Facile synthesis of two-dimensional copper terephthalate for efficient electrocatalytic CO₂ reduction to ethylene

Ying Zhang, Yangmei Li, Qiang Tan, Song Hong and Zhenyu Sun

ABSTRACT
Electrochemical CO₂ reduction (ECR) powered by renewable electricity is reckoned to provide an effective strategy to alleviate environmental issues and energy crisis, enabling a potential carbon neutral economy. To boost the ECR to fuels and value-added chemicals, the design of highly active and selective catalysts is important. In this study, we demonstrate facile ultrasonication-facilitated synthesis of two-dimensional copper terephthalate for efficient ECR. High faradaic efficiencies (FEs) of up to 72.9% for hydrocarbons are achieved at a mild overpotential in an H-type cell. In particular, the FE for ethylene (C₂H₄) formation approaches 50.0% at an applied potential of −1.1 V (vs. the reversible hydrogen electrode), outperforming commercial Cu, Cu₂O, CuO, Cu(OH)₂ and many recently reported Cu-based materials. The C₂H₄ partial geometric current density is as high as ~6.0 mA cm⁻². This work offers a simple avenue to developing advanced electrocatalysts for converting CO₂ into high-value hydrocarbons.

1. Introduction
CO₂ concentration has been progressively increasing since the preindustrial era (~280 ppm) due to anthropogenic activities, reaching over 419 ppm levels in 2021 [1–4]. This intensifies environmental issues. Electrochemical CO₂ reduction (ECR) driven by electricity generated from intermittent renewable resources provides a potential strategy to produce fuels and value-added chemicals, enabling a sustainable future [5]. Since the pioneering work dated back to the 1950s, massive efforts have been made to design and screen materials for efficient ECR [6–10].

In comparison to methane (CH₄) [11], carbon monoxide (CO) [12–17], or formic acid (HCOOH or formate [HCOO⁻] in alkaline electrolyte) [18,19] that are typically the major C₁ products of CO₂ reduction, converting CO₂ into C₂+ (encompassing two or more...
carbon atoms) hydrocarbons and oxygenates is desirable from both ecological and economic viewpoints [20–23]. Among various materials, Cu is the only active metal to electrochemically catalyse CO₂ into multi-electron transferred products because of its negative adsorption energy for CO* and positive adsorption energy for H* [24]. Cu has a suitable affinity for *CO in accordance with the Sabatier principle, thus facilitating further step-wise transformation to yield up to 12 C₂+ products [4,25–27]. However, Cu is intrinsically limited by the scaling relations between the binding energies (BEs) of different reaction intermediates on the metallic surface. This results in wide product distributions and undesired H₂ evolution, therefore inhibiting large-scale implementation. From this scenario, endeavours have been initiated to improve the activity and selectivity by crystal facet engineering [28], heteroatom doping [29,30], alloying [31,32], construction of hybrids [33–36] or through control of morphology [37], oxidation state [38] of Cu catalysts. Despite rapid progress that has been made in ECR after decades of exploration, the viability of CO₂ electrolysis from a commercial perspective still needs to overcome key hurdles such as large kinetic overpotential (up to 1.0 V for C₂+ products), insufficient current density and low selectivity for C₂+ products, among others. To this end, the design and development of new and advanced electrocatalysts are important.

Herein, we reported the synthesis of a two-dimensional (2D) Cu-based porous structure through a facile ultrasonication-assisted coordination strategy at room temperature. The as-obtained materials facilitated the ECR to hydrocarbons at mild overpotentials. Especially, the faradaic efficiency (FE) for the formation of ethylene (C₂H₄) reached up to 50.0% at an applied potential of −1.1 V vs. the reversible hydrogen electrode (RHE) in an H-type cell with 0.1 M aqueous KHCO₃ electrolyte solution, superior to commercial Cu, Cu₂O, CuO, Cu(OH)₂ and many other Cu-based electrocatalysts demonstrated in prior literature.

2. Experimental

2.1. Reagents and materials

All chemicals used in this work were of analytical grade and used without further treatments. Anhydrous ethanol, isopropanol (IPA), terephthalic acid (TPA), 1,3,5-benzenetricarboxylic acid (BTC) and N,N-dimethylformamide (DMF) were obtained from Aladdin. CuCl₂•2H₂O and commercial Cu, Cu₂O, CuO, Cu(OH)₂ were purchased from Aladdin. Carbon black was provided by Beijing Chemical Reagent Company. Nafion solution (5.0 wt%) was supplied by Sigma-Aldrich. Toray Carbon Paper (TGP-H-060, thickness of 0.19 mm, resistivity of ~5.8 mΩ cm, porosity of 78.0%) and Nafion 117 membranes were bought from Alfa Aesar. Deionised water (18.2 megohm-cm) was obtained from a Millipore system. Carbon dioxide gas (99.999% purity) and argon gas (99.999% purity) were both provided by Beijing Haipu Gas Co., Ltd.

2.2. Synthesis of Cu/TPA-DMF and Cu/BTC-DMF

To obtain Cu/TPA-DMF, 32 mL of DMF, 2 mL of ethanol and 2 mL of deionised water were first mixed in a 100 mL flask at 25°C under magnetic stirring. Then 0.75 mmol of TPA was dissolved into the above mixture under bath ultrasonication to yield a homogeneous dispersion. Subsequently, 0.75 mmol of CuCl₂•2H₂O was added and the system was subjected to bath ultrasonication (40 kHz) for 8 h. Finally, the products were obtained after repeating washing with water and ethanol followed by vacuum drying at 60°C.
overnight. Cu/BTC-DMF was prepared via a similar procedure except the use of BTC rather than TPA.

2.3. Characterisation

X-ray powder diffraction (XRD) was performed with a D/MAX-RC diffractometer operated at 30 kV and 100 mA with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) experiments were carried out using Thermo Scientific ESCALAB 250Xi instrument. The instrument was equipped with an electron flood and scanning ion gun. All spectra were calibrated to the C 1s BE at 284.8 eV. Scanning electron microscopy (SEM) was conducted using a field emission microscope (JEOL JSM-7800F) operated at 5 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed using a JEM-ARM200F microscope with 200 kV accelerating voltage. STEM samples were prepared by depositing a droplet of suspension onto an Au grid coated with a Lacey Carbon film.

2.4. Electrochemical tests

Typically, 10 mg of a catalyst was dispersed in 2 mL of a solution containing IPA, deionised water and Nafion solution (5.0 wt%) with a corresponding volume ratio of 100:100:1 under bath ultrasonication for 30 min to form a homogeneous ink. 200 μL of the dispersion was then deposited onto a carbon paper electrode with a size of 1 cm × 1 cm, which was dried in the air. For linear sweep voltammograms (LSVs) in Ar- or CO2-saturated 0.1 M KHCO3 electrolyte, 6 mg of a catalyst was dispersed in a mixture of ethanol (600 μL), deionised water (600 μL) and Nafion solution (5.0 wt%, 600 μL). Subsequently, the mixture was ultrasonicated for 30 min to form a homogeneous ink. 7.95 μL of the dispersion was then dropped onto a glassy carbon electrode (geometric area: 0.19625 cm2; catalyst loading content: 0.135 mg cm−2) and dried at room temperature.

Controlled potential electrolysis of CO2 was carried out in an H-type cell separated by a Nafion 117 membrane. Before ECR experiments, the Nafion membrane was pre-treated by heating in H2O2 aqueous solution (5.0%) and H2SO4 (0.5 M) at 80 °C for 1 h, respectively. Then the Nafion membrane was immersed in deionised water under ambient conditions for 30 min and then washed with deionised water. Toray Carbon fibre paper with a size of 1 cm × 1 cm was used as working electrode. Pt wire and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. Applied potentials were controlled by an electrochemical working station (CHI 760E, Shanghai CH Instruments Co., China). All potentials in this study were measured against the Ag/AgCl reference electrode (in KCl solution, 3.5 M) and converted to the RHE reference scale by

\[ E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197 + 0.0591 \times \text{pH} \]  

ECR was initiated in CO2-saturated KHCO3 solution (0.1 M) at room temperature and atmospheric pressure. CO2 was purged into the KHCO3 solution for 30 min to expel residual air in the reservoir, then controlled potential electrolysis was conducted at each voltage for 60 min. LSVs in Ar- or CO2 atmosphere were carried out in a three-electrode system using Ag/AgCl as reference electrode, Pt wire as counter electrode, and glassy carbon as working electrode on a CHI 760E potentiostat. Rotating disk electrode (RDE) experiments were run on an AFMSRCE RDE control system (Pine Inc., USA). The electrolyte is 0.1 M KHCO3 solution purged with Ar or CO2 for 30 min.
2.5. Quantitative analysis of gaseous and liquid products

The ECR gas-phase products were probed by an Agilent 7890B gas chromatography (GC) with two thermal conductivity detectors (TCD) and one flame ionisation detector (FID). The liquid products were quantified by \(^1\)H NMR (nuclear magnetic resonance, Bruker Avance III 400 HD spectrometer) using a solvent presaturation technique to suppress the water peak. NMR samples were prepared by mixing 0.5 mL of the product-containing electrolyte and 0.1 mL DMSO-\(d_6\) as the internal standard. FE was determined from the amount of charge passed to produce each product divided by the total amount of charge passed at a specific time or during the overall run.

3. Results and discussion

In this work, we developed a very simple method for the preparation of 2D crystalline Cu/TPA-DMF via ultrasonication treatment of a mixture of CuCl\(_2\)•2H\(_2\)O and TPA in DMF.

3.1. Structural characterisation

The phase and structural features of the as-made samples were characterised using XRD analysis. The XRD patterns given in Figure 1(a) showed the formation of a phase of Cu/TPA-MOF along with standard XRD profiles for CuO, Cu\(_2\)O and CuCl\(_2\).

![XRD Pattern](image)

**Figure 1.** (a) XRD pattern of Cu/TPA-MOF along with standard XRD profiles for CuO, Cu\(_2\)O and CuCl\(_2\). (b) Wide-survey, (c) Cu 2p and (d) O 1s XP spectra of Cu/TPA-DMF.
TPA-DMF with good crystallinity. No reflection peaks originating from the CuCl₂ precursor, CuO and Cu₂O were found.

XPS was employed to investigate the surface composition and chemical state of the Cu moieties. Depicted in Figure 1(b–d) are the wide-survey, Cu 2p and O 1s XP spectra of Cu/TPA-DMF, respectively. The sample was predominantly composed of copper, oxygen, carbon and nitrogen. No other heteroelement including element Cl was detectable, suggesting that there are no unreacted precursors or byproducts in the product. The Cu 2p core-level spectrum of Cu/TPA-DMF indicated the presence of Cu²⁺ in the Cu/TPA-DMF, manifesting prominent Cu 2p₁/₂ and 2p₃/₂ peaks with respective BEs centred at around 955.1 and 935.4 eV, along with their strong satellite peaks [39]. No apparent peaks ascribed to Cu⁺ can be observed. The O 1s XP spectrum was deconvoluted into three components, corresponding to C–O (533.4 eV), C=O (532.5 eV) and Cu–O (531.9 eV) (Figure 1(d)). The Cu-O bond can be attributed to the coordination between copper metal ions and carboxylate-based ligands.

To decipher the morphology and microstructure of Cu/TPA-DMF, SEM (Figure 2(a)) and aberration-corrected HAADF-STEM along with energy-dispersive X-ray analysis (Figure 2(b–j)) were conducted. Large quantities of flakes that stacked on top of each other with lateral sizes of 300.0 nm – 3.0 µm were observed. Further high-resolution STEM imaging revealed that some nanosheets were decorated with CuO nanocrystals of about 7.0 nm plausibly resulting from oxidation of copper precursor in DMF. Furthermore, the energy-dispersive X-ray spectroscopy (EDS) maps (Figure 2(g–j)) together with the EDS spectrum (Figure 2(d)) confirmed that the nanosheets were composed of C, Cu, O and N elements.
3.2. Electrochemical measurements

ECR is sensitive to operating environments including the nature and properties of electrocatalyst, electrolyte type and concentration and electrochemical cell type [40]. To probe the intrinsic catalytic properties of the Cu/TPA-DMF, we performed the ECR in CO2-saturated 0.1 M KHCO3 aqueous solution (pH 6.8) using an H-type cell with continuous CO2 bubbling at room temperature and atmospheric pressure [41]. The potential-dependent geometric current densities of Cu/TPA-DMF in the voltage range of 0.0 to −1.3 V were measured by LSV, as illustrated in Figure 3(a). Invariably larger cathodic currents were observed in a CO2 environment than in an Ar environment throughout the potential range. No liquid compounds were detected over the applied potential region. Products of CO, H2, CH4 and C2H4 were identified in the potential range of −1.0 to −1.3 V in a CO2-saturated 0.1 M KHCO3 electrolyte. The ECR dominated over hydrogen evolution reaction (HER) at potentials between −1.0 and −1.15 V (Figure 3(b,c)). The FEs for hydrocarbons including C2H4 and CH4 reached up to 70.0% at −1.1 V with about 8.4 mA cm−2 partial geometric current density. Further elevation of overpotential resulted in decrease of C2H4 FE likely owing to more severe competition with hydrogen evolution reaction at more negative voltages. It is worth noting that the FE for C2H4 formation is as high as 50.0%, substantially outperforming that of TPA (FE_{C2H4} ≈ 0.0%), carbon paper (FE_{C2H4} ≈ 0.0%), commercial Cu (FE_{C2H4} ≈ 10.6%), Cu2O (FE_{C2H4} ≈ 7.9%), CuO (FE_{C2H4} ≈ 23.8%) and Cu(OH)2 (FE_{C2H4} ≈ 13.3%) (Figure 3(d)), and many recently reported Cu-based electrocatalysts at similar overpotentials (Figure 3(e) and Supplementary Table S1). The Tafel slope for C2H4 production over Cu/TPA-DMF was measured to be about 160.9 mV−dec−1 (Supplementary Figure S1) lower than defective CuO demonstrated in prior literature,23 indicating that the as-synthesised catalyst has good reaction kinetics for ECR. The formation of the *CO intermediate on the surface of the catalyst appeared to control the reaction rate. Chronoamperometric measurements showed that the FE for C2H4 remained above 40.0% even after 7.0 h of successive polarisation at −1.1 V (Figure 3(f)).

The ECR performance was readily tuned by controlling the added amount of the linker and metal precursor and ultrasonic temperature (Figure 3(g)). The optimal mole ratio of TPA and CuCl2 for ECR was found to be 1:1. The catalyst synthesised at 25 °C exhibited superior ECR activity than those obtained at both 5 °C and 45 °C. Likewise, manipulating the type of solvent during materials synthesis allowed one to regulate the ECR property. The Cu/TPA-DMF produced in a mixture of DMF, ethanol, and water displayed considerably better activity for ECR than either in pure ethanol or water (Figure 3(g)). The type of ligand would affect the bonding mode and structure of materials, thus affecting its catalytic performance. The linker species in a metal-organic frameworks (MOF) structure can also modify the adsorption and binding of water and CO2 reduction intermediates, providing the opportunity for fine-tuning of the ECR selectivity. Indeed, the TPA ligand imparted remarkably better activity in terms of ECR FE and C2H4 selectivity than the BTC, probably due to the concomitant reduction in the numbers of unsaturated active Cu sites in the Cu/BTC-DMF (Figure 3(g)). We also
prepared Cu/TPA-DMF by using a magnetic fixing and hydrothermal treatment at 120 °C at equivalent periods akin to the protocol of ultrasonication, which exhibited lower ECR activity in both cases (Figure 3(g)).

4 Conclusions

In summary, we showed for the first time a facile and effective ultrasonication-facilitated strategy to synthesise 2D Cu/TPA-DMF. The as-obtained materials significantly promoted the ECR to hydrocarbons at low overpotentials in an H-type cell with 0.1 M KHCO₃ solution, affording FEs exceeding 72.0%. The catalytic property was readily tuned by manipulating reaction conditions. A high FE for C₂H₄ of up to 50.0% and a C₂H₄ partial geometric current density of about 6.0 mA cm⁻² were attained at −1.1 V (vs. RHE), surpassing many reported Cu-based electrocatalysts. This work provides a new possibility for designing 2D copper terephthalate to enhance the conversion of CO₂ into C₂H₄.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the National Natural Science Foundation of China (no. 21972010), Beijing Natural Science Foundation (no. 2192039) and the Foundation of Key Laboratory of Low-Carbon Conversion Science & Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences (no. KLLCCSE-201901, SARI, CAS).

References

1. Tao H, Fan Q, Ma T, et al. Two-dimensional materials for energy conversion and storage. Prog Mater Sci. 2020;111:100637.
2. Tao H, Gao Y, Talreja N, et al. Two-dimensional nanosheets for electrocatalysis in energy generation and conversion. J Mater Chem A. 2017;5(16):7257–7284.
3. Shen H, Choi C, Masa J, et al. Electrochemical ammonia synthesis: mechanistic understanding and catalyst design. Chem. 2021;7(7):1708–1754.
4. Zhou W, Guo J-K, Shen S, et al. Progress in photoelectrocatalytic reduction of carbon dioxide. Acta Phys Chim Sin. 2020;36(3):1906048.
5. Sun Z, Ma T, Tao H, et al. Fundamentals and challenges of electrochemical CO₂ reduction using two-dimensional materials. Chem. 2017;3(4):560–587.
6. Ma T, Fan Q, Li X, et al. Graphene-based materials for electrochemical CO₂ reduction. J CO₂ Util. 2019;30:168–182.
7. Ma T, Fan Q, Tao H, et al. Heterogeneous electrochemical CO₂ reduction using nonmetallic carbon-based catalysts: current status and future challenges. Nanotechnology. 2017;28(47):472001.
8. Centi G. Smart catalytic materials for energy transition. SmartMat. 2020;10(1):e1005.
9. Liu Z. Highly efficient electroreduction of carbon dioxide to formate over copper dendrites derived from in situ electrosynthesized copper-metal-oxide frameworks. Acta Phys Chim Sin. 2020;36(11):2006006.
10. Yang C, Nosheen F, Zhang Z. Recent progress in structural modulation of metal nanomaterials for electrocatalytic CO₂ reduction. Rare Met. 2021;40(6):1412–1430.
11. Zhang H, Chang X, Chen J, et al. Computational and experimental demonstrations of one-pot tandem catalysis for electrochemical carbon dioxide reduction to methane. Nat Commun. 2019;10(1):3340.
12. Jia M, Choi C, Wu T-S, et al. Carbon-supported Ni nanoparticles for efficient CO₂ electroreduction. Chem Sci. 2018;9(47):8775–8780.
13. Li G, Qin Y, Wu Y, et al. Nitrogen and sulfur dual-doped high-surface-area hollow carbon nanospheres for efficient CO\textsubscript{2} reduction. Chinese J Catal. 2020;41(5):830–838.
14. Jia M, Hong S, Wu T-S, et al. Single Sb sites for efficient electrochemical CO\textsubscript{2} reduction. Chem Commun (Camb). 2019;55(80):12024–12027.
15. Zhou Y, Han N, Li Y. Recent progress on Pd-based nanomaterials for electrochemical CO\textsubscript{2} reduction. Acta Phys Chim Sin. 2020;36(9):2001041.
16. Tao H, Sun X, Back S, et al. Doping palladium with tellurium for the highly selective electrocatalytic reduction of aqueous CO\textsubscript{2} to CO. Chem Sci. 2018;9(2):483–487.
17. Chen J, Li J, Xu J, et al. Phthalocyanine-derived catalysts decorated by metallic nanoclusters for enhanced CO\textsubscript{2} electroreduction. Green Energy Environ. 2021.
18. Chu S, Ou P, Pan Y. Efficient photoelectrochemical conversion of CO\textsubscript{2} to syngas by photocathode engineering. Green Energy Environ. 2020.
19. Wang S, Wang J, Xin H. Insights into electrochemical CO\textsubscript{2} reduction on tin oxides from first-principles calculations. Green Energy Environ. 2017;2(2):168–171.
20. Fan Q, Zhang M, Jia M, et al. Electrochemical CO\textsubscript{2} reduction to C\textsubscript{2}+ species: heterogeneous electrocatalysts, reaction pathways, and optimization strategies. Mater Today Energy. 2018;10:280–301.
21. Yang Y, Zhang Y, Hu J-S, et al. Progress in the mechanisms and materials for CO\textsubscript{2} electroreduction toward C\textsubscript{2}+ products. Acta Phys Chim Sin. 2020;36(1):1906085.
22. Chen Y, Liu C, Guo S, et al. CO\textsubscript{2} capture and conversion to value-added products promoted by MXene-based materials. Green Energy Environ. 2020.
23. Jia S, Zhu Q, Wu H, et al. Efficient electrocatalytic reduction of carbon dioxide to ethylene on copper–antimony bimetallic alloy catalyst. Chinese J Catal. 2020;41(7):1091–1098.
24. Hao L, Sun Z. Metal oxide-based materials for electrochemical CO\textsubscript{2} reduction. Acta Phys Chim Sin. 2021;37(7):2009033.
25. Nitopi S, Bertheussen E, Scott SB, et al. Progress and perspectives of electrochemical CO\textsubscript{2} reduction on copper in aqueous electrolyte. Chem Rev. 2019;119(12):7610–7672.
26. Gao Z, Wang C, Li J, et al. Conductive metal-organic frameworks for electrocatalysis: achievements, challenges, and opportunities. Acta Phys Chim Sin. 2020;37(7):2010025.
27. Meng Y, Kuang S, Liu H, et al. Recent advances in electrochemical CO\textsubscript{2} reduction using copper-based catalysts. Acta Phys Chim Sin. 2020;37(5):2006034.
28. Wu YA, McNulty I, Liu C, et al. Facet-dependent active sites of a single Cu\textsubscript{2}O particle photocatalyst for CO\textsubscript{2} reduction to methanol. Nat Energy. 2019;4(11):957–968.
29. Jiang Y, Choi C, Hong S, et al. Enhanced electrochemical CO\textsubscript{2} reduction to ethylene over CuO by synergistically tuning oxygen vacancies and metal doping. Cell Rep Phys Sci. 2021;2(3):100356.
30. El-Tantawy A, Daoush W, El-Nikhaily A. Microstructure and properties of BN/Ni-Cu composites fabricated by powder technology. J Exp Nanosci. 2018;13(1):174–187.
31. Walker J, Rees NV, Mendes PM. Progress towards the ideal core@shell nanoparticle for fuel cell electrocatalysis. J Exp Nanosci. 2018;13(1):258–271.
32. Shao J, Wang Y, Gao D, et al. Copper-indium bimetallic catalysts for the selective electrochemical reduction of carbon dioxide. Chinese J Catal. 2020;41(9):1393–1400.
33. Chu S, Hong S, Masa J, et al. Synergistic catalysis of CuO/In\textsubscript{2}O\textsubscript{3} composites for highly selective electrochemical CO\textsubscript{2} reduction to CO. Chem Commun (Camb)). 2019;55(82):12380–12383.
34. Chu S, Li X, Robertson AW, et al. Electrocatalytic CO\textsubscript{2} reduction to ethylene over CeO\textsubscript{2}-supported Cu nanoparticles: effect of exposed facets of CeO\textsubscript{2}. Acta Phys Chim Sin. 2021;37(5):2009023.
35. Meenakshi R, Suresh P. WEDM of Cu/WC/SiC composites: development and machining parameters using artificial immune system. J Exp Nanosci. 2020;15(1):12–25.
36. Sagadevan S, Vennila S, Singh P, et al. Exploration of the antibacterial capacity and ethanol sensing ability of Cu–TiO\textsubscript{2} nanoparticles. J Exp Nanosci. 2020;15(1):337–349.
37. Tan D, Zhang J, Yao L, et al. Multi-shelled CuO microboxes for carbon dioxide reduction to ethylene. Nano Res. 2020;13(3):768–774.
38. Chu S, Yan X, Choi C, et al. Stabilization of Cu\textsuperscript{2+} by tuning a CuO–CeO\textsubscript{2} interface for selective electrochemical CO\textsubscript{2} reduction to ethylene. Green Chem. 2020;22(19):6540–6546.
39. He X, Wang W-N. MOF-based ternary nanocomposites for better CO\textsubscript{2} photoreduction: roles of heterojunctions and coordinatively unsaturated metal sites. J Mater Chem A. 2018;6(3):932–940.
40. Wang N, Miao RK, Lee G, et al. Suppressing the liquid product crossover in electrochemical CO\textsubscript{2} reduction. SmartMat. 2021;2(1):12–16.
41. Fan Q, Hou P, Choi C, et al. Activation of Ni particles into single Ni–N atoms for efficient electrochemical reduction of CO\textsubscript{2}. Adv Energy Mater. 2020;10(5):1903068.