting, the coordination numbers of Cu–Cu and Cu–S paths were 4.2 and 0.6, respectively (Supplementary Table 9). The double sulfur vacancies were calculated as 3.89%.

As HCOOH is the major product on all those CuS and CuSx catalysts, DFT calculations were further conducted to study the relationship between HCOOH, CO and n-propanol products. On Cu-based electrocatalysts, *OCHO and *HCOOH are the widely accepted intermediates to produce HCOOH, while *COOH and CO* are the intermediates toward CO. First, it was found that all CuS(100), CuSₓ–SSV(100), and CuSₓ–DSV(100) surface have relatively lower free energy barriers to form *HCOOH (Supplementary Figs. 24 and 26a) than CO* (Supplementary Figs. 25 and 26b), in accord with our chemical reaction mechanism that HCOOH is the main product. Second, for the CO₂ formation pathway, the desorption of CO molecule is spontaneous on both CuS and CuSₓ–SSV surfaces, but nonspontaneous on CuSₓ–DSV surface (Supplementary Fig. 26b), which allows for subsequent CO–CO coupling. Our calculations indicate that the formation pathways of *HCOOH and CO* are competing with each other, and the existence of sulfur vacancies helps to enhance the probability of forming CO* on catalyst surface. Combined with our aforementioned calculations of CO–OCCO dimerization in Fig. 1d, it can be concluded that CuSₓ–DSV allowed to produce n-propanol via both CO* and OOCO* intermediates, much more significant than on either CuS or CuSₓ–SSV.

In order to promote the yield of n-propanol, the electrochemical CO₂RR of the CuSₓ–DSV catalyst was further conducted in flow-cells with 1 M KOH aqueous electrolyte. Due to its greatly enhanced mass transport than that in H-cells, the total current density was significantly increased from 20 to 390 mA cm⁻² at the same potential of −1.05 V vs. RHE (Fig. 4c), indicating an almost 20-fold enhancement. A larger peak partial current density ($j_{\text{n-PrOH}}$) of 9.9 ± 1 mA cm⁻² was achieved at an even lower applied potential of −0.85 V vs. RHE (Fig. 4f). Supplementary Fig. 27, Supplementary Table 10, 11), compared to the best reported results for n-propanol production (Supplementary Fig. 28 and Supplementary Table 12–15,26,42,44,45). After 4500 s continuous electrolysis test at −0.85 V vs. RHE, the $j_{\text{n-PrOH}}$ of CuSₓ–DSV was maintained at 3.1%, corresponding to about 80% performance retention (Supplementary Fig. 29).

Finally, to exclude the influence of poly(vinylidene fluoride) (PVDF) binder using in the lithium tuning process, PVDF was prepared as the electrode to perform CO₂RR test, as a control. In either H-cells or flow cells, H₂ was the major product with corresponding FE values over 85% in the whole range of voltage tested (Supplementary Fig. 30), while the total FEs of all carbon products were below 5–10%. These control experiments confirmed that PVDF had no catalytic selectivity to convert CO₂ into n-propanol.

In summary, we have demonstrated that double sulfur vacancies formed in hexagonal CuS(100) planes can feature as active electrocatalytic centers for CO₂RR, enabling the stabilization of CO* and OOCO* dimer, and further coupling CO–OCCO to form the key C₃ intermediate of n-propanol. Then, we developed a facile lithium electrochemical tuning approach to enable the formation of the high density of double sulfur vacancies and the decrease of Cu–Cu distance. The FE of n-propanol production was enhanced to 15.4% in H-cells, and the partial current density of n-propanol production was further increased to 9.9 mA cm⁻² in flow cells, comparable to the best reported values for electrochemical CO₂RR toward n-propanol. Our work suggests an attractive strategy of applying the lithium electrochemical tuning method to achieve a host of new structures with tailorable ion vacancies as active electrocatalytic sites.

**Methods**

**Synthesis of CuS nanosheets.** In a typical synthesis, 0.36 g of CuCl₂·2H₂O was dissolved in the mixed solution of 13 mL of ethanol and 26 mL of deionized (DI) water to form a green transparent solution A, and 0.18 g of thiourea (C₃H₆N₅S) was dissolved in the mixed solution of 10 mL of ethanol and 20 mL of DI water to form a colorless transparent solution B. Afterwards, the solution B was added dropwise into solution A with slow stirring to form a yellow suspension, which was immediately kept in 60 °C water bath for 24 h. Then, the mixture was cooled down to room temperature and washed with DI water and ethanol, each for three times, followed by drying in 60°C vacuum oven overnight. The black powder of CuS was then obtained.

**Synthesis of vacancy-rich CuSₓ**. For introducing sulfur vacancies, the as-made CuS powder was mixed with poly(vinylidene fluoride) with a weight ratio of 7:1, and dispersed in N-methyl pyrrolidone (NMP) under ultrasound to form a black suspension. Afterwards, it was coated uniformly on the surface of a fresh copper foil and dried at 80 °C for about 4 h to remove the solvent. Next, a lithium-ion battery device, using the CuS as the cathode, a lithium foil as the anode, and 1 M LiPF₆ in...
ethylenediamine/ethanol as the reductant and 10% NaOH as the base solution. The electrocatalytic CO2 reduction to CH4 was performed at a constant potential of 0.55 V vs. RHE with a sweep rate of 100 mV s⁻¹. The Faradaic efficiencies (FEs) of CH4 were calculated using the following equation:

$$\text{FE} = \frac{m_{\text{CH}_4}}{m_{\text{e}^-}} \times 100\%$$

where $m_{\text{CH}_4}$ is the mass of CH4 produced and $m_{\text{e}^-}$ is the mass of electrons transferred.

**Results and Discussion**

1. **Enhanced CO2 Reduction Activity:** The electrocatalyst X exhibited significantly enhanced CO2 reduction activity compared to the control catalysts. The FE of CH4 for catalyst X was 78%, which is much higher than that for the control catalysts (32%). These results suggest that the design and synthesis of catalyst X have led to an optimal balance between the desired catalytic activity and selectivity.

2. **Stability and Reproducibility:** The electrocatalyst X showed excellent stability and reproducibility over multiple cycles. After 50 cycles, the FE of CH4 remained almost unchanged, indicating the stability of the catalyst under electrochemical conditions.

3. **Role of Nanoporous Structure:** The unique nanoporous structure of catalyst X is believed to facilitate the mass transport of reactants and products, thereby enhancing the CO2 reduction efficiency. The high activity is attributed to the large specific surface area and well-distributed active sites.

4. **Electrocatalytic Mechanism:** The electrocatalytic mechanism of CO2 reduction to CH4 on catalyst X involves the formation of an active intermediate and the subsequent hydrogenation of the intermediate to CH4. The reaction likely follows a pathway similar to the WGS reaction, involving the formation of CO and subsequent hydrogenation to CH4.

**Conclusion**

The design and synthesis of catalyst X have led to a significant enhancement in the CO2 reduction activity and selectivity. The unique nanoporous structure and optimized active site distribution contribute to the high performance of this electrocatalyst. Further studies are needed to elucidate the detailed reaction pathways and to optimize the catalyst for practical applications in CO2 reduction technologies.

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**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Author contributions**

G.Z. and Y.L. proposed, designed, and supervised the project. G.Z., Y.L., C.P., and G.L. wrote the manuscript. C.P., J.Z., M.C., Z.W., T.S., and L.Z. performed the experiments and analyzed the data. G.L. and Y.L. performed the theoretical calculations. All the authors discussed, commented on, and revised the manuscript.

**Competing interests**

The authors declare no competing interests.

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**Nature Communications** | https://doi.org/10.1038/s41467-021-21901-1 | www.nature.com/naturecommunications
**Additional information**

**Supplementary information** The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-21901-1.

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**Peer review information** Nature Communications thanks Pussana Hirunsit, Tong-Bu Lu, and other, anonymous, reviewers for their contributions to the peer review of this work.

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