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Cooperative promotion of electroreduction of CO to *n*-propanol by *CO enrichment and proton regulation†

Rongxing Qiu,^a Linxiao Cui,^a Li Peng,^{*a} Olga A. Syzgantseva,^b Jiaran Li,^a Nan Fang,^a Maria A. Syzgantseva,^c Yuan Jiang,^a Jie Zhang,^d Bingxing Zhang,^e Lingzhi Ding,^a Yangyang Dong,^a Tianwei Xue,^a Cheng Li,^a Jin-Chao Dong,^a Jinyu Ye,^a Isil Akpınar,^f Shuliang Yang,^g Jun Li,^g Jun Li,^g Jianling Zhang,^g Jian-Feng Li^g and Buxing Han^g

The CO₂/CO electroreduction reaction (CO₂RR/CORR) to liquid products presents an enticing pathway to store intermittent renewable electricity. However, the selectivity for desirable high-value C₃ products, such as *n*-propanol, remains unsatisfactory in the CO₂RR/CORR. Here, we report that *CO enrichment and proton regulation cooperatively enhance C₁–C₂ coupling by increasing CO pressure and utilizing proton sponge modification, promoting the production of *n*-propanol over a Cu⁰/Cu⁺ nanosheet catalyst in the CORR. We obtain an impressive faradaic efficiency (FE) of 44.0% ± 2.3% for *n*-propanol at a low potential of –0.44 V vs. reversible hydrogen electrode (RHE) under 3 bar CO. Experimental results demonstrated that *H intermediates could be regulated by proton sponge modification. *In situ* characterization combined with density functional theory (DFT) calculations validate that Cu⁺ species exist stably in proton sponge-modified Cu-based catalysts along with appropriate *CO coverage. This design facilitates the potential-determining C₁–C₁ and C₁–C₂ coupling steps and contributes to the *n*-propanol production.

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Introduction

Electrochemical CO₂ reduction reaction (CO₂RR) to high value-added chemical feedstocks and fuels is a promising route for the storage of renewable electricity.¹ Presently, much progress has been made in the CO₂RR, however, the major products with satisfying performance reported are limited to C₁ (CO,^{2,3} CH₄,^{4–6}

HCOO[–],⁷ and CH₃OH^{8,9}) and C₂ (C₂H₄,^{10–12} C₂H₅OH,^{13–15} and CH₃COOH¹⁶) products. C₃ products such as *n*-propanol, a high value-added and high energy-density chemical, have been produced with low FE in previous reports in the CO₂RR.^{17–19} Besides, electrolytes with alkaline or neutral pH are typically employed in the CO₂RR, which leads to undesired carbonate formation easily, causing energy/carbon losses and performance degradation.²⁰ Given the conspicuous progress of the highly efficient CO₂RR to CO,²¹ the *n*-propanol chemical produced by the electrochemical reduction reaction of CO (CORR) following the high-performance CO₂ reduction to CO, could efficiently alleviate these problems.^{22,23}

Cu-based materials have been reported to be efficient electrocatalysts for producing C₃ products such as *n*-propanol. Recently, various strategies have been adopted to enhance the FE of *n*-propanol with Cu-based catalysts, including the engineering of the oxidation state of Cu atoms,²⁴ morphological tuning,^{25–27} Cu-based multimetallic materials,^{28–31} grain boundary control,³² selective formation of the desired facets,³³ *etc.* However, these catalysts still suffer from several challenges, such as limited selectivity in producing *n*-propanol (Table S1†). Thus, developing new approaches to enhance *n*-propanol selectivity in the CORR is still highly challenging and desirable.

As demonstrated in the published reports, high *CO coverage is beneficial for the formation of C₂₊ alcohol products

^aCollege of Chemistry and Chemical Engineering, College of Energy, Xiamen University, Xiamen, 361005, Fujian, P. R. China. E-mail: li.peng@xmu.edu.cn; ysl@xmu.edu.cn; junnyxm@xmu.edu.cn

^bLomonosov Moscow State University, Peoples' Friendship University of Russia, Russia/Department of Chemistry, Moscow, 119991, Russia

^cDepartment of Physics, Mendeleev University of Chemical Technology, Moscow, 125047, Russia

^dInstitute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), 1951 Sion, Switzerland

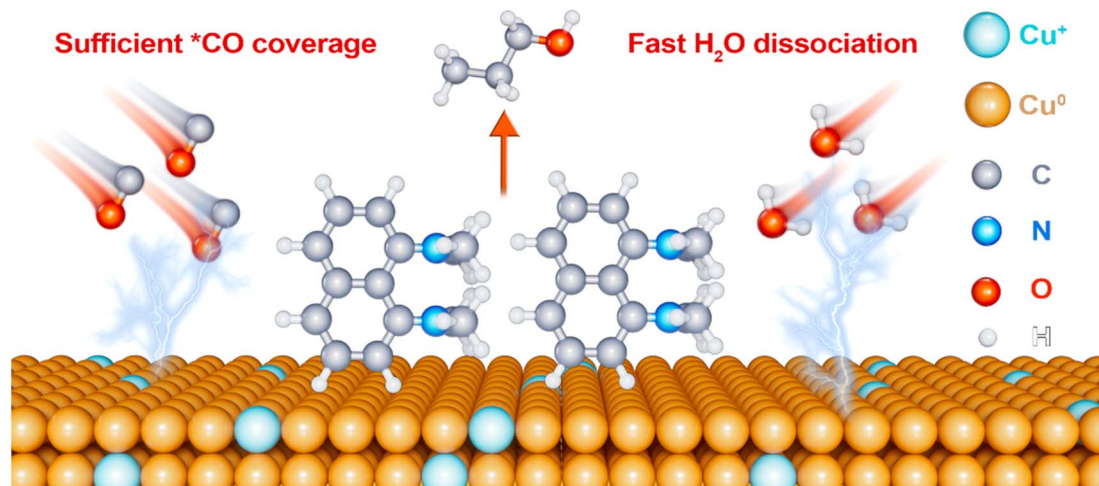
^eSchool of Materials Science and Engineering, Zhejiang University, Hangzhou, 310058, Zhejiang, P.R. China

^fDepartment of Chemistry and International Institute of Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

^gBeijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P.R. China. E-mail: hanbx@iccas.ac.cn

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Scheme 1 Schematic illustration of CO electrolysis to *n*-propanol with proton sponge-modified Cu nanosheets as the catalyst under the assistance of CO pressures.

in CO₂/CO electrolysis.^{34–37} Interestingly, our previous study of the CO₂RR showed that higher CO₂ pressure could enrich *CO coverage on the catalyst surface, which was beneficial to obtain the ethanol product rather than ethylene.³⁸ Considering that the pathway of the CORR to *n*-propanol is a multiple proton-coupled electron transfer process, sufficient supplies of *CO and *H intermediates are essential to produce *n*-propanol during the process. *CO coverage usually could be regulated by pressure variation, while *H intermediates could be modulated *via* a reductive concerted proton–electron transfer (CPET) mediator.^{39,40} Proton sponge (1,8-bis(dimethylamino)naphthalene) shows exceptional proton affinity through bidentate-type coordination by the two dimethylamino groups located at the peri position of the naphthalene skeleton.^{41–43} The general feature of all proton sponges is the presence of two basic nitrogen centers in the molecule, which have an orientation that allows the uptake of one proton to yield a stabilized intramolecular hydrogen bond (IMHB). The strength of the IMHB calculated for proton sponges is in the range of 16–21.5 kcal mol^{−1},^{42,44} which is similar to that of the CPET mediator.

Herein, a cooperative strategy of applying pressure coupled with the use of a proton regulator (proton sponge, PS) for an efficient CORR to *n*-propanol was developed. A series of proton sponge-modified Cu nanosheet catalysts (denoted as Cu-NS-*x*% PS, *x* = 0, 10, 20, 30 and 50, where *x* is the mass percentage of proton sponge in the catalyst) were constructed. The CORR experiments were carried out under different CO pressures (0.5, 1, 2, 3 and 5 bar) with the as-prepared catalysts. Among these, the Cu-NS-20% PS catalyst for the CORR showed an *n*-propanol FE of 44.0% ± 2.3% at −0.44 V *vs.* RHE under 3 bar CO, representing ~1.4-fold improvement relative to the unmodified Cu-NS under the same CO pressure. Experimental results showed that *H intermediates could be adjusted *via* proton sponge modification. *In situ* attenuated-total-reflection surface-enhanced infrared absorption spectroscopy (*in situ* ATR-SEIRAS) indicated that sufficient *CO coverage could be

provided by elevating CO pressure on the proton sponge modified Cu-NS catalyst for subsequent C–C coupling. *In situ* Raman spectra combined with DFT calculations further verified that Cu⁺ species in the Cu-NS-20% PS catalyst was persistent during the CORR under 3 bar CO, which was also beneficial for stabilizing *CO, and facilitating both C₁–C₁ and C₁–C₂ coupling to produce the desired *n*-propanol. This work creatively demonstrated that the cooperative design of a proton regulator with appropriate CO pressure was highly capable of improving the electro-synthesis of *n*-propanol from CO and H₂O (Scheme 1).

Results and discussion

Catalyst preparation and characterization

Proton sponge-modified Cu nanosheet catalysts were prepared as displayed schematically in Fig. 1a. Firstly, CuO nanosheets (CuO-NS) were synthesized *via* a wet chemical method. Proton sponge-modified CuO nanosheets (CuO-NS-*x*% PS) were then obtained by the addition of 1,8-bis(dimethylamino)naphthalene (proton sponge) dissolved in isopropanol to CuO nanosheets. The representative scanning electron microscopy (SEM) (Fig. 1b) and transmission electron microscopy (TEM) images (Fig. 1c) displayed CuO-NS-20% PS with a nanosheet morphology, which was similar to that of CuO-NS and other CuO-NS-*x*% PS (Fig. S1 and S2†). The lattice distances of CuO-NS-20% PS and CuO-NS were observed clearly in the high-resolution transmission electron microscopy (HR-TEM) images (Fig. 1d, S3 and S4†), which corresponded to CuO (111) and CuO (110), respectively. Moreover, energy-dispersive X-ray spectroscopy (EDX) elemental mapping of CuO-NS-20% PS showed that the characteristic Cu, O and N elements were uniformly dispersed in CuO-NS-20% PS, indicating that the proton sponge was integrated very well (Fig. 1e). The successful proton sponge modification was further confirmed *via* Fourier-transform infrared spectroscopy (FT-IR), where representative absorption peaks from proton sponge were also well detected in



CuO-NS-20% PS (Fig. 1f). Powder X-ray diffraction patterns (PXRD) of CuO-NS- x % PS ($x = 10, 20, 30$ and 50) were consistent with those of CuO-NS (Fig. 1g). Raman spectra further demonstrated the characteristic peak of CuO at $276, 320,$ and 605 cm^{-1} for both CuO-NS and CuO-NS-20% PS (Fig. S5†).⁴⁵ These results revealed that the mild proton sponge-modification method would not affect the crystallinity of CuO. Additionally, X-ray photoelectron spectroscopy (XPS) was used to monitor the valence state of the catalysts. XPS spectrum of CuO-NS-20% PS revealed characteristic peaks of Cu^{2+} species at 954.3 eV ($\text{Cu } 2p_{1/2}$) and 934.3 eV ($\text{Cu } 2p_{3/2}$) (Fig. S6†). The N 1s XPS spectra further evidenced the successful proton sponge-modification (Fig. S7†). Moreover, the mole percentages of proton sponge in CuO-NS- x % PS were cross-checked by thermal gravimetric analysis (TGA), XPS, and SEM-EDX, indicating that the amount of modified PS could be easily regulated (Fig. S8 and Table S2†).

Cu-NS- x % PS catalysts ($x = 0, 10, 20, 30$ and 50) were obtained *via in situ* electroreduction of CuO-NS- x % PS upon four runs of linear sweep voltammetry (LSV) with a scan speed of

20 mV s^{-1} over a potential range from open-circuit potential (OCP) to -0.64 V vs. RHE . As observed in SEM and TEM images (Fig. 2a and b), Cu-NS-20% PS displayed a rougher surface with distinguishable nanoparticles on the nanosheet when compared with the precursor, CuO-NS-20% PS (Fig. 1b and c).⁴⁶ Due to the unavoidable oxidation during sample transfer in *ex situ* XRD, Cu_2O species were detected in both Cu-NS and Cu-NS-20% PS following electroreduction. The PXRD pattern of the Cu-NS-20% PS proved the formation of Cu^0 and Cu^+ species, and the major exposed planes were Cu_2O (111), Cu (111) and Cu (200) of face-centered cubic Cu (fcc-Cu), while Cu (111) was the most remarkable characteristic peak in the PXRD pattern of the pure Cu-NS sample (Fig. 2c). Cu LMM Auger spectra in Cu-NS-20% PS further confirmed the existence of Cu^+ species (Fig. S9†). To acquire more accurate surface features of the Cu-NS and proton sponge modified Cu-NS, we investigated the electrochemical adsorption of OH^- on the Cu-NS and Cu-NS-20% PS catalysts considering their facet-dependent OH^- adsorption behaviors. The cyclic voltammetry curves in

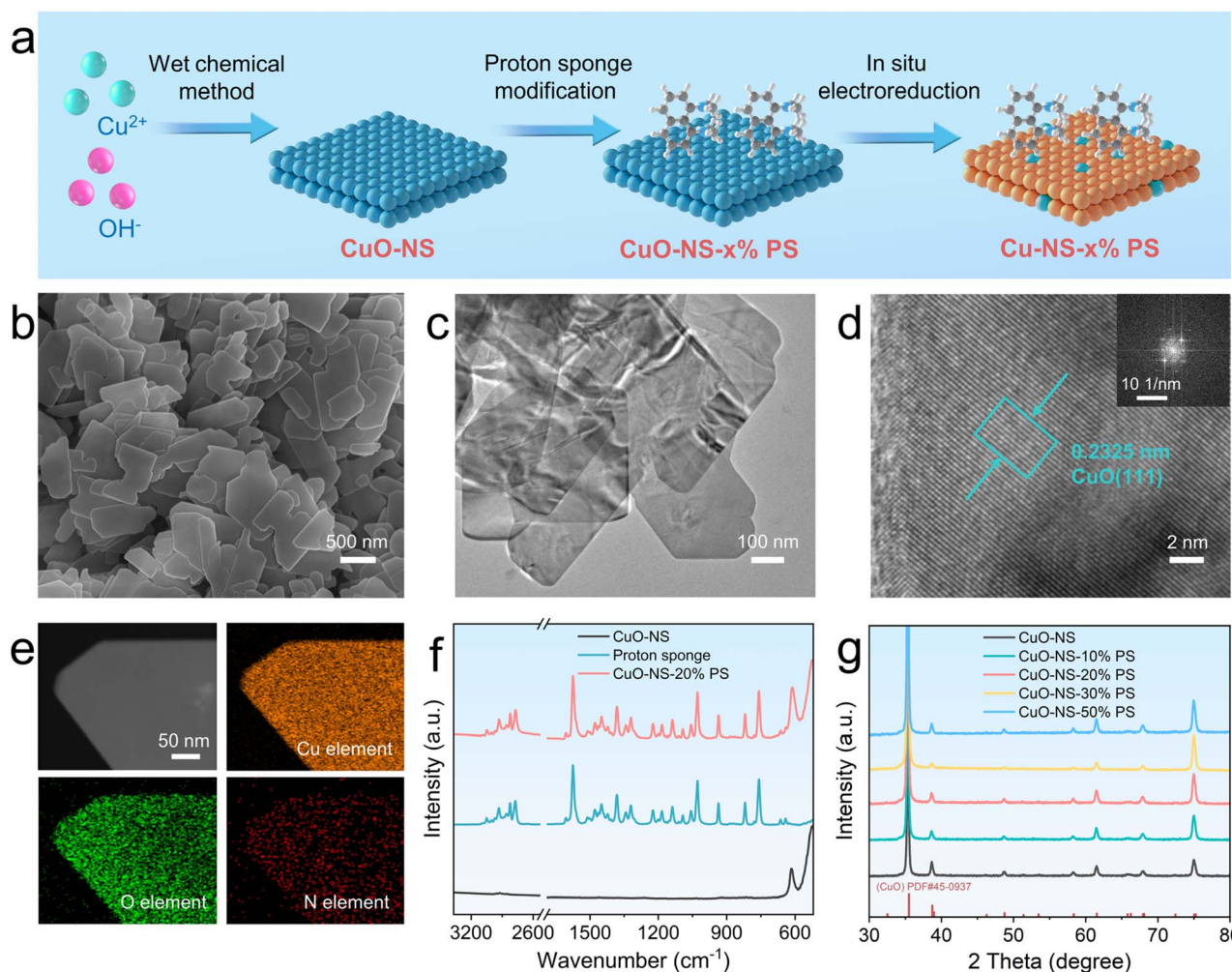


Fig. 1 Synthesis and characterization of CuO-NS- x % PS catalysts ($x = 0, 10, 20, 30$ and 50). (a) Schematic illustration of the synthetic procedure of Cu-NS-PS catalysts. (b) SEM, (c) TEM and (d) HRTEM images of CuO-NS-20% PS. (e) EDX elemental mappings of Cu, O and N in a single nanosheet of CuO-NS-20% PS. (f) FT-IR spectra of pure CuO-NS, proton sponge and CuO-NS-20% PS. (g) PXRD patterns of CuO-NS and CuO-NS- x % PS with different proton sponge loadings.



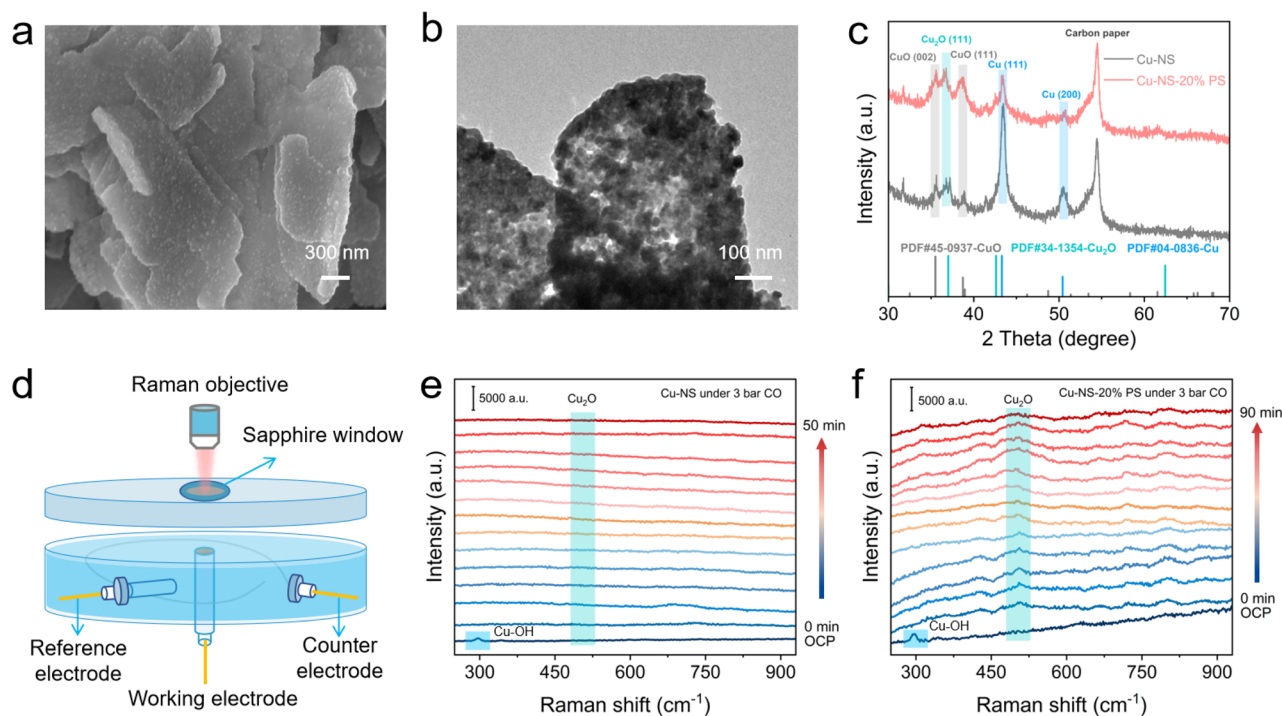


Fig. 2 Synthesis and characterization of Cu-NS-20% PS catalysts. (a) SEM and (b) TEM images of Cu-NS-20% PS. (c) PXRD patterns of Cu-NS and Cu-NS-20% PS. (d) Schematic illustration of the custom-made high-pressure *in situ* Raman cell setup for the CORR. (e) *In situ* Raman spectra of Cu-NS under 3 bar CO at -0.44 V vs. RHE for 50 min. (f) *In situ* Raman spectra of Cu-NS-20% PS under 3 bar CO at -0.44 V vs. RHE for 90 min. The electrode was pretreated via *in situ* electroreduction before recording the amperometric curve and *in situ* Raman spectra testing.

Fig. S10† showed OH^- adsorption peaks at around 0.40, 0.44 and 0.50 V vs. RHE for Cu-NS and Cu-NS-20% PS, corresponding to the OH^- adsorption on the Cu (100), Cu (110) and Cu (111) surfaces, respectively.^{47–49} These results indicate that both Cu-NS and Cu-NS-20% PS are dominated by Cu {100}, {110} and {111} facets.

In situ Raman spectra were collected in a high-pressure *in situ* Raman cell setup (Fig. 2d), and Raman bands that appeared around 510 cm^{-1} belonging to Cu_2O ^{50–52} remained in the proton sponge-modified Cu-based catalysts (Cu-NS-20% PS and Cu-NS-50% PS) at -0.44 V vs. RHE during the *in situ* observation (Fig. 2f and S11†), while no Cu_2O was detected for the pure Cu-NS sample during the CORR process (Fig. 2e). These results validated that Cu^+ species existed stably in the proton sponge-modified Cu-based catalysts during the CORR process, which was obviously different from Cu-NS without proton sponge modification. In order to observe the detailed changes in the valence state of Cu species during the *in situ* electroreduction process, *in situ* PXRD and *in situ* Raman characterization were conducted. Results showed that the Cu-NS catalyst possessed both Cu^+ and Cu^0 before converting to Cu^0 completely (Fig. S12 and S13†).

CORR performance on proton sponge modified Cu-NS under different pressures

The electrocatalytic activity and selectivity for the CORR under different pressures were systematically evaluated in a custom-made pressurized cell with a two-compartment

polytetrafluoroethylene (PTFE) lining separated by a proton exchange membrane (Fig. 3a and S14†). The CORR product distributions from Cu-NS and Cu-NS-20% PS under 1 bar and 3 bar CO are presented in Fig. 3b. As the CO pressure elevated from 1 bar to 3 bar, both Cu-NS and Cu-NS-20% PS exhibited an increase in $\text{FE}_{n\text{-propanol}}$ and $\text{FE}_{\text{acetate}}$, while the $\text{FE}_{\text{C}_2\text{H}_4}$ and FE_{H_2} decreased. Notably, compared with pure Cu-NS, the FE_{H_2} of proton sponge modified Cu-NS increased under ambient pressure, which was attributed to low $^*\text{CO}$ coverage and high $^*\text{H}$ intermediates caused by the proton sponge. While the FE_{H_2} of Cu-NS-20% PS under 3 bar CO was similar to that of Cu-NS under the same CO pressure, Cu-NS-20% PS exhibited higher $\text{FE}_{n\text{-propanol}}$ and lower $\text{FE}_{\text{acetate}}$. This was because the higher $^*\text{CO}$ coverage under 3 bar CO could match the higher $^*\text{H}$ intermediates to produce *n*-propanol rather than acetate. Overall, the $\text{FE}_{n\text{-propanol}}$ reached $44.0 \pm 2.3\%$ over Cu-NS-20% PS under 3 bar CO at -0.44 V vs. RHE, which was ~ 1.4 -fold higher than that over the pure Cu-NS catalyst under the same CO pressure. Moreover, the total current density (j_{total}) and partial current density for *n*-propanol ($j_{n\text{-propanol}}$) of Cu-NS or Cu-NS-20% PS could be enhanced during the CORR when CO pressure elevated from 1 bar to 3 bar (Fig. 3c). The positive feedback further indicated that higher activity for producing *n*-propanol in the CORR could be achieved with the assistance of proton sponge under elevating CO pressure.

To explore the effects of CO pressure on CORR performance, CORR experiments with Cu-NS-20% PS at 0.5, 1, 2, 3 and 5 bar CO were further conducted (Fig. S19†). According to the



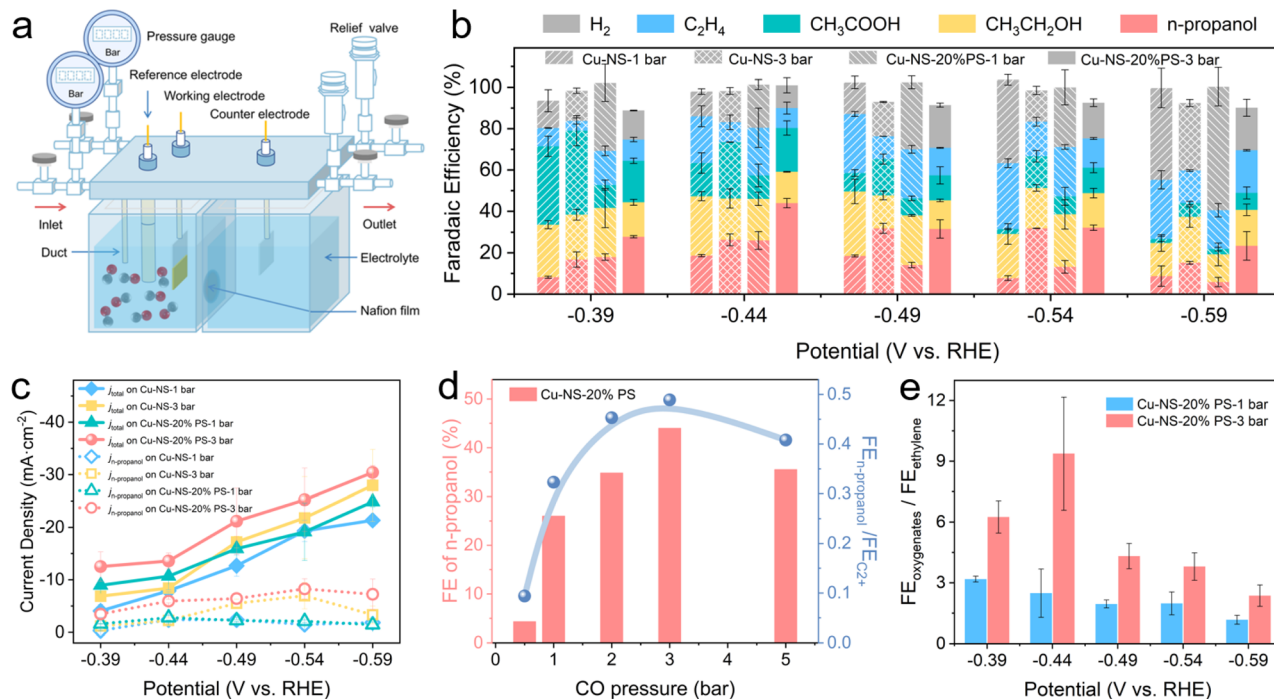


Fig. 3 Electrochemical CORR performances of Cu-NS and Cu-NS-20% PS under ambient and high CO pressures. (a) Schematic CORR setup under both ambient and high CO pressures. (b) CORR product distributions for Cu-NS and Cu-NS-20% PS under 1 bar and 3 bar CO, respectively. (c) The total current density (j_{total}) and partial current density for n -propanol ($j_{n\text{-propanol}}$) on Cu-NS-20% PS and Cu-NS catalysts under 1 bar, 3 bar CO vs. the cathodic potentials, respectively. (d) $\text{FE}_{n\text{-propanol}}$ and $\text{FE}_{n\text{-propanol}}/\text{FE}_{\text{C}_2^+}$ ratios on Cu-NS-20% PS under different CO pressures (0.5, 1, 2, 3 and 5 bar CO). (e) $\text{FE}_{\text{oxygenates}}/\text{FE}_{\text{ethylene}}$ ratios on Cu-NS-20% PS under different CO pressures (1 bar vs. 3 bar CO). Error bars represent the standard deviation of three independent measurements.

experimental data, we built the correlations between $\text{FE}_{n\text{-propanol}}$ and CO pressures in the CORR with the Cu-NS-20% PS catalyst (Fig. 3d). $\text{FE}_{n\text{-propanol}}$ presented a volcanic trend with the CO pressures increased from 0.5 to 5 bar CO, in which $\text{FE}_{n\text{-propanol}}$ rose steeply with CO pressure increasing from 0.5 to 3 bar. $\text{FE}_{n\text{-propanol}}$ exhibited a drop when the CO pressure was further elevated to 5 bar, which could be attributed to excessive $^*\text{CO}$ coverage and insufficient $^*\text{H}$ intermediates required for the n -propanol production pathway. These results indicated that an appropriate $^*\text{CO}$ coverage was beneficial for $\text{C}_1\text{-C}_1$ coupling and $\text{C}_1\text{-C}_2$ coupling to produce n -propanol during the CORR process. We observed that the $\text{FE}_{\text{oxygenates}}/\text{FE}_{\text{ethylene}}$ ratio on Cu-NS-20% PS increased with the CO pressures elevated from 1 bar to 3 bar CO (Fig. 3e), and a similar trend appeared on Cu-NS (Fig. S20[†]). These results proved that oxygenated products could be enhanced accompanied by decreased ethylene by facilely increasing the CO pressure.^{53,54} The CO pressure regulation could also remarkably affect the C_2 and C_3 selectivities in the CORR. In detail, with the CO pressure elevated, the FE of C_2H_4 and $\text{CH}_3\text{CH}_2\text{OH}$ decreased, while the FE of CH_3COOH and n -propanol increased on the majority of nano Cu-based catalysts (Table S3[†]).

The role of proton sponge was then investigated. We conducted a series of CORR experiments on Cu-NS without proton sponge and Cu-NS- $x\%$ PS with different loadings of proton sponge ($x = 10, 20, 30$ and 50) under 3 bar CO pressure (Fig. 4a and S21[†]). Initially, with the increased amount of proton

sponge in Cu-NS, the $\text{FE}_{n\text{-propanol}}$ was promoted efficiently, and reached the peak until Cu-NS combined with 20% of proton sponge, and then showed a downward trend. We also constructed the relationship between $\text{FE}_{n\text{-propanol}}/\text{FE}_{\text{C}_2^+}$ ratio and the amount of proton sponge (Fig. 4a). The $\text{FE}_{n\text{-propanol}}/\text{FE}_{\text{C}_2^+}$ ratio over Cu-NS-20% PS reached almost 0.5 under 3 bar CO, while the ratio was only 0.38 for Cu-NS under 3 bar CO, which evidenced that the n -propanol production was synergistically promoted by the proton sponge and elevating CO pressure. Interestingly, both $\text{FE}_{\text{acetate}}$ and the $\text{FE}_{\text{acetate}}/\text{FE}_{\text{oxygenates}}$ ratio dropped after being modified with 20% proton sponge on Cu-NS compared with the pure Cu-NS under the same CO pressure (Fig. 3b and 4b). Meanwhile, the proton sponge modified Cu-NS increased HER selectivity especially under ambient CO pressure (Fig. S22[†]). According to the above results, it can be concluded that acetate formation with the least proton requirement per carbon among the produced oxygenates could be favored because the proton donor was in short supply on Cu-NS without modification of the proton sponge. However, the n -propanol production pathway, in demand for more proton introduction, is adaptively regulated and enhanced accordingly by the Cu-NS with modification of proton sponge.

The $\text{FE}_{n\text{-propanol}}$ of the CORR on a catalyst with higher amount of proton sponge and CO pressure (Cu-NS-30% PS under 5 bar CO pressure) was further investigated. Cu-NS-30% PS exhibited $\text{FE}_{n\text{-propanol}}$ of 30.6% at -0.49 V vs. RHE under 5 bar CO, which was lower than that of Cu-NS-20% PS under 3 bar CO



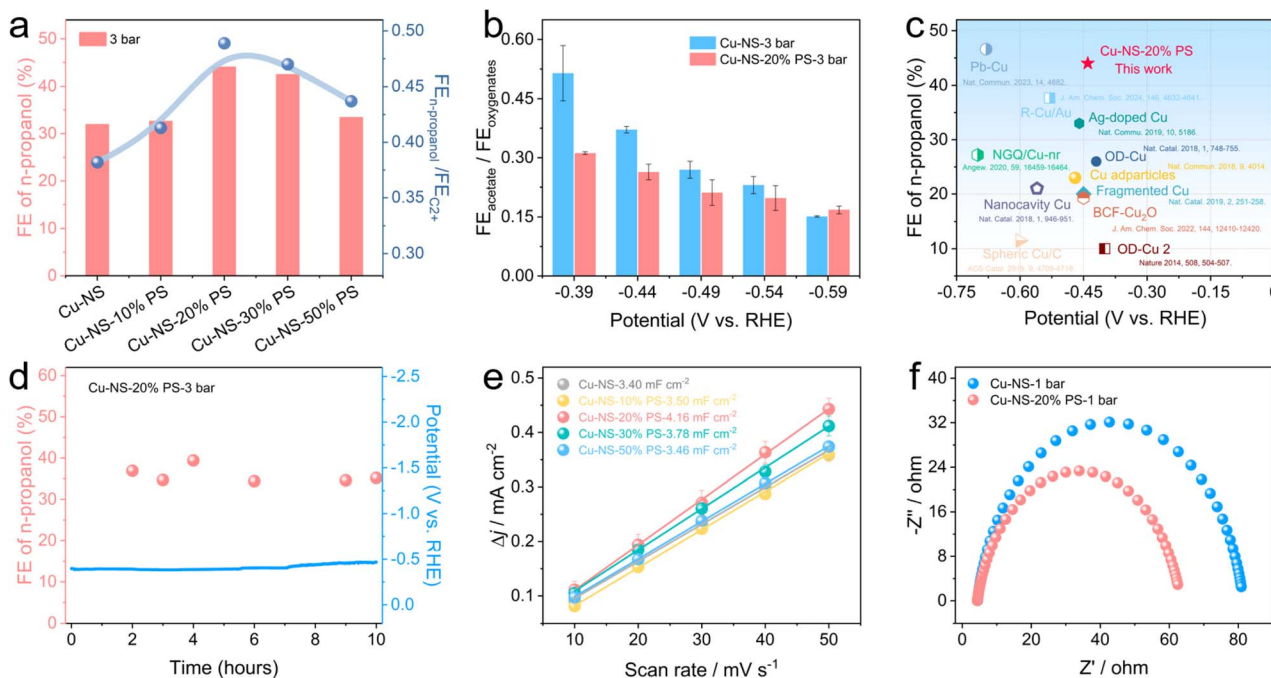


Fig. 4 Electrochemical CORR performance of Cu-NS-*x*% PS (*x* = 0, 10, 20, 30 and 50) under ambient and high CO pressures. (a) $FE_{n\text{-propanol}}$ and $FE_{n\text{-propanol}}/FE_{C_{2+}}$ ratios on Cu-NS-*x*% PS (*x* = 0, 10, 20, 30 and 50) under 3 bar CO. (b) The comparison of $FE_{\text{acetate}}/FE_{\text{oxygenates}}$ ratios on Cu-NS and Cu-NS-20% PS under 3 bar CO pressure. (c) $FE_{n\text{-propanol}}$ vs. potentials for various Cu-based catalysts in the CORR. (d) The chronopotentiometric potential time curve for Cu-NS-20% PS under 3 bar CO at -12 mA cm^{-2} along with the corresponding $FE_{n\text{-propanol}}$. (e) The charging current density differences against scan rates with Cu-NS-*x*% PS (*x* = 0, 10, 20, 30 and 50) as catalysts. (f) Nyquist plots for Cu-NS and Cu-NS-20% PS electrodes in CO-saturated 1 M KOH electrolyte under 1 bar CO.

pressure and higher than that of Cu-NS under 1 bar CO pressure (Fig. 3b and S23[†]). These results revealed that an excess amount of proton sponge could cover the active sites of the Cu-based catalyst and further suppress the *n*-propanol production. Besides, the CORR performance of Cu-NS-20% PS using different concentrations of KOH (0.5 M and 2 M) as the electrolyte was also scrutinized under 3 bar CO (Fig. S24[†]). The $FE_{n\text{-propanol}}$ and $FE_{C_{2+}}$ of Cu-NS-20% PS using 1 M KOH as the electrolyte were higher than those of the same catalyst using 0.5 M or 2 M KOH as the electrolyte under 3 bar CO pressure (Fig. S25[†]). This observation suggests that in higher concentrated alkaline media (*e.g.*, 2 M KOH), the limited proton availability may suppress CO reduction, thereby diminishing C_{2+} product selectivity. Compared with the two catalysts from commercial CuO and proton sponge modified commercial CuO, the as-prepared Cu-NS and Cu-NS-20% PS exhibited higher activity and selectivity towards *n*-propanol during the CORR, which could be attributed to the more abundant active sites in the nanosheet CuO precursor (Fig. S1 and S26[†]). In order to investigate the CORR performance of CuO-based catalysts from different proton sponge modification methods, CuO-NS was first *in situ* reduced at -0.44 V vs. RHE for 30 min, then 20% proton sponge was added to the surface of the Cu-NS to form the Cu-NS-after 20% PS catalyst. As displayed in the results in Fig. 3b and S27[†], the $FE_{n\text{-propanol}}$ from Cu-NS-after 20% PS was lower than that from Cu-NS-20% PS at different tested potentials.

Moreover, we directly compared the catalytic performance of Cu-NS-20% PS for *n*-propanol production with that of the reported catalysts (Fig. 4c and Table S1[†]). It was clearly demonstrated that Cu-NS-20% PS possessed one of the highest $FE_{n\text{-propanol}}$ values to date, and revealed one of the lowest potentials amongst results reported thus far. And the partial current density for *n*-propanol was also greatly improved compared with the bare Cu-NS catalyst under ambient CO pressure, exhibiting pretty good results in H-type cells (Fig. 3c and S28[†]).

The stability of Cu-NS-20% PS was also evaluated *via* a long-term chronopotentiometry testing. It was found that there was no apparent decay of activity within 10 h operation time (Fig. 4d). Furthermore, the PXRD, XPS, SEM and TEM data of the electrode after the CORR under 3 bar CO test were collected. The characteristic peaks of Cu_2O and Cu observed obviously from the PXRD patterns were found to be similar to the original Cu-NS-20% PS (Fig. 2c and S29[†]). XPS spectra of the Cu-NS-20% PS after the CORR also exhibited the presence of Cu^+ peaks (Fig. S30[†]). Besides, the SEM and TEM images showed that the sample still retained the nanosheet morphology (Fig. S31[†]).

Based on the results and analysis above, the selectivity and activity of *n*-propanol were raised distinctly by rationally introducing a certain amount of proton sponge and appropriate CO pressure. This prompted us to investigate the intrinsic reasons for the enhanced CO conversion to *n*-propanol. To verify the importance of the Cu-NS-20% PS structure, we determined the double-layer capacitance (C_{dl}), which was obtained from the



charging current density at -0.026 V *vs.* RHE against the slope of scan rate (Fig. 4e and S32†). The C_{dl} values of Cu-NS-*x*% PS ($x = 0, 10, 20, 30$ and 50) presented a volcanic trend, and Cu-NS-20% PS showed the highest electrochemically active surface area (ECSA) (Fig. S33 and Table S4†). The trend was similar to the relationship between $FE_{n\text{-propanol}}$ and proton sponge amount on Cu-NS, which further indicated that the active sites of the Cu-based catalyst and the activity of the CORR to *n*-propanol could be enhanced with an optimized proton sponge/Cu ratio, while an excess amount of proton sponge would shield the active sites of the Cu-based catalyst indeed. The Nyquist plots were also measured (Fig. 4f and S34†), and the charge-transfer resistance (R_{ct}) of Cu-NS-20% PS was found to be smaller than that of Cu-NS, suggesting that the proton sponge-modified Cu-based catalyst could efficiently promote the charge transport during the electrocatalytic process in contrast to the control Cu-NS.⁵⁵

Mechanism analysis

To gain in-depth insights into the mechanism of proton sponge-modification of Cu-NS and the pressure-driven electrochemical CORR to *n*-propanol, *in situ* ATR-SEIRAS data were further collected on a custom-made high-pressure spectroelectrochemical setup to probe the intermediates associated with CORR reactivity on Cu-NS-20% PS and Cu-NS under CO pressures of 1 bar and 3 bar, respectively (Fig. S35–S37†). A prominent absorption band in the range of $2072\text{--}2025$ cm^{-1} , attributed to the C=O stretching mode of atop-adsorbed CO (CO_{atop}), was observed on the Cu-NS-20% PS and Cu-NS at potentials from 0.1 to -0.6 V *vs.* RHE under both 1 bar and 3 bar CO (Fig. 5a, b, d and e). The CO_{atop} band red-shifted as the potential decreased from 0.1 to -0.6 V *vs.* RHE, which was ascribed to the Stark shift.^{56,57}

Meanwhile, the peak position of the CO_{atop} band could serve as a proxy to compare absolute CO coverages.⁵⁸ The wavenumber of the CO_{atop} band was higher under 3 bar than those under 1 bar for both Cu-NS-20% PS and Cu-NS (Fig. 5c), indicating that the absolute CO_{atop} coverage at 3 bar of CO was higher than that under ambient CO pressure at a controlled potential.⁵⁸ Besides, the CO_{atop} band areas of Cu-NS-20% PS and Cu-NS were normalized to the maximum value under both 1 bar and 3 bar CO pressures, respectively (Fig. 5f). We speculated that the elevated CO pressure and modification with proton sponge on Cu-NS could enrich the $^*\text{CO}$ intermediates, and cause moderate impact of rapid CO_{atop} consumption at large overpotentials. On the other hand, the bands in the range of $1839\text{--}1763$ cm^{-1} can be assigned to the C=O stretching mode of the bridge-adsorbed CO (CO_b). The Cu-NS-20% PS catalyst presented the strongest CO_b peaks during the CORR from 0.1 to -0.6 V *vs.* RHE under 3 bar CO compared with those of control experiments (Fig. 5a, b, d and e), and it was reported that the cooperation of CO_{atop} and CO_b could facilitate C–C coupling.⁵⁹

To further understand how the $^*\text{H}$ supply affected the C_2 and C_3 products, well-controlled sets of experiments including linear sweep voltammetry tests, kinetic isotopic effect (KIE) of H/D measurements and $^*\text{H}$ trapping experiments were conducted.

Firstly, the intrinsic H_2O dissociation activity of Cu-NS, with and without proton sponge modification, was investigated by comparing the normalized polarization curves of Cu-NS and Cu-NS-20% PS per ECSA in 1 M KOH under an Ar atmosphere (Fig. 5g and S38†). Both the ECSA-normalized current density and geometric current density of Cu-NS-20% PS were higher than those of Cu-NS, demonstrating that modifying Cu-NS with a proton sponge enhanced the dissociation of H_2O ,⁶⁰ in good agreement with experimental results (Fig. S22†). Besides, we measured the KIE of H/D on the Cu-NS and Cu-NS-20% PS catalysts. The KIE of H/D is defined as the ratio of $FE_{\text{C}_2\text{H}_4}$ in H_2O and D_2O , a KIE value larger than 1.5 indicates that water activation affects the reaction rate.⁶¹ The Cu-NS catalyst showed large KIE values of 1.53 and 1.85 at 1 bar and 3 bar CO, respectively, indicating that the sluggish kinetics of H_2O dissociation limited the electrocatalytic CORR process.⁶² The Cu-NS-20% PS catalyst exhibited lower KIE values of 1.02 and 1.35 at 1 bar and 3 bar CO, respectively, indicating that the Cu-NS catalyst modified with proton sponge could effectively accelerate H_2O dissociation and promote proton transfer at both 1 bar CO and 3 bar CO pressures (Fig. 5h).^{63,64} To further investigate whether $^*\text{H}$ supply of Cu-NS-20% PS tuned the *n*-propanol selectivity, we conducted the $^*\text{H}$ trapping experiments using *tert*-butanol (*t*-BuOH) as the $^*\text{H}$ trapping agent.^{64,65} The decrease in the ratio of $FE_{n\text{-propanol}}/FE_{\text{C}_2^+}$ on Cu-NS-20% PS was much larger than that on Cu-NS when *t*-BuOH was added to the reaction system (Fig. 5i). This result indicates that the generation of *n*-propanol is closely related to the $^*\text{H}$ supply on the catalyst surface, and a faster $^*\text{H}$ supply (proton-sufficient supply) could directionally promote the CORR to produce *n*-propanol.⁶⁴

Density functional theory (DFT) calculations

To further rationalize the impact of the proton sponge on the catalyst performance towards the selective and efficient propanol synthesis, DFT simulations related to the impact of the proton sponge on the oxidation state of the Cu-NS and on the key C-chain growth stage were performed. The proton sponge could adsorb on the Cu_2O surface in different configurations, including the one depicted in Fig. 6a. The proton sponge was mainly attracted to the Cu_2O surface *via* carbon copper interactions, as well as weak interactions of hydrogen atoms with the surface. The presence of the proton sponge substantially increased the energy of formation of oxygen vacancy on the Cu_2O surface (Fig. 6b and S39–S41†), as compared with the pristine Cu_2O (111) surface,⁶⁶ preventing the removal of oxygen from the reactive surface and thus preserving the oxidation state of the Cu^+ , which coexisted with the metallic Cu^0 . The hydrophobic nature of the proton sponge heightened the chemical potential of water⁶⁶ in the vicinity of the catalyst surface, therefore, making its formation unfavorable. That also contributed to the coexistence of Cu^+ and Cu^0 oxidation states. Moreover, its non-polar fragments could serve to attract the non-polar hydrogen molecules. Therefore, Cu^+/Cu^0 became stabilized in the presence of the proton sponge.

Given that only $^*\text{CO}$ was observed and hydrogen-containing species were not detected in the *in situ* ATR-SEIRAS, we are more inclined to rationally follow the $^*\text{CO} + ^*\text{CO}$ and $^*\text{CO} + ^*\text{OCCO}$



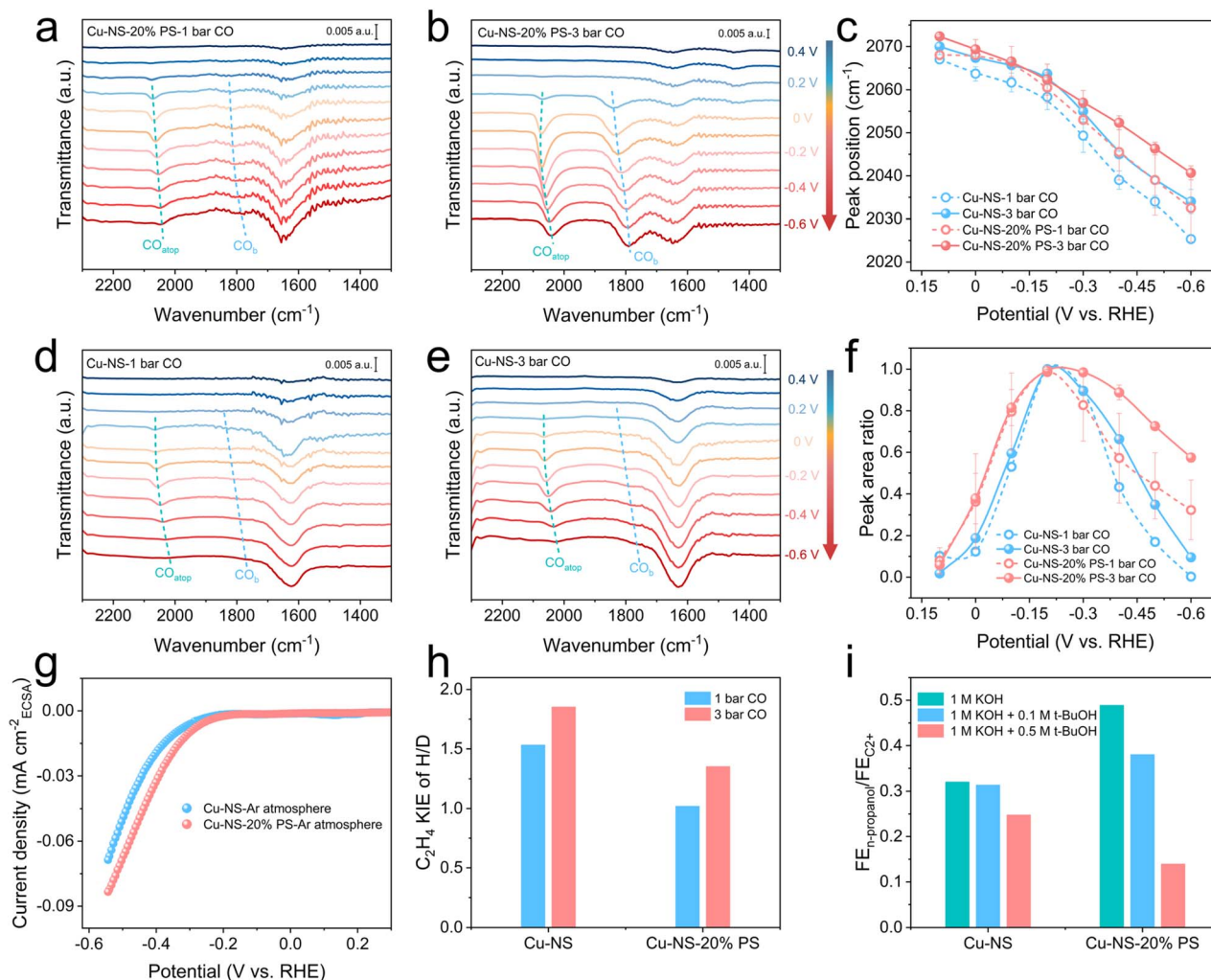


Fig. 5 Mechanism investigation. Potential-dependent SEIRAS investigation of CO_{atop} and CO_{b} bands on Cu-NS-20% PS under (a) 1 bar CO, (b) 3 bar CO in 0.1 M KOH electrolyte. (c) Potential-dependent SEIRAS investigation of CO_{atop} peak positions on Cu-NS-20% PS and Cu-NS under CO pressures of 1 bar and 3 bar, respectively. Potential-dependent SEIRAS investigation of CO_{atop} and CO_{b} bands on Cu-NS under (d) 1 bar CO, (e) 3 bar CO in 0.1 M KOH electrolyte. (f) Potential-dependent SEIRAS investigation of CO_{atop} band areas on Cu-NS-20% PS and Cu-NS under pressures of 1 bar and 3 bar CO, respectively. The maximum peak area at each CO pressure was scaled to 1.0. Error bars represent the standard deviation of three independent measurements. (g) The linear sweep voltammetry curve per ECSA in 1 M KOH under an Ar atmosphere for the Cu-NS-20% PS and Cu-NS catalysts, respectively. (h) KIE of H/D in the CORR to C_2H_4 performance on Cu-NS and Cu-NS-20% PS at -0.44 V vs. RHE under 1 bar and 3 bar CO, respectively. (i) Ratios of $\text{FE}_{n\text{-propanol}}/\text{FE}_{\text{C}_2^+}$ on Cu-NS and Cu-NS-20% PS at -0.44 V vs. RHE in 1 M KOH solution with the addition of 0 M, 0.1 M and 0.5 M *t*-BuOH under 3 bar CO pressure.

coupling mechanisms to generate *n*-propanol.^{28,67} Considering the C-chain growth on the Cu^+/Cu^0 and Cu^0 surfaces, it turned out that the adsorption of $^*\text{CO}$, $^*\text{OCCO}$ and $^*\text{OCCOCO}$ intermediates on Cu^+/Cu^0 was more favorable than that on the fully reduced (111) surface of fcc-Cu (Fig. 6c and S42–S44†). Indeed, for $^*\text{OCCOCO}$, the adsorption energy on Cu^+/Cu^0 was -1.76 eV; while for the metallic Cu system, it was -0.66 eV. In both Cu^+/Cu^0 and Cu^0 systems, $^*\text{OCCOCO}$ attached to the surface *via* the terminal carbon atoms on both sides interacting with surface copper atoms, while neither the middle carbon atom nor oxygen atoms participated in the adsorption. However, in particular, for the mixed valence Cu^+/Cu^0 system, the distance between copper sites perfectly matched with the length of the C_3 chain of the $^*\text{OCCOCO}$ intermediates (Fig. S45 and S46†), which was

another factor responsible for its enhanced selectivity and activity towards the C_3 product.

On the other hand, the proton sponge can locally stabilize the dissociated water molecules, collecting the H^+ inside. The $[\text{proton sponge-H}]^+$ complex attracts OH^- along with hydration water molecules due to the electrostatic interaction. The system with H^+ in the proton sponge and hydrated OH^- is less energetically favorable by 0.43 eV than the proton sponge–water system (Fig. S47†). However, the electrochemical overpotential applied to the system during the reaction (-0.44 V vs. RHE) is sufficient to overcome this energy barrier, that is, the negatively charged catalyst surface by electrostatic interaction provokes water dissociation; the proton sponge collects the resulting protons and promotes proton supply (Fig. S48†).



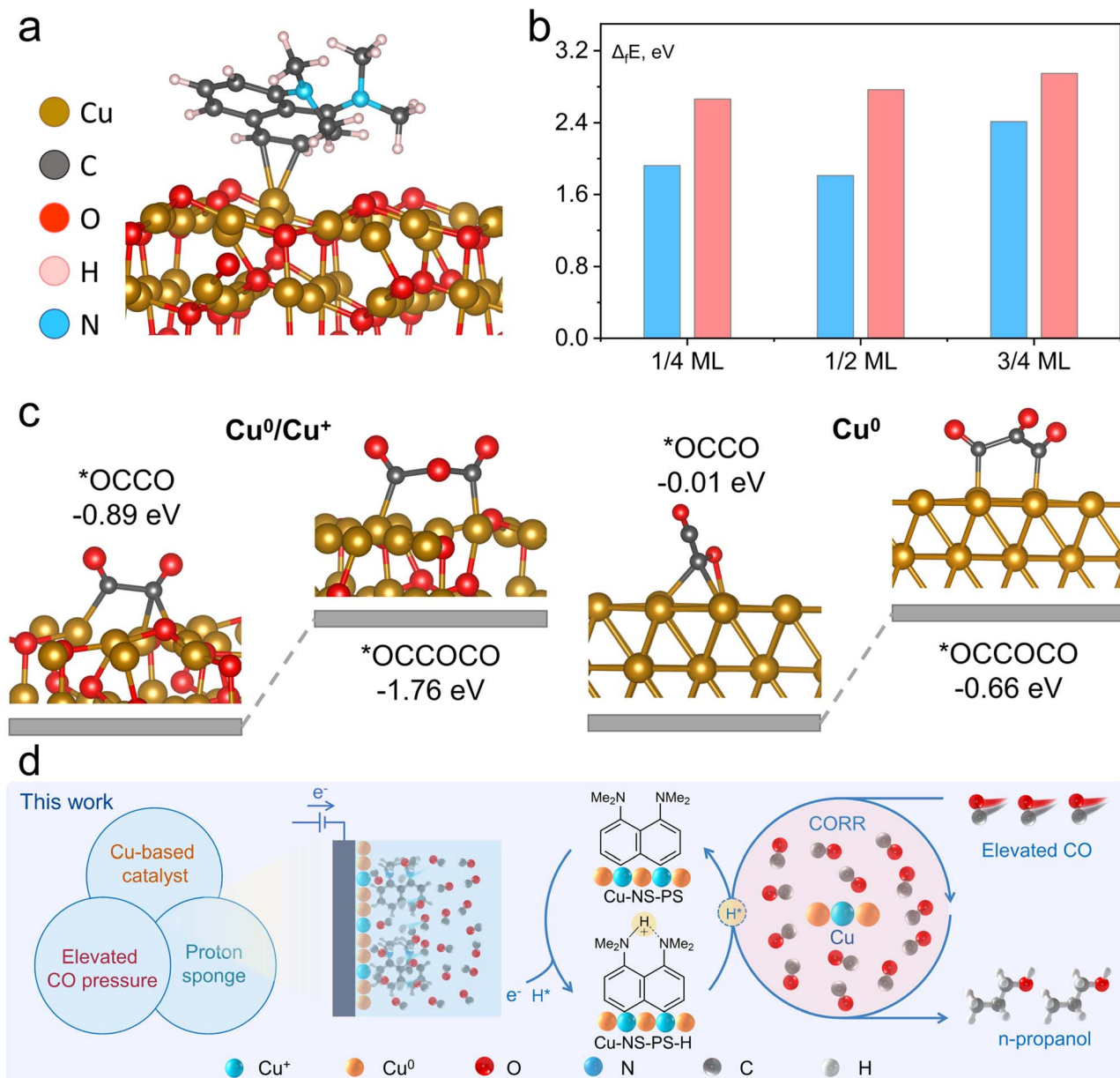


Fig. 6 The impact of the proton sponge on the copper oxidation state on the surface and the adsorption energetics of the key C-chain growth intermediates. (a) Adsorption of the proton sponge molecule on the Cu_2O (111) surface. (b) The formation energies of oxygen vacancies on the pristine Cu_2O (111) surface (blue, from ref. 66) and Cu_2O (111) surface covered with proton sponge (pink). (c) Adsorption intermediates and energies on the Cu^0/Cu^+ (111) Cu_2O surface and Cu (111) surface. (d) Schematic illustration of the cooperative promotion of electroreduction of CO to *n*-propanol on Cu-based catalysts by the proton regulator and elevated pressure.

Based on a series of control experiments and DFT calculations above, it could be observed that both the elevated CO pressure and proton sponge-modification on Cu-based catalysts played indispensable roles in enhancing $^*\text{CO}$ coverage and $^*\text{H}$ supply for subsequent $^*\text{CO} + ^*\text{CO}$ and $^*\text{CO} + ^*\text{OCCO}$ coupling. Besides, the mixed-valence Cu^+/Cu^0 system exhibits an optimal geometric configuration, where the interatomic spacing between adjacent copper sites aligns precisely with the molecular dimensions of the C_3 backbone in the $^*\text{OCCOCO}$ intermediate. The synergistic optimization of multiple reaction

parameters in proton sponge-functionalized Cu catalysts leads to significantly enhanced *n*-propanol generation efficiency in the CORR (Fig. 6d).

Conclusions

In summary, we present a strategy to significantly improve the selectivity of *n*-propanol in CO electrolysis by cooperation of the binding proton sponge on Cu-NS and the CO pressure regulation. Through conveniently regulating the amount of proton



sponge and CO pressure, we demonstrate a CO to *n*-propanol conversion with an FE of $44.0\% \pm 2.3\%$ for *n*-propanol on the Cu-NS-20% PS catalyst at -0.44 V vs. RHE under 3 bar CO pressure, which is ~ 1.4 -fold higher than that on the pure Cu-NS catalyst under the same CO pressure. The oxygenated products are enhanced accompanied by a decrease of ethylene selectivity by increasing the CO pressure for both pure Cu-NS and Cu-NS-20% PS. Simultaneously, the selectivity of the multiple proton coupled electron transfer product (*n*-propanol) was enhanced effectively on Cu-NS-20% PS compared with the pure Cu-NS. This is due to the appropriate *CO coverage, matched with the suitable *H intermediates, and the perfect distance between copper sites matching the length of the C₃ chain of the *OCCOCO intermediates after modification with proton sponge under elevated CO pressure. Experimental results and *in situ* ATR-SEIRAS demonstrated that sufficient *CO coverage and *H intermediate could be provided by appropriate CO pressure and proton sponge-modification, respectively, for subsequent C₁-C₁ and C₁-C₂ coupling. *In situ* Raman spectra and DFT calculations further revealed that Cu⁺ species existed stably in the proton sponge-modified Cu-based catalyst, leading to a low energy barrier in the potential-determining C₁-C₁ and C₁-C₂ coupling steps.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

L. P., S. Y., J. L. and B. H. supervised the project. R. Q. designed the high-pressure *in situ* Raman cell setup and *in situ* ATR-SEIRAS cell setup. R. Q. and B. Z. synthesized the catalysts. R. Q., L. C., J. L., C. L. and J. Z. carried out electrochemical experiments. R. Q., L. C., L. D. and Y. D. characterized the materials. O. A. S. and M. A. S. carried out DFT calculations. R. Q., N. F. and J. Y. conducted the *in situ* ATR-SEIRAS experiment. R. Q., Y. J., J.-C. D. and J.-F. L. conducted the *in situ* Raman spectroscopy experiment. T. X., I. A. and J. Z. contributed to data analysis. R. Q., J. L., L. P., J. L., S. Y. and B. H. co-wrote the manuscript. All authors discussed the results and contributed to the preparation of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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