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Vanadium Oxide Integrated on Hierarchically Nanoporous Copper for Efficient Electroreduction of CO₂ to Ethanol

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Electrochemical reduction of CO₂ into ethanol product is regarded as a highly promising route for CO₂ utilization. However, the poor selectivity is still a critical challenge for increasing the yield of the specific ethanol. As CO₂ reduction catalyst, the hierarchically nanoporous copper integrated with vanadium oxide can achieve a 30.1% Faradaic efficiency for CO₂-to-ethanol production and an ethanol partial current density of -16 mA cm⁻² at -0.62 V vs. RHE, corresponding to a 4-fold increase in activity compared to the bare nanoporous Cu. It even delivers ethanol partial current density that exceeds -39 mA cm⁻² at -0.8 V vs. RHE in a flow-cell reactor. The hierarchically nanoporous Cu skeleton not only facilitates both electron and electrolyte transports but also provides large specific surface area for high active site density. Density functional theory reveals that the vanadium oxide decorated Cu surface can facilitate water dissociation and optimize the hydrogen adsorption energy on Cu, lowering the energy barrier of protonation of carbon dioxide and C-C coupling. Meanwhile, it can increase hydrogen proton coverage on the catalyst surface and inhibit dehydration, which are beneficial for breaking the C=C bond of the *HCCOH intermediate, thus enhancing the Faradaic efficiency of ethanol significantly. The highly efficient conversion of CO₂ to ethanol demonstrates that the hybrid electrocatalyst is considered as a promising candidate for practical electrocatalytic CO₂RR applications.

Introduction

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Electrochemical conversion of carbon dioxide (CO₂) into commercially valuable fuels and chemicals utilizing renewable electricity is an appealing way for reducing atmospherical CO₂ emissions.^{1, 2} Recently, various valuable products have been obtained through electrochemical CO₂ reduction reaction (CO₂RR), while the C₂₊ products are more attractive owing to their ultra-high energy densities and high economic value. Especially, ethanol is highly desirable, which can be either used directly as a fuel or indirectly as fuel precursors.³⁻⁶ However, producing ethanol via electrochemical CO₂RR is far away from commercialization because of the high overpotential, low activity, selectivity and poor stability of catalysts.⁷ Therefore, efficient catalysts are

needed to reduce reaction overpotential and improve catalytic activity and selectivity.

Copper is the most promising electrocatalysts for the reduction of CO₂ to C₂ products due to its appropriate binding energy to many intermediates.⁷⁻ ¹³ To improve the selectivity of ethanol production, several strategies have been developed to modify the copper catalysts surface, such as roughness effect,¹⁴ interface engineering,¹⁵ dopant modification,^{16,17} bimetallic catalysis,¹⁸⁻²¹ and tandem catalysis,^{22,23} These methods mainly control the production of the key C₁ intermediate (*CO) by another component to further enhance the production of C₂₊ species, because the C₂₊ selectivity can be tuned by CO coverage. However, most of the research indicate that methods of modifying copper catalysts surface focus on improving selectivity of C₂ mixed products rather than single target products,¹⁹⁻²⁴ Currently, the selectivity of ethanol still remains low, thus it is imperative to design catalysts to improve ethanol selectivity.

it is well known that ethanol production is a typical twelve-electrons transfer process, which means more hydrogenation steps in comparison to other products.^{25,26} H coverage plays an important role in the hydrogenation

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process.^{27,28} Thus, enhancing H adsorption on the catalyst surface is a potential strategy to promote the formation of key intermediate and ethanol. Actually, the elements near the sixth subfamilies have good affinity for hydrogen, such as Cr. Mo. V. W and so on. Previous reports have shown that the doping of chromium oxide or vanadium oxide can accelerate the hydrolysis kinetics and provide hydrogen protons.^{29,30} Previous works have indicated that Cu surfaces decorated by oxides or hydroxides can accelerate H₂O dissociation and provide strong affinity to H atoms, which can boost hydrogenation reaction in CO₂RR.³¹⁻³⁴ Herein, we construct a vanadium oxide integrated on hierarchically nanoporous copper hybrid electrocatalysts with a three-dimensional (3D) bicontinuous nanoporous architecture for highperformance CO2RR. These hybrid electrocatalysts are composed of amorphous vanadium oxide, which are in situ grown on 3D bicontinuous nanoporous Cu skeleton (denoted as np-Cu@VO₂) by one-step chemical dealloying. Such hierarchical architecture offers suitable pathways for both electron and reactants transports. In addition, nano-sized interconnective Cu ligaments and bimodal nanopore channels remarkably increase the number density of highly active sites for promoting the reactant accessibility.^{35,36} Therefore, the np-Cu@VO₂-5% hybrid electrocatalyst enables a 30.1%Faradaic efficiency (FE) for CO₂-to-ethonal production and an ethanol partial current density of -16 mA cm⁻² at -0.62 V versus reversible hydrogen electrode (RHE), corresponding to a 4-fold increase in activity compared to the bare nanoporous Cu. It even delivers ethanol partial current density that exceeds -39 mA cm⁻² much higher than that of np-Cu at -0.8 V vs. RHE in a flow-cell reactor. Density functional theory (DFT) results reveal that the vanadium oxide integrated on surface of nanoporous Cu can promote the water dissociation and change the adsorption energy of hydrogen on Cu, thus reducing the pivotal energy barriers of carbon dioxide protonation and C-C coupling steps in the ethanol formation pathway. Meanwhile, it can also increase the surface hydrogen proton (*H) coverage of the catalyst and inhibit dehydration, which are beneficial for breaking the double bond of the *HCCOH intermediate, leading to the enhancement of ethanol FE significantly.

Experimental

Fabrication of hierarchical np-Cu and np-Cu@VO2

All catalysts with nanoporous structures were fabricated by a facile alloying/dealloying procedure.^{37,38} The $AI_{80}Cu_{20-x}V_x$ (x=0, 0.2, 1, 2) precursor ribbon with ~50 µm thickness and ~5 mm wide were first produced by a melting-spinning method in Ar gas from their ingots, which were made by arc melting using pure Cu, V, and Al in Ar atmosphere. The as-prepared alloy ribbons were chemically dealloying in Ar-purged 2.0 M NaOH aqueous electrolyte for 2 h. These produced catalysts were rinsed in pure water for multiple times to remove chemical substance in nanopore channels. After vacuum drying, the catalysts obtained by chemical corrosion were self-supporting materials, which could be used directly as cathodes in H-type cell without ink preparation process.

Material Characterizations

X-ray diffraction (XRD) patterns were obtained using a Right MATHER 2743 polycrystalline powder diffractometer with Cu K α ray (λ =0.15418 nm). Observation and Analysis of Microstructure and Morphology were probed with a HitachiS-4800 HD SEM (at 10 kV and 8.5 mm work distance). The transmission electron microscopy (TEM) was conducted by a Tecnai G2 F20 S-TWIN whose limit point resolution is 0.17 nm. High-angle annular dark fieldscanning TEM (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDS) mapping were conducted on a JEM-ARM 200F with acceleration voltage of 200 kV. Chemical states of surface atoms were studied by X-ray photoelectron spectroscopy (XAS) were obtained on beamline BL01C1 at National Synchrotron Radiation Research Center in the fluorescence mode using a Lytle detector with a step-size of 0.25 eV at room temperature. The specific surface area was obtained from the results of N₂ physisorption at 77 K (Micromeritics ASAP 2020) by using the BET (Brunauer-Emmet-Teller).

Electrochemical measurements

A CHI660 electrochemical workstation with three-electrode cell was used to control the external reaction conditions. Electrochemical performance of the samples was tested by electrochemical workstation in a three-electrode system which had a working electrode (catalysis), a Ag/AgCl reference electrode filled with saturated KCI solution and a Pt counter electrode. All potentials applied by electrochemical workstation were transformed to the potentials relative to reversible hydrogen electrode (RHE) as a criterion with a formula ($E_{RHE} = E_{Ag/AgCl} + 0.0591 \text{ pH} + 0.197 \text{ V}$). The electrolyte, 0.1 M KHCO₃ solution, was bubbled with CO₂ at least 30 min to ensure formation of CO₂saturated solution before experiments. 1.0 M KOH solution and Hg/HgO reference electrode was used in flow cell. Linear sweep voltammetry (LSV) measurements in CO₂-saturated or Ar-saturated electrolytes were taken at a given potential range with the sweep rate of 50 mV/s. Carbon dioxide electrochemical reduction experiments were measured in a H-type cell (separated by Nafion 117 proton exchange membrane) and flow cell (anion exchange membrane) with a CHI660 electrochemical workstation, respectively. Before testing, ten cycles cyclic voltammetry were performed to activate the catalyst and remove the residual impurities. The open circuit voltage was tested for half an hour with fresh solution as the blank group, which eliminated the interference of impurities. Gas products (hydrogen and small molecular hydrocarbons) are detected by gas chromatograph (GC2014 Shimadzu) equipped with TCD and FID detector with argon as carrier gas which connected with the cathodic compartment. Liquid products were characterized by 1H NMR on Bruker Avance III 400MHz HD spectrometer. Liquid products were also analyzed by GC whose FID detector equipped with Bond-Q column. The Faradaic efficiency of the products was calculated through GC and NMR data. The Faradaic efficiency (FE) and energy efficiency (EE) for the products was calculated as following formula: $FE = x^*F^*n/Q$ =x*F*n/(I*t), where x is the number of electrons transferred, F is the Faraday

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constant, Q is the total transferred charge, I is the current, t is the running time and n is the total amount of product (in mole); $EE_{product} = (1.23-E_{product})*FE_{product}/(1.23-E_{applied})$, $E_{product}$ represents the equilibrium potential of CO_2 electroreduction to each products, which is 0.09 V for ethanol.

Working introduction of flow cell

To prepare the electrode in flow cell, 5 mg of ground precatalyst was dispersed in 0.48 ml methanol, and then 20 μ l Nafion solution was added. Next, the ink was ultrasonically treated for 10 min. 100 uL as-prepared suspension was then dripped evenly onto hydrophobic carbon paper (0.5 cm x 2 cm), which ensured that catalyst loading should be around 1.0 mg/cm². Finally, the catalysts dried for at least 6 h in vacuum before use.

The hydrophobic carbon paper consisted of mesoporous layer and microporous layer which enhanced the gas diffusion, and the high conductivity also improved the current density. In the process of electrolysis, CO₂ gas first diffused through the mesoporous layer and then entered into the microporous layer. At the junction of the microporous layer and the catalyst layer, the catalyst formed interface contact and directly participates in the reaction.

Density functional theory calculations

All density functional theory (DFT) calculations were performed by Vienna Abinitio Simulation Package (VASP).^{39,40} The exchange-correlation functional was generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE).⁴¹⁻⁴³ The cutoff energy was set as 450 eV. Minimum force convergence was -0.02 eV. Minimum energy iterative convergence was set as 0.0001 eV. The bared Cu (111) surface was modeled by a four-layers (4X4) supercell with 20 Å vacuum. The bottom two layers were fixed as the bulk phase and the upper two layers were allowed to relax. For VO₂ modified Cu surface, a VO₂ molecule was placed on Cu (111)-(4X4) surface supercell , and the vanadium content was about 3 at%. Cu-O bond was found after the structure optimization. In the CO₂RR process, the adsorption of *COOH resulted in the reconstruction of VO₂. Monkhorst-Pack method was used to generate $3\times3\times1$ k-point mesh.⁴⁴

Results and Discussion

The np-Cu@VO₂ hybrid electrocatalysts are fabricated through facile alloying/dealloying processes (see Methods), during which the chemical compositions are tuned by controlling precursor alloy ribbons of $Cu_{20-x}V_xAI_{80}$ (x = 0.2, 1, and 2 at%). These precursor ribbons are first produced by meltspinning in vacuum from their alloy ingots made of pure Cu and Al with different amounts of V, which are consisted of a α -Al and CuAl₂ phase (**Figure S1**). This precursor alloy is expected to produce a bimodal nanoporous architecture of hybrid electrocatalysts when selectively etching less-noble Al component from the α -Al and CuAl₂ phase in 2.0 M NaOH solution. With the formation of np-Cu skeleton via fully chemical dealloying processes, the metallic V is exposed to alkaline solution, and then oxidized on the surface of np-Cu to form vanadium oxide species (VO₂). According to the V atom ratio in

the precursor alloy, the products are defined as the np-Cu@VO2-1%, 5% and 10%, respectively. Scanning electron microscope (SEM) images of the app Cu@VO2-5% hybrid electrocatalyst fabricated by chemically dealloying Cu₁₉V₁Al₈₀ precursor exhibit a uniform bicontinuous nanoporous architecture consisting of interconnective metallic ligaments and bimodal nanopore channels with characteristic lengths of ~120 nm first ordered pore and ~15 nm secondary pore (Figure 1a, 1b and Figure S2-3). High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) further confirms the hierarchically porous structure of np-Cu@VO2-5% (Figure 1c). The representative high resolution HAADF-STEM image of np-Cu@VO2-5% shows well-defined lattice fringes (Figure 1d and 1e), further confirming the crystalline structure of np-Cu. The lattice fringe of np-Cu with a d-spacing of ~0.21 nm could be assigned to be (111) plane of cubic Cu (JCPDS 04-0836). The fast Fourier transform (FFT) pattern indicates that the tetragonal CuAl₂ transforms to the cubic Cu (insets of Figure 1e). These are confirmed by X-ray diffraction (XRD) patterns (Figure S4), wherein the characteristic diffraction peaks correspond to the cubic Cu (JCPDS 04-0836). In addition, it is observed that crystalline np-Cu is surrounded by amorphous-like vanadium oxide nanoparticle (Figure 1d). The elemental



Figure 1. Structural and composition characterizations of np-Cu@VO₂-5%. (a) SEM image of catalytic surface. (b) High magnification SEM images. (c) low-magnification HAADF-STEM image. (d) HAADF-STEM image. (e) Fast Fourier transformation filtered HAADF-STEM image. (f) EDS element mappings of np-Cu@VO₂-5%. (g) V 2p XPS spectra for np-Cu@VO₂ with different vanadium components. (h) Vanadium K-edge XANES spectra before and after CO₂RR and the edge position-amplification view. (i) FT of the EXAFS spectra before and after 12h CO₂RR testing at a constant potential of -0.62 V vs. RHE. Scale bars: (a) 400 nm, (b) 100 nm, (c) 100 nm, (d) 2 nm, (e) 1 nm, (f) 40 nm.

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distribution of the np-Cu@VO₂-5% is examined by energy-dispersive X-ray spectroscopy (EDS). Element mappings show that vanadium is homogeneously distributed in the surface of copper skeleton (Figure 1f).

The X-ray photoelectron spectroscopy (XPS) of np-Cu@VO₂-5% further verifies the existence of metallic Cu states (Figure S5). In contrast, the V 2p spectrum of np-Cu@VO2-5% shows the co-existence of V4+ and V5+, implying that the vanadium species is indeed formed (Figure 1g). The O 1s spectra confirms that the vanadium species exist as oxide (Figure S6). Further, X-ray adsorption spectroscopy (XAS) is performed to probe the electronic structure of np-Cu@VO2-5% (Figure 1h, 1i and S7). The V K-edge XANES and EXAFS spectra of np-Cu@VO₂-5% confirm that vanadium specie exists as an oxide in the surface of nanoporous copper. Moreover, once a potential of -0.62 V vs. RHE is applied, the chemical state of vanadium remains unchanged (Figure 1i). We found that, in agreement with the XPS results, Cu species are slightly oxidized before the reaction (Figure S7). However, once a negative potential is applied during CO₂RR, only peaks corresponding to metallic Cu are observed on the hybrid electrocatalyst, which excludes the presence of copper oxide on the surface. Thus, all results enable us to tentatively describe the surface of the np-Cu as an amorphous-like vanadium oxide species.

The electrocatalytic CO₂RR performance of np-Cu@VO₂ is investigated by using a customized H-type cell with a standard three-electrode system. The linear sweep voltammetry (LSV) curves of np-Cu@VO₂-5% and monometallic np-Cu are shown in Figure S8. Compared with monometallic np-Cu, the current densities of np-Cu@VO₂-5% obviously increase under Ar and CO₂ conditions, implying a higher intrinsic activity toward CO2RR than that of monometallic np-Cu. The gas chromatographic (GC) analysis for gas-phase products and nuclear magnetic resonance (NMR) analysis for liquid products are shown in Figure S9-11. Figure 2a and 2b depict the CO2RR products of np-Cu and np-Cu@VO₂-5%, respectively. It is found that the np-Cu exhibits a similar product distribution to that of metallic copper reported previously.45-⁴⁷ Excluding H₂, np-Cu shows six reduction products (CO, HCOOH, CH₃OH, C₂H₄, C_2H_6 , C_2H_5OH). Hydrocarbon products that include C_2H_4 and C_2H_6 exist extremely low faradaic efficiency (FE). Meanwhile, C1 products of CO, HCOOH and CH_3OH possess the Faraday efficiency within ten at a potential range from -0.52 V vs. RHE (Reversible Hydrogen Electrode) to -0.92 V vs. RHE. The diversity of products leads to low FE of C₂H₅OH. Obviously, vanadium doping nanoporous copper not only reduces the type of products, but also reduces the FE of other CO₂ products (Figure 2b). Hydrocarbon products directly disappear and CO product is close to none. while the np-Cu@VO₂-5% shows higher faradaic efficiency (FE) for H₂ and C₂H₅OH with a proper potential. The H_2 and ethanol product profiles as a function of applied potential for each catalyst are shown in Figure 2c, revealing that vanadium oxide could promote the H_2 and C_2H_5OH selectivity of eletrochemical CO_2RR and restrain the formation of other reduction products at a proper potential condition (Figure S12 and S13). Meanwhile, the difference of specific surface area between np-Cu and np-Cu@VO₂-5% is small, even the np-Cu has higher specific surface

area, which indicates that the enhancement of CO2RR performance of npCu@VO₂ is not caused by specific surface area. Thus, the BET results exclude the influence of specific surface area on performance, which proves the contribution of VO₂ modification in enhancing performance (Figure S14). The partial current density for ethanol of the np-Cu@VO₂-5% and np-Cu product are further measured (Figure 2c and 2d). For the np-Cu@VO2-5% hybrid catalyst, the FE for ethanol increase to 30.1%. Accordingly, the partial current densities for ethanol reaches the maximum value of ~ -16 mA cm⁻² at -0.62 V vs. RHE (Figure 2d), indicating a 4-fold increase in CO₂RR activity compared to the bare nanoporous Cu. The lowest charge-transfer resistance (R_{CT}) of np-Cu@VO₂-5% among the catalysts results in the fastest chargetransfer process, which may contribute to the increase of current density (Figure S15). Therefore, the np-Cu@VO₂-5% hybrid catalyst shows one of the best selectivities among the reported electrocatalysts for ethanol production (Figure S16 and Table S2). The better performance of np-Cu@VO₂-5% can be attributed to the stronger hydrogen affinity of vanadium oxide, which results in a high H coverage on the catalyst surface. 7,28,34 It also shows that the increase of ethanol FE is not at all potential, which indicates that there is a competition between the formation of H₂ and C₂H₅OH (Figure 2c). In addition, the sharp increase of the partial current density of H₂ at low potential further illustrate the better formation of H₂ and the higher H coverage of np-Cu@VO₂-5%, which is caused by the strong affinity of vanadium oxide to hydrogen (Figure S17). More interestingly, the ethanol FE of np-Cu@VO2 gradually



increases when the V ratio increases from 1% up to

Figure 2. Electrochemical CO₂RR performance for np-Cu@VO₂ in a typical Htype cell. (a) The Faradaic efficiency of main products for np-Cu at different specific potentials. (b) The Faradaic efficiency of main products for np-Cu@VO₂-5% at different specific potentials. (c) H₂ and ethanol Faraday efficiency distribution of np-Cu@VO₂-5% and np-Cu at the critical potential. (d) The comparison of ethanol partial current density between np-Cu and np-Cu@VO₂-5%. (e) Ethanol Faradaic efficiency of np-Cu@VO₂ with different V component. (f) Chronoamperometry result and ethanol FE of np-Cu@VO₂-5% in CO₂-saturated 0.1 M KHCO₃ solution at -0.62 V vs. RHE.

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10

-0.5 -0.6 -0.7 -0.8 -0.9

80 60

40

Electrolvte

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Potential (V vs. RHE)

-0.7

Potential (V vs. RHE)

ntial (V vs. RHE

-*- np-Cu -*- np-Cu@VO2-5%

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5% (Figure 2e). Further increase of the V content leads to the decline of ethanol FE because of the more H₂ formation. Long-term stability is confirmed by 12 h electrolysis of np-Cu@VO₂-5% at -0.62 V vs. RHE (Figure 2f). Stable current density and average FE reached 30.1% for the overall run are achieved. Furthermore, structural features and chemical compositions of the np-Cu@VO₂-5% are maintained as well (Figure S18-20, Table S1).

To achieve practical applications, the use of flow cell reactors could be an effective solution.⁴⁸⁻⁵⁰ Therefore, the CO₂RR performance of np-Cu and np-Cu@VO₂-5% is further measured in a self-designed flow cell reactor (Figure 3a). The current densities measured in 1.0 M KOH continuously increased with decreasing the applied potential (Figure S21). Figure 3b and 3c show the Faraday efficiency of main products at different specific potential for np-Cu and np-Cu@VO₂-5%, respectively. Obviously, it has similar phenomenon that vanadium doping nanoporous copper reduces the type of products and the FE of other CO₂ products. It is easy to see that the ethanol selectivity of np- $Cu@VO_{2}-5\%$ is greatly improved at the same potential compared to np-Cu. which further proves above view that V doping has a positive effect on ethanol production (Figure 3d). The ethanol FE of the flow cell reactor can even reach the highest level of 38.2% at -0.8 V vs. RHE with a high partial current density of -39 mA cm⁻². It is worth noting that the ethanol partial current density of np-Cu@VO₂-5% is all significantly higher than that of np-Cu (Figure 3e). This is attributed to unique gas-liquid interface and porous conductive framework for mass transfer in the electrode. Meanwhile, energy conversion efficiency could achieve 21.3% in the flow cell (Figure 3f). Notably, np-Cu@VO₂-5% is capable of delivering stable current densities of -102 mA cm⁻² at low applied potentials of -0.80 V vs. RHE, with ethanol FE close to 38.2% (Figure 3g), indicating that the commercial application could be realized close. Consequently, the extraordinary electrocatalytic performance of the as-prepared np-Cu@VO2-5% makes it is comparable with recently reported Cu-based electrocatalysts for CO₂-to-ethonal production in flow cell (Table S3).

To understand the origin of such high electrocatalytic performances, the CO_2RR mechanisms of np-Cu@VO₂ are investigated by first-principles calculations. We first examine the water dissociation energy and the H adsorption energy on both bare Cu (111) and Cu (111)@VO₂ (**Table S4**). As shown in **Figure 4a**, there is a supramaximal difference of 1.33 eV in the dissociation energy of hydrolysis between the Cu and Cu@VO₂, which indicates that water dissociation is more favorable on the vanadium oxide modified-Cu surface in comparison with that on the bare Cu. While, H₂O adsorption of vanadium oxide modified-Cu is stronger than that of monometallic Cu. This validates that the surface of oxide modified-Cu is surrounded by more protons, which are from water dissociation in comparison to bare Cu. The more negative adsorption energy of H on Cu@VO₂ hybrid catalyst indicates that the building such hybrid catalyst could enable us to investigate and exploit *H in CO₂RR.



CO.

Potential (V vs. RHE)

--- np-Cu --- np-Cu@VO2-5%

-0.7 -0.8

• C2H5OH

-0.8 V vs RHE

tial (V vs. RHE)

3

Time / h

(%) (%)

30

20

30

20

-50

-100

-150

Tota

Figure 3. CO₂RR performance of np-Cu and np-Cu@VO₂-5% catalyst in the

flow cell. (a) Schematic diagram of gas diffusion electrode in flow cell (red and

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white balls stand for carbon, oxygen, respectively. Orange atomic layer is catalyst layer). (b) The Faraday efficiency of main products for np-Cu at different specific potential. (c) The Faraday efficiency of main products for np-Cu@VO₂-5% at different specific potential. (d) The ethanol Faraday efficiency distribution of np-Cu and np-Cu@VO₂-5% at different specific potential. (e) The comparison of ethanol partial current density between two catalysts at different specific potential (f) The comparison of energy conversion efficiency between two catalysts at the critical potential. (g) Chronoamperometry result and ethanol FE in 1.0 M KOH solution at -0.8 V vs. RHE.

Moreover, adsorptions of intermediate products on catalyst surfaces are also theoretically investigated by means of the first-principles approach. (Figure 4b, Figure S22 and S23). It is observed that CO_2 forms C_2 intermediate on the copper surface through protonation firstly to form *COOH, then dehydrate to *CO, and finally copolymerize to *OCCO.^{2,48,51} In the initial CO_2 protonation process, compared with bare Cu (0.5 eV), Cu@VO₂ exhibits lower energy barrier (0.29 eV), which is considered as the rate-determining step (Figure 4c, Table S5). In further reaction process for Cu@VO₂, *COOH intermediate hydrogenation and dehydration to *CO intermediate abnormally appears footsteps. This is basically certain that dehydration is inhibited by strong water adsorption for Cu@VO₂, which caused small energy

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barrier to the formation of *CO. It is worth noting that Cu@VO₂ has lower *CO coupling energy barrier (0.94 eV) in comparison to Cu (1.39 eV, Table S4). Meanwhile, the higher *CO adsorption energy can inhibit the desorption of *CO, leading to the *CO coupling, 52-54 which is consistent with experimental result that the FE of CO sharply declines after introducing vanadium oxide. Based on the above analysis, the possible CO₂RR mechanism of np-Cu@VO₂ is proposed (Figure 4d). The strong hydrolytic ability of the vanadium oxide grown on the Cu surface leads to the great increase of the *H coverage. The high *H coverage reduces the hydrogenation reaction energy barrier of protonation of carbon dioxide. Furthermore, the higher *CO adsorption energy of Cu@VO₂ are accompanied with a distinct decrease of free energy for the *COCO formation, which is deemed as the rate-determining step in the ethanol formation path. In addition, the *HCCOH hydrogenates into *HCCHOH is a key process in the ethanol pathway *HCCOH, 34,55,56 The accelerated water dissociation and strong hydrogen adsorption of vanadium oxide increase the surface *H coverage of the hybrid catalyst so as to break the double bond of the *HCCOH intermediate to form *HCCHOH, which results in the improvement of ethanol selectivity.



Figure 4. DFT calculation. (a) Calculated H_2O adsorption energies, H_2O dissociation reaction energies, hydrogen adsorption energies on Cu and Cu@VO₂ surfaces. (b) DFT calculated reaction state on Cu@VO₂ model, from left to right is *COOH adsorbed state, *CO adsorbed state and *OCCO adsorbed state. (c) The free energy diagram for electrochemical CO₂RR path. (d) schematic diagram of key steps in the CO₂RR process. red, white, green, gray and blue spheres stand for copper, oxygen, vanadium, carbon, and hydrogen atoms, respectively.

Besides the intrinsically catalysis of the VO₂ modified np-Cu, the hierarchically nanoporous structure fabricated by the chemical dealloying plays important roles in electrochemical CO₂RR of np-Cu@VO₂. The large surface area and bimodal bicontinuous porous structure, together with nanosize Cu ligaments and thus reduced diffusion length, promote timely fast diffusion of the both electrons and reactants.³⁵⁻³⁷ The bimodal pore has a limiting effect on the diffusion of C₁ intermediate and hydroxyl radical on the catalyst surface. Thereby, the increase of local pH and C₁ intermediate concentration caused by bimodal nanopore can reduce the reaction barrier view Article Online of C-C coupling and promote the reaction kinetics. BG: 10.1039/D0TA09522B

Conclusion

In summary, we have successfully developed a new np-Cu@VO2 hybrid catalyst toward high-efficiency CO2RR by one-step dealloying method. The hierarchically bicontinuous nanoporosity, produced by chemical dealloying, offers a large specific surface area, bimodal porous structure and excellent electrochemical stability, leading to remarkably CO₂RR performance and longterm catalytic lifetime. The resultant np-Cu@VO₂-5% exhibits a 30.1% Faradaic efficiency for CO₂-to-ethonal production and an ethanol partial current density of -16 mA cm⁻² at -0.62 V versus reversible hydrogen electrode (RHE), corresponding to a 4-fold increase in activity compared to the bare nanoporous Cu. It even delivers ethanol partial current density that exceeds -39 mA cm⁻² at -0.8 V vs. RHE in a flow-cell reactor, which is much higher than that of np-Cu. DFT studies reveal that VO₂ modified Cu surface can facilitates the dissociation of water and adsorption of hydrogen on Cu. which would decrease energy barrier in two rate-determining steps reaction and promote the key *HCCHOH intermediate species forming on copper surfaces in the ethanol production pathway. The present results hold a great promise for the design of multi-step CO₂ electroreduction catalysts with great potential for practical application.

Conflicts of interest

The authors declare no competing financial interest.

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TOC Figure

A vanadium oxide integrated on hierarchically nanoporous copper hybrid electrocatalyst with three-dimensional bicontinuous nanoporous architecture is exploited for high-performance electrochemical CO₂ reduction. The obtained np-Cu@VO₂-5% hybrid electrocatalyst enables a 30.1% Faradaic efficiency for CO₂-to-ethonal production and an ethanol partial current density of -16 mA cm⁻² at -0.62 V vs. RHE, corresponding to a 4-fold increase in activity compared to the bare nanoporous Cu.

