Electrocatalytic CO₂ Reduction to Ethylene over CeO₂-Supported Cu Nanoparticles: Effect of Exposed Facets of CeO₂

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Abstract: Fossil fuels are expected to be the major source of energy for the next few decades. However, combustion of nonrenewable resources leads to the release of large quantities of CO₂, the primary greenhouse gas. Notably, the concentration of CO₂ in the atmosphere is increasing annually at an astounding rate. Electrochemical CO₂ reduction (ECR) to value-added fuels and chemicals using electricity from intermittent renewable energy sources is a carbon-neutral method to alleviate anthropogenic CO₂ emissions. Despite the steady progress in the selective generation of C₁ products (CO and formic acid), the production of multi-carbon species still suffers from low selectivity and efficiency. As an ECR product, ethylene (C₂H₄) has a higher energy density than do C₁ species and is an important industrial feedstock in high demand. However, the conversion of CO₂ to C₂H₄ is plagued by low productivity and large overpotential, in addition to the severe competing hydrogen evolution reaction (HER) during the ECR. To address these issues, the design and development of advanced electrocatalysts are critical. Here, we demonstrate fine-tuning of ECR to C₂H₄ by taking advantage of the prominent interaction of Cu with shape-controlled CeO₂ nanocrystals, that is, cubes, rods, and octahedra predominantly covered with (100), (110), and (111) surfaces, respectively. We found that the selectivity and activity of the ECR depended strongly on the exposed crystal facets of CeO₂. The overall ECR Faradaic efficiency (FE) over Cu/CeO₂(110) (FE $\approx$ 56.7%) surpassed that of both Cu/CeO₂(100) (FE $\approx$ 51.5%) and Cu/CeO₂(111) (FE $\approx$ 48.4%) in 0.1 mol·L⁻¹ KHCO₃ solutions with an H-type cell. This was in stark contrast to the exclusive occurrence of the HER over pure carbon paper, CeO₂(100), CeO₂(110), and CeO₂(111). In particular, the FE toward C₂H₄ formation and the partial current density increased in the sequence Cu/CeO₂(111) < Cu/CeO₂(100) < Cu/CeO₂(110) within applied bias potentials from -1.00 to -1.15 V (vs. the reversible hydrogen electrode), reaching 39.1% over Cu/CeO₂(110) at a mild overpotential (1.13 V). The corresponding values for Cu/CeO₂(100) and Cu/CeO₂(111) were FE_{C₂H₄} $\approx$ 31.8% and FE_{C₂H₄} $\approx$ 29.6%, respectively. The C₂H₄ selectivity was comparable to that of many reported Cu-based electrocatalysts at similar overpotentials. Furthermore, the FE for C₂H₄ remained stable even after 6 h of continuous electrolysis. The superior ECR activity of Cu/CeO₂(110) to yield C₂H₄ was attributed to the metastable (110) surface, which not only promoted the effective adsorption of CO₂ but also remarkably stabilized Cu⁺, thereby boosting the ECR to produce C₂H₄. This work offers an alternative strategy to enhance the ECR efficiency by crystal facet engineering.

Key Words: CO₂; Electrochemical reduction; Ethylene; Cu; CeO₂; Exposed facet

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CeO₂ 负载 Cu 纳米粒子电催化 CO₂ 还原产乙烯: CeO₂ 不同暴露晶面对催化性能的影响

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摘要: 化石燃料在未来几十年仍然是主要的能量来源, 但是这种不可再生资源的燃烧释放出大量的CO₂ (主要的温室气体), 空气中CO₂的浓度每年仍然持续增加。使用间歇性可再生能源转化的电能驱动电化学CO₂还原生成高附加值产品为其减排提供了一种有前景、CO₂“零排放”的方法。本文通过利用Cu和不同形状的CeO₂纳米晶之间的相互作用, 即分别暴露(100)、(110)、(111)晶面的立方体、棒状和八面体CeO₂, 实现了对电化学CO₂还原产乙烯的有效调控。研究发现, 电化学CO₂还原的选择性和活性与CeO₂暴露的晶面密切相关, 生成乙烯的法拉第效率和偏电流密度在1.00到1.15 V (相对于可逆氢电极)的施加电势范围内呈现出Cu/CeO₂(111) < Cu/CeO₂(100) < Cu/CeO₂(110)的趋势。在H-型电解池中, 以0.1 mol·L⁻¹ KHCO₃溶液为电解质, Cu/CeO₂(110)电催化CO₂还原的法拉第效率为56.7%, 这与纯碳纸、CeO₂(100)、CeO₂(110)、CeO₂(111)纳米颗粒上只发生析氢副反应形成了鲜明对比, 并且Cu/CeO₂(110)可在较温和的过电势下(1.13 V)电催化CO₂还原产乙烯, 其法拉第效率达到39.1%, 和文献报道的很多Cu-基材料的性能相当, 而Cu/CeO₂(100)与Cu/CeO₂(111)产乙烯的法拉第效率分别为31.8%和29.6%。此外, 经过6 h的持续电解后, 乙烯的法拉第效率基本保持稳定。Cu/CeO₂(110)还原CO₂产乙烯的活性可能与CeO₂(110)表面的亚稳态性质有关, 其不仅能有效促进CO₂的吸附, 还能有效稳定Cu⁺, 从而促进了CO₂还原为乙烯。本工作为增强电化学CO₂还原提供了晶面工程途径。

关键词: 二氧化碳; 电化学还原; 乙烯; 铜; 二氧化铈; 暴露晶面

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1 Introduction

Anthropogenic global warming is a dire consequence of excess emissions of greenhouse gases, mostly carbon dioxide (CO₂)¹⁻³. The steady increase in the concentration of atmospheric CO₂, from 270 × 10⁻⁶ in the preindustrial era to more than 407 × 10⁻⁶ by 2019, and probably approaching 600 × 10⁻⁶ by 2100, intensifies such catastrophic effect. Electrochemical CO₂ reduction (ECR) powered by renewably generated electricity offers a mild and clean way to mitigate this issue⁴⁻¹⁰. ECR also offers an avenue to resolving energy security and energy sustainability. ECR can proceed *via* multiple concerted proton-electron transfer processes. Based on the number of electrons and protons transferred, CO₂ can be converted to different products. However, CO₂ has remarkable thermodynamic stability and requires high energy to be activated. Efficient conversion of CO₂ is only achievable through the design of advanced electrocatalysts with optimized structures¹¹⁻¹⁴.

ECR to C₁ species such as carbon monoxide (CO)¹⁵⁻¹⁷ and formic acid (HCOOH)¹⁸ has been achieved at a very high Faradaic efficiency (FE) exceeding 90%, while production of multi-carbon compounds remains a grand challenge¹⁹. Among the reported electrocatalysts, Cu appears to be the only metal that is capable of catalyzing the ECR to not only HCOOH and CO but also a range of hydrocarbons and oxygenates (aldehydes, and alcohols)¹². Cu possesses a suitable binding strength of *CO

(affinity not too weak and not too strong) to obey the Sabatier principle, favoring further C–C coupling transformation. Also, it has a negative adsorption energy for CO* but a positive adsorption energy for H* (an intermediate formed in the hydrogen evolution reaction, HER)²⁰. C₂H₄ is a widely used feedstock for producing plastics, ethylene oxide, and diesel fuels. However, due to the concurrent generation of H₂ and other C₁ compounds, the FE for the production of C₂H₄ (FE_{C₂H₄}) on metallic Cu is low. Efforts to improve the FE_{C₂H₄} have been made on optimizing the sizes, morphologies, and exposed crystal lattices of metallic Cu nanoparticles (NPs)²¹⁻²³. In addition, Cu/oxide interfaces are considered to play a role in impeding the undesired HER during ECR. In our previous work, we found that tuning the composition and interface of CuO and Sb₂O₃ or In₂O₃ enabled substantially enhanced CO₂-to-CO conversion^{24,25}. The CO FE was as high as 93.0% over CuO-In₂O₃ composite catalysts²⁶. CeO₂ has been regarded as a remarkable catalyst or support owing to its redox behavior and oxygen storage capacity²⁷⁻³⁴. Of particular interest, CeO₂ was found to effectively stabilize Cu⁺, thereby boosting the ECR selectively to yield C₂H₄ over CuO³⁵. Despite these advances, effects of the interaction between metallic Cu and CeO₂ with varying exposed facets on ECR have not been explored thus far.

Herein, we investigated the ECR performance of Cu NPs supported on different shaped-controlled CeO₂ nanocrystals. The ECR selectivity and activity was found to be significantly

affected by the exposed crystal facets of CeO₂. Furthermore, the FEED_{C₂H₄} was shown to increase following the trend of Cu/CeO₂(111) < Cu/CeO₂(100) < Cu/CeO₂(110). We found that CeO₂ changed the oxidation state of Cu atoms toward Cu⁺ at the CuO-CeO₂ interface with CeO₂(110) being more remarkably than CeO₂(100) and CeO₂(111). The existence of Cu⁺ species was supposed to be likely the adsorption and active sites for CO₂ activation followed by further C-C coupling to yield C₂H₄.

2 Experimental

2.1 Materials

Ce(NO₃)₃·6H₂O (Product number: C105376, 99.5%), Na₃PO₄·12H₂O (Product number: S112445, 98.0%), Cu(Ac)₂·H₂O (Product number: C108085, 99.95%), NaBH₄ (Product number: S108355, 98.0%) and ethanol (Product number: E111963, 99.9%) were purchased from Aladdin (Shanghai, China). NaOH (Product number: S817970, 97.0%) was provided by Maclin (Shanghai, China). All raw materials were used as received without additional treatments.

2.2 Synthesis of CeO₂ cubes, rods, and octahedra predominantly covered with (100), (110), and (111) surfaces, respectively

CeO₂ cubes were synthesized using a hydrothermal method³⁶. Typically, 9.6 g of NaOH and 40.0 mL of deionized (DI) water were added in a Teflon-lined steel reactor (100 mL) and mixed with 0.868 g of Ce(NO₃)₃·6H₂O under magnetic stirring for 30 min to yield a white suspension. The reactor was sealed and heated at 453 K for 24 h. The resulting precipitate was separated by centrifugation and washed with excess DI water and ethanol four times, followed by drying at 353 K for 8 h. The obtained powder was then treated at 673 K for 4 h at a heating rate of 5 K·min⁻¹.

CeO₂ nanorods were prepared by adapting a similar hydrothermal method³⁷. Specifically, 8.44 g of NaOH and 15.0 mL of DI water were added in a Teflon-lined steel reactor (100 mL) and mixed with 0.88 g of Ce(NO₃)₃·6H₂O and 20.0 mL of DI water under magnetic stirring for 30 min to form a white slurry. The reactor was sealed and heated at 453 K for 24 h. The resulting precipitate was separated by centrifugation and washed with a mixture of excess DI water and ethanol four times, and subsequently dried at 333 K for 6 h. The obtained powder was subsequently treated at 773 K for 4 h under Ar at a heating rate of 5 K·min⁻¹.

CeO₂ octahedra were produced using a modified hydrothermal method³⁶. 0.0038 g of Na₃PO₄·12H₂O and 40.0 mL of DI water were loaded in a Teflon-lined steel reactor (100 mL), followed by mixing with 0.434 g of Ce(NO₃)₃·6H₂O under vigorous magnetic stirring for 30 min. The reactor was sealed and heated at 473 K for 20 h. The resulting precipitates were separated by centrifugation and washed with excess DI water and ethanol four times, followed by drying at 353 K for 8 h. The obtained powder was then calcined at 673 K for 4 h at a heating rate of 5 K·min⁻¹.

2.3 Preparation of Cu/CeO₂ catalysts

Cu nanoparticles were immobilized on the surface of CeO₂ through an ultrasonication-facilitated deposition method using sodium borohydride as a reductant. Typically, 20.0 mg of CeO₂ powder with controlled shapes and a specific amount of Cu(Ac)₂·H₂O were dissolved in 20.0 mL of ethanol. The resultant solution was subjected to ultrasonication for 10 min to ensure a complete mixing. 10.0 mL of 0.1 mol·L⁻¹ NaBH₄ ethanol solution was added into the solution under nitrogen, which was ultrasonicated for another 20 min. The resulting precipitate was separated by centrifugation and washed with a mixture of excess DI water and ethanol four times, and then dried in a vacuum oven at 273 K for 8 h.

2.4 Characterization

X-ray powder diffraction (XRD) was carried out with a D/MAX-RC diffractometer (Japan) operated at 30 kV and 100 mA with Cu K_α radiation (λ = 0.15418 nm). X-ray photoelectron spectroscopy (XPS) experiments were conducted using Thermo Scientific ESCALAB 250Xi instrument (UK) equipped with an electron flood and scanning ion gun. All spectra were calibrated to the C 1s binding energy at 284.8 eV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was recorded using a JEOL ARM200 microscope (Japan) operated at 200 kV voltage. High-resolution (HR) transmission electron microscopy (TEM) was performed using a JEOL 3000F (Japan). TEM and STEM samples were obtained by dropping a droplet of suspension onto a Ni grid coated with a lacey carbon film. The Brunauer-Emmett-Teller specific surface areas of samples were determined using a physical adsorption instrument (Micromeritics ASAP 2020, USA) at 77 K. The sample was subjected to degassing at 120 °C for 12 h.

2.5 Electrochemical measurements

Controlled potential electrolysis was performed in a conventional H-type cell reactor separated by a cationic polymeric membrane (Nafion 117). Prior to ECR measurements, the Nafion membrane was heated in H₂O₂ aqueous solution (5.0%) and H₂SO₄ (0.5 mol·L⁻¹) at 80 °C for 1 h, respectively. Subsequently, the Nafion membrane was soaked in DI water at room temperature and left for 30 min and then washed with DI water. 12.0 mg of a catalyst was suspended in 2.4 mL of a mixture of isopropanol, DI, and Nafion solution (5.0% (w, mass fraction)) with a respective volume ratio of 100 : 100 : 1 under ultrasonication for 30 min to yield a homogeneous dispersion. 240 μL of the dispersion was then deposited onto a Toray Carbon fiber paper electrode (1.2 cm × 1 cm), and dried under room temperature. A Pt wire and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The potentials were controlled by an electrochemical working station (CHI 760E, Shanghai CH Instruments Co., China). All voltages in this study were provided relative to the Ag/AgCl reference electrode (in KCl solution, 3.5 mol·L⁻¹) and converted to the RHE reference scale based on the equation

$$E \text{ (vs RHE)} = E \text{ (vs Ag/AgCl)} + 0.197 + 0.0591 \times \text{pH} \quad (1)$$

ECR was conducted in CO₂-saturated 0.1 mol·L⁻¹ KHCO₃ (pH 6.8) under ambient conditions. CO₂ was bubbled in the KHCO₃ electrolytes for 30 min to expel residual air in the solution, and controlled electrolysis was carried out at each potential for 60 min.

Linear sweep voltammograms in Ar- or CO₂ environment were obtained by using a three-electrode configuration with an Ag/AgCl reference electrode, Pt wire counter electrode, and glassy carbon working electrode on a CHI 760E potentiostat. Rotating disk electrode (RDE) experiments were performed on an AFMSRCE RDE control system (Pine Inc., USA). The electrolyte is 0.1 mol·L⁻¹ KHCO₃ solution bubbled with Ar or CO₂ for 30 min. To attain linear sweep voltammograms, 6 mg of a catalyst was suspended in a solution containing ethanol (600 μL), DI water (600 μL), and Nafion solution (1.0% (w), 600 μL). Then, the mixture was treated under ultrasonication for 30 min to yield an ink. 7.95 μL of the ink was subsequently loaded onto a glassy carbon electrode and dried at room temperature.

2.6 Quantitative determination of gaseous and liquid products

The gas-phase products after ECR were analyzed by an Agilent 7890B gas chromatography (GC) with two thermal conductivity detectors (TCD) and one flame ionization detector (FID). To probe the gas products, 20 mL of produced gas in the dead volume of a gas bag (~2 L) was injected into the GC at equivalent conditions with a sample lock syringe. CO, C₂H₄, CH₄, and H₂ mole fractions of injected samples could be determined based on GC calibration curves. The amounts of liquid products (n in moles) were measured using nuclear magnetic resonance (NMR, Bruker Avance III 400 HD spectrometer). NMR samples were made by blending 0.5 mL of the product-containing electrolyte and 0.1 mL of DMSO-*d*₆ as the internal standard. The FE of a product was determined using the equation:

$$FE = Q_{\text{product}}/Q_{\text{total}} = (mF \times n)/(I \times t) \quad (2)$$

Where F represents the Faraday constant (96485 C·mol⁻¹), n

the number of moles for a product, m (in number) the electrons needed for the formation of one product molecule. The amount of charge (Q in Coulomb) passed to generate products was determined. I (in ampere) stands for the constant current at an applied potential. t (in second) corresponds to the electrolysis time.

3 Results and discussion

3.1 Morphology and structure analysis

The X-ray diffraction (XRD) analysis results of the as-obtained Cu/CeO₂ samples, along with the patterns of standard CeO₂, metallic Cu, and CuO_x, are provided in Fig. 1a. The diffraction peaks appearing around 28.1°, 32.5°, 47.1°, 55.9°, 58.6°, 69.0°, 76.2°, and 78.7°, could be well indexed to the (111), (200), (220), (311), (222), (400), (331), and (420) planes of CeO₂ (PDF#43-1002), respectively. This suggests the yield of fluorite (*Fm3m*) CeO₂ with a face-centered cubic (*fcc*) structure in the composites³⁸. No typical reflections of Cu, Cu₂O, and CuO were observed in all cases, plausibly resulting from the low loading and/or small sizes of Cu in the samples.

To probe the surface composition and chemical state of Cu and Ce, as well as their interactions, XPS was performed. The Cu 2*p* XPS spectrum of Cu/CeO₂(110) was provided in Fig. 1b. Pronounced peaks of Cu 2*p*_{1/2} with binding energies (BEs) at 952.3 and 954.2 eV were clearly observed, generally associated with the Cu⁰/Cu⁺ and Cu²⁺ species, respectively³⁵. Three satellite peaks at about 940.9, 943.6, and 962.5 eV (Figs. 1b and S1a and S1b) originated from Cu²⁺, while a satellite peak at about 571.2 eV (Fig. S1c–e) corresponded to Cu⁺³⁹. The existence of oxidized Cu is probably due to oxidation of the sample after exposure in the air. Interestingly, the content of Cu⁺ was found to follow the sequence of Cu/CeO₂(110) > Cu/CeO₂(100) > Cu/CeO₂(111) in the Cu LMM Auger spectra (Fig. S1c–e). This suggests that CeO₂(110) has a more remarkable capability to stabilize Cu⁺ compared to CeO₂(100) and CeO₂(111). Fig. 1c shows the Ce 3*d* signals of

Fig. 1 (a) XRD patterns of Cu/CeO₂(111), Cu/CeO₂(110), and Cu/CeO₂(100); (b) Cu 2*p* and (c) Ce 3*d* XPS spectra of Cu/CeO₂(110).

Cu/CeO₂(110), which display a satellite structure arising from hybridization of Ce 3d orbitals with O 2p orbitals and partial occupation of the 4f levels. The 3d_{5/2} and 3d_{3/2} spin-orbit peaks (spin-orbit splitting, about 18.5 eV) are depicted as ν and ν' , respectively, attributed to Ce⁴⁺. The peaks of ν_0 and ν_1 were assigned to a mixing configuration of the 3d⁹4f² (O 2p⁴) and 3d⁹4f¹ (O 2p⁵) Ce⁴⁺ states and ν_2 to the 3d⁹4f⁰ (O 2p⁶) Ce⁴⁺ state. A similar assignment was used to analyze the ν' structures, in accordance with the Ce 3d_{3/2} level. This manifests the predominated state of Ce⁴⁺ in the samples, matching with the XRD results. Four peaks u_0 (BE $\approx$ 884.5 eV), u_1 (BE $\approx$ 881.6 eV), u_0' (BE $\approx$ 903.4 eV), and u_1' (BE $\approx$ 899.5 eV) corresponding to Ce³⁺ could be observed, suggesting the formation of Ce₂O₃ in the samples⁴⁰. Fig. S1f displays N₂ adsorption-desorption isotherms of the Cu/CeO₂ samples. A typical type I-isotherm can be observed according to the BDDT (Brunauer, Deming, Deming, and Teller) classification⁴¹. The BET (Brunauer-Emmett-Teller) surface area is 90.1, 46.3, and 101.1 m²·g⁻¹ for Cu/CeO₂(111), Cu/CeO₂(100), and Cu/CeO₂(110), respectively.

The morphological features of the resulting CeO₂ nanocrystals and Cu/CeO₂ samples were examined by TEM and HAADF-STEM. As revealed by TEM (Fig. 2), well-defined CeO₂ samples with a morphology of cubes, rods, and octahedra were formed. The as-synthesized CeO₂ has good crystallinity. Predominant CeO₂ {100} and {200} planes were observed, as confirmed by their lattice spacing³⁶, with the CeO₂ cubes exhibiting an average size of about 18.0 nm (Fig. 2a,b). Whereas

Fig. 2 TEM and HRTEM images of CeO₂ with different shapes: (a, b) cubes; (c, d) rods; and (e, f) octahedra. The inset in image (f) illustrates the corresponding FFT.

{220} planes with a d -spacing of 0.19 nm³⁷ were identified for CeO₂ rods with a mean diameter and length of about 6.7 and 27.6 nm, respectively (Fig. 2c,d). By fast Fourier transformation (FFT) (inset of Fig. 2f), the exposed facet of {111}³⁶ was indexed for a CeO₂ octahedra (Fig. 2e,f), with a size of $\sim$ 180.0 nm. Fig. 3a–f shows the STEM images and electron energy loss spectroscopy (EELS) spectra of Cu/CeO₂(100), Cu/CeO₂(110), and Cu/CeO₂(111). It can be seen that the morphology of respective CeO₂ retained regardless of Cu decoration (Fig. 3a,c,e). The EEL spectra at Ce $M_{5,4}$ edges matched what we expected for CeO₂ (Fig. 3b,d,f)⁴². The EEL spectra at the Cu $L_{2,3}$ edges manifested adsorption jumps at $E(L_3)$ of about 930 eV and $E(L_2)$ of about 950 eV, corresponding to transitions from 2p core levels to unoccupied 3d levels present in oxidized Cu. Based on HRTEM and FFT, fcc CuO NPs of about 5 nm surrounded by CeO₂ nanocrystals were discerned (Fig. 3g–i). The formation of CuO is likely due to oxidation of metallic Cu after exposure of the samples in the air.

3.2 Investigation of Cu/CeO₂ for electrochemical CO₂ reduction

The catalytic properties of Cu/CeO₂ catalysts toward CO₂ reduction were tested in CO₂-saturated 0.1 mol·L⁻¹ KHCO₃ solutions (pH 6.8) using an H-type cell under continuous CO₂ bubbling. The geometric current densities of Cu/CeO₂ samples were examined by linear sweep voltammetry (LSV) with applied voltages in the range from 0.00 to -1.40 V, as displayed in Figs. 4a and S2a. Of note, for all three Cu/CeO₂ samples remarkably higher cathodic current densities were attained in a CO₂ environment compared with an Ar atmosphere throughout the

Fig. 3 STEM images and EELS spectra of (a, b) Cu/CeO₂(100), (c, d) Cu/CeO₂(110), (e, f) Cu/CeO₂(111); (g) HRTEM image of Cu/CeO₂(111); (h) enlarged image of the white rectangle in image (g); (i) FFT of the region shown in image (h).

Fig. 4 (a) LSV results of Cu/CeO₂(110) on a glassy carbon electrode in Ar- (dashed black line) or CO₂ (solid red line)-saturated 0.1 mol·L⁻¹ KHCO₃ at a scan rate of 5 mV·s⁻¹. (b) Faradaic efficiencies for ECR products of Cu/CeO₂(100), Cu/CeO₂(110), and Cu/CeO₂(111) at -1.05 V. (c) Overall ECR Faradaic efficiencies and (d) C₂H₄ geometric current densities over Cu/CeO₂(111) (named as ①), Cu/CeO₂(110) (named as ②), and Cu/CeO₂(100) (named as ③) at various applied potentials. (e) ECR Faradaic efficiencies at -1.05 V as a function of Cu loading over Cu/CeO₂(110). (f) Tafel plots of the partial geometric current density for C₂H₄ production over Cu/CeO₂(100), Cu/CeO₂(110), and Cu/CeO₂(111). (g) C₂H₄ FEs (column) and corresponding partial geometric current densities (ball) for Cu/CeO₂(110) during cycles with an interval of 1 h in CO₂- and Ar-saturated 0.1 mol·L⁻¹ KHCO₃. (h) Current density and C₂H₄ FE of Cu/CeO₂(110) during long-time electrolysis at -1.05 V.

potential range applied. CO, H₂, CH₄, C₂H₄ were probed at working voltages from -1.00 to -1.20 V in a CO₂-saturated 0.1 mol·L⁻¹ KHCO₃ solution. In sharp contrast, pure carbon paper, CeO₂(100), CeO₂(110), and CeO₂(111) exclusively produced H₂ within the applied potentials (Fig. S2b–e), indicating their poor activities for ECR. At -1.05 V, the ECR took place over HER for all the three Cu/CeO₂ samples. The overall ECR FE over Cu/CeO₂(110) (FE ≈ 56.7%) outperformed that of both Cu/CeO₂(100) (FE ≈ 51.5%) and Cu/CeO₂(111) (FE ≈ 48.4%) (Fig. 4b,c). Strikingly, Cu/CeO₂(110) exhibited the highest selectivity for C₂H₄ formation (FE_{C₂H₄} ≈ 39.1%) at -1.05 V compared to Cu/CeO₂(100) (FE_{C₂H₄} ≈ 31.8%) and Cu/CeO₂(111) (FE_{C₂H₄} ≈ 29.6%). The C₂H₄ selectivity is comparable to many reported Cu-based materials under similar overpotentials such as Cu nanocubes with exposed (100) facets (FE_{C₂H₄} ≈ 32.0%)⁴³, Ag-Cu nanodimers (FE_{C₂H₄} ≈ 40.0%)⁴⁴, and carbon electrocatalysts such as N-doped graphene quantum dots (FE_{C₂H₄} ≤ 31.0%)⁴⁵. Likewise, Cu/CeO₂(110) also displayed

significantly larger C₂H₄ partial geometric current density than the other two catalysts (Fig. 4d). Comparably lower CO generation was observed for Cu/CeO₂(110) attributed to its higher hydrocarbon production, which consumed the CO intermediate. The high intrinsic activity of the Cu/CeO₂(110) sample may be closely correlated to the nature of the metastable (110) surface⁴⁶. On the one hand, CeO₂ facilitated effective adsorption of CO₂, forming carbonates and hydrogen carbonates, thereby benefiting ECR³⁵. On the other hand, CeO₂(110) could significantly stabilize Cu⁺, which was believed to play a critical role in the ECR to produce C₂H₄³⁵. The ceria nanocrystals with different facets synthesized here were all larger than 5 nm, therefore, the size of ceria was unlikely to affect the catalytic performance⁴⁷. These point to the possibility that the exposed CeO₂(110) facets favored ECR over Cu selectively to C₂H₄.

At applied overpotentials more positive than -1.05 V, more CO than CH₄ was produced while CH₄ dominated in the ECR products at more negative potentials than -1.15 V for the three

catalysts. At voltages ≤ -1.20 V, the FE of evolved H_2 surpassed 50.0%, which tended to increase with increasing overpotential. This is most probably due to restricted CO_2 mass transport and thus more protons available for facile occurrence of the competing HER. Moreover, the effect of Cu loading in Cu/CeO₂(110) on ECR was investigated (Fig. 4e). It was found that the ECR FE increased with improving the content of Cu from 2.5% (w) to 5.0% (w). This may be due to the increase of the interface between Cu and CeO₂. However, further increase in Cu loading from 5.0% (w) to 7.5% (w) resulted in drop of ECR performance, which was probably attributed to aggregation of Cu NPs and thus decrease of the interfacial area of Cu with CeO₂.

The reaction kinetics were studied by Tafel analysis. A Tafel slope of 192.8 mV·dec⁻¹ was derived for Cu/CeO₂(110), smaller than 194.4 mV·dec⁻¹ for Cu/CeO₂(100) and 207.1 mV·dec⁻¹ for Cu/CeO₂(111) (Fig. 4f). This indicates that the Cu/CeO₂(110) has a faster kinetics for ECR to generate C₂H₄. The generation of the *CO intermediate for subsequent reactions on the surface of the catalysts may be the rate-controlling process. The Nyquist plots showed a lower charge transfer resistance of Cu/CeO₂(110) NPs than both Cu/CeO₂(100) and Cu/CeO₂(111) (Fig. S2f), indicating its more favorable electron exchange between the catalyst on the electrode surface and dissolved CO₂ in the electrolyte, benefiting ECR.

The stability of the ECR process over Cu/CeO₂(110) was evaluated by alternated electrolysis between Ar- and CO₂-saturated electrolytes (Fig. 4g) as well as continuous electrolysis under CO₂ environment at a fixed potential of -1.05 V for 6 h (Fig. 4h). It is worth noting that the catalyst remained steady for C₂H₄ formation in both cases.

4 Conclusions

To be concluded, we have demonstrated facile synthesis of Cu NPs supported on CeO₂ nanocrystals (cubes, rods, and octahedra) with different exposed facets. The Cu/CeO₂ nanocomposites were observed to exhibit facet dependent catalytic properties for ECR in 0.1 mol·L⁻¹ KHCO₃ solutions at ambient conditions. The Cu/CeO₂(110) catalyst delivered higher ECR performance than both Cu/CeO₂(100) and Cu/CeO₂(111) in terms of ECR FE and partial geometric current density. Especially, the FE_{C₂H₄} and J_{C₂H₄} over Cu/CeO₂(110) reached up to 39.1% and 2.5 mA·cm⁻² at -1.05 V, respectively, in contrast to 31.8% and 2.2 mA·cm⁻² for Cu/CeO₂(100), 29.6% and 1.7 mA·cm⁻² for Cu/CeO₂(111). The superior ECR activity of Cu/CeO₂(110) could be attributed to a strong synergy between Cu NPs and CeO₂(110) facets, which resulted in more stabilized Cu¹⁺ species, thus promoting C-C coupling, formation and desorption of C₂H₄. Our work provides a simple and effective avenue for enhancing the ECR toward C₂H₄ formation by crystal facet engineering.

internet at <http://www.whxb.pku.edu.cn>.

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