



Identification of champion transition metals centers in metal and nitrogen-codoped carbon catalysts for CO₂ reduction



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ABSTRACT

Transition metal is known to influence electrochemical activities over transition metals (M) and nitrogen (N)-codoped carbon (M–N–C) catalysts. However, champion transition metals centers in M–N–C for catalyzing CO₂ reduction reaction (CO₂RR) remain unclear, hindering further catalyst development with enhanced performance. Herein, we report the investigation of effects of five transition metals (Cr, Mn, Fe, Co, Ni) on CO₂RR activities and mechanisms using metal-doped nitrogenated carbon nanosheets as model catalysts fabricated via a novel space-confinement-assisted molecular-level complexing approach. Analyzing N 1s XPS spectra confirmed the formation of M–N complexes via the coordination of metals atoms with pyridinic N, which was identified as the active species in CO₂RR. According to activity descriptors including overpotentials, Faradaic efficiency (FE) and Turnover Frequency (TOF) per metal site, we here established that Fe and Ni are more active than Co, Mn, and Cr in M–N–C for the reduction of CO₂ to CO. The main role of Fe is to reduce overpotentials, exhibiting the lowest onset overpotential of 0.19 V to yield CO on Fe–N–C. Ni can drastically improve CO selectivity and reaction rates, yielding the highest CO Faradaic efficiency of 96%, partial current density of -8.2 mA cm^{-2} , and TOF of 1060 h^{-1} at a moderate overpotential of 0.65 V. Mechanism explorations reveal that CO₂RR on M–N–C (M = Fe, Cr, Mn) undergoes the formation of a ^{*}COOH intermediate as the rate-determining step, whereas M–N–C (M = Ni, Co) catalyzes CO₂RR via the transfer of the first electron to form a ^{*}CO₂^{•-} species. On the basis of the findings, we suggest doping Fe and/or Ni to design advanced M–N–C for CO₂ electroreduction.

1. Introduction

Growing global warming and energy demands have triggered a great interest in reusing the greenhouse gas CO₂ to reach an anthropogenic carbon cycle and utilizing renewable energy sources such as solar, wind and tidal to power human's activities. Room-temperature electrochemical CO₂ reduction by using water as a reaction medium and clean energy-generated electricity as the power input can not only convert CO₂ but also store intermittent renewable energy in value-added fuels simultaneously, which is believed to be one of the most attractive strategies to remit environmental and energy issues [1,2]. This desired technology, however, is technically hindered owing to the thermodynamically stable nature of CO₂ and the strong competition with hydrogen evolution reaction (HER) in aqueous electrolytes, leading to a prohibitive overpotential and a poor selectivity for CO₂ reduction reaction (CO₂RR) in practice [3,4]. Although selective electroreduction of CO₂ to CO and formic acid has been achieved, it requires the use of noble metals (Ag, Au, Pd) [5–7]. The core challenge of CO₂RR remains on the development of inexpensive, selective and stable

catalysts operating at low overpotentials.

Toward this goal, heat-treated transition metals (M) and nitrogen (N)-codoped carbon (M–N–C) catalysts have attracted numerous attention by virtue of their advantages including high CO₂-to-CO selectivity, rich reserve, chemical stability, and good conductivity [8–11]. Doping transition metals and nitrogen into the carbon matrix can break electroneutrality of carbons and increase charge and spin densities, thus transforming inert carbons into active electrocatalysts. So far, lots of M–N–C families, including Fe(Mn)/N-doped carbon black [12], N,P,Co-doped mesoporous carbon [13], Fe(Ni)/N-doped porous carbon [14,15] have been developed for CO₂RR to produce CO, in which nitrogen coordinated metal complexes (M–N) were proposed to be likely catalytic active sites owing to their optimal binding strength with the chemical species involved in CO₂RR [12,14–16]. Despite the reported advancements in the literature, M–N–C is still far from their practical applications due to poor activity, primarily suffering from large overpotentials and low currents [12–16]. Because different metals in M–N–C exhibit various behaviors in CO₂RR, it is imperative to identify the champion metal centers in M–N–C among various popular

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transition metals for CO₂ electroreduction. Nevertheless, the reported M–N–C catalysts functionalized by Fe, Co, Mn, and Ni were synthesized using various carbon/nitrogen precursors and different methods, resulting in huge differences in carbon architectures, metal species structures, and nitrogen doping level (contents and configurations) [12–15]. These discrepancies make it infeasible to identifying the most active metal center of M–N–C based on reported results because electrocatalytic activities of M–N–C are highly dependent on carbon structures, N/M chemical states and contents [14,17,18]. Moreover, the differences in CO₂RR pathways on different transition metals are not well understood, precluding the selection of most active M–N–C catalysts. Therefore, it is demanding to explore the electrocatalytic reactivity and behaviors of different transition metals in M–N–C, which will provide in-depth mechanistic understanding and guide the design of high-efficiency M–N–C electrocatalysts for CO₂ reduction by selectively doping M–N–C with the most efficient transition metal.

The objective of this paper is to identifying champion metals centers among five popular transition metals (Cr, Mn, Fe, Co, Ni) in M–N–C synthesized by the same method and understanding their specific catalytic roles in CO₂ reduction. Metal-doped nitrogenated carbon nanosheets were prepared by a space-confinement-assisted molecular-level complexing synthesis and studied as model catalysts. The structure, compositions, and nitrogen/metal chemical states were characterized by TEM, XRD, ICP-MS, and XPS. Electrochemical CO₂RR behaviors were then systematically evaluated and compared against undesired hydrogen evolution reaction. Catalytic properties including overpotentials, Faradaic efficiency, and turnover frequency per metal site for CO production were used as descriptors to rank the electrocatalytic reactivity of the five transition metals for CO₂ reduction. Moreover, Tafel analyses were performed to unveil electrocatalytic CO₂RR pathway, which provides mechanistic insights of the role of five metals on CO₂RR.

2. Experimental section

2.1. Synthesis of M–N–C

M–N–C was prepared via a simple solid-phase pyrolysis route. In a typical synthesis of Fe–N–C, urea (10 g), citric acid (0.334 g) and iron nitrate nonahydrate (0.035 g) were dispersed in deionized water (15 mL) with continuous stirring for 2 h and then dried at 80 °C to obtain a dried solid. The solid was ground into a uniform powder, which was put in a combustion boat and transferred into a tube furnace. Then, the temperature of the furnace was increased to 550 °C for 2 h and further raised to 900 °C for 1 h at a heating rate of 3 °C min⁻¹ under argon flow. After cooling down to room temperature, final powder sample was collected. The iron contents and pyrolysis temperatures were adjusted to optimize CO₂RR activity of Fe–N–C; we found that 8.66×10^{-5} mol Fe in precursors and a heating temperature of 900 °C yielded the best CO₂RR activity (Fig. S1). Other M–N–C samples were prepared using the same procedure as for Fe–N–C except for employing different metal nitrate precursors but keeping the same metal content at 8.66×10^{-5} mol, and the metal-free N–C was synthesized using urea and citric acid as precursors for comparison purpose.

2.2. Physical characterization

Morphology, structure, and composition of catalysts were characterized by scanning electron microscopy (SEM, JEOL JSM7500F), transmission electron microscopy (TEM, FEI Tecnai G2 F20 ST), X-ray diffraction (XRD, BRUKER D8) and X-ray photoelectron spectroscopy (XPS, Omicron). Metal amounts in catalysts were determined by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 300D Quadrupole); five replicates of each sample were analyzed to yield the average.

2.3. Electrochemical CO₂RR activity measurements

Electrocatalytic CO₂RR was evaluated in a two-compartment three-electrode electrochemical cell in CO₂-saturated 0.1 M KHCO₃ electrolyte (pH = 6.8). A Pt mesh and an Ag/AgCl (3 M KCl) were used as the counter electrode and reference electrode, respectively. The measured potentials after iR compensation were rescaled to the reversible hydrogen electrode by $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.210 \text{ V} + 0.0591 \text{ V} \times \text{pH}$. The working electrode was prepared by drop casting 60 μL of catalyst ink onto a carbon paper (1 cm²) with mass loading of 0.3 mg cm⁻². The ink was prepared by dispersing 3 mg catalysts in a mixture solution of 200 μL DI-water, 370 μL ethanol, and 30 μL 5% Nafion solution via sonication for 3 h. The working and reference electrodes were placed in the cathode chamber, while the counter electrode was placed in the anode chamber, which was separated by a piece of Nafion 115 ionic exchange membrane to avoid the re-oxidation of CO₂RR-generated products. The high-purity CO₂ was introduced in the cathode chamber for 1 h to saturate electrolyte before electrolysis with a flow rate of 34 mL min⁻¹ and maintained this flow rate during measurements. The gas-phase products were analyzed via an online gas chromatograph (GC, Fuel Cell GC-2014ATF, Shimadzu) equipped with a thermal conductivity detector (TCD) and a methanizer assisted flame ionization detector (FID). The GC calibration is provided in Supporting Information. The liquid-products were characterized by a nuclear magnetic resonance (NMR) spectrometer (Bruker avance III 500 MHz). 2,2,3,3-d(4)-3-(trimethylsilyl)propionic acid sodium salt (TSP) was used as the internal standard, and the 0.6 mM TSP standard solution was prepared in D₂O [19]. The representative sample for ¹H NMR was prepared by depositing 500 μL of the KHCO₃ solution collected after 550 min CO₂RR tests on Ni–N–C at –0.75 V in an NMR tube followed by adding 100 μL of STP standard solution.

The activity descriptors including Faradaic efficiency (FE), partial current density, mass activity, production rates, and turnover frequency (TOF) per metal site for CO production were calculated to reveal the catalytic properties, and the calculation methods are provided in Supplementary Materials.

3. Results and discussion

3.1. Synthesis, structure, and composition of M–N–C

Since previous reports have suggested that M–N species serves as primary active sites in CO₂RR [12,14], the preparation of M–N–C with high-density M–N dopants is thereby the premise to compare their CO₂RR activities. In this work, we synthesized metal/nitrogen-doped carbon nanosheets as presenting M–N–C by atomically constructing the M–N coordination via a molecular-level complexing chemistry design with space-confinement assistance. As depicted in Fig. 1a, citric acid, urea, and metal nitrate were used as starting feedstock, and a solid-phase pyrolysis route was carried out to fabricate M–N–C. Citric acid was the carbon precursor, which also served as the complexing agent to chelate the transition metals in water because of its high affinity to metal ions [20,21], guaranteeing a uniform dispersion of the metals species. During the carbonization at 550 °C, urea surrounding around citric acid-metal composites polycondensed into layer-structured graphitic carbon nitride (g-C₃N₄), which thus functioned as a space-confined nanoreactor to direct the formation of two-dimensional graphene-like carbon and further hindered the aggregation of the metals species due to space-limited effects from g-C₃N₄ interlayers [22,23]. When the temperature reached 750 °C, the decomposition of thermally unstable g-C₃N₄ templates liberated carbon nanosheets. In the meantime, numerous nitrogen-containing gases (NH₃, C₂N₂⁺, C₃N₂⁺, C₃N₃⁺) were generated during the process of the thermolysis of urea and g-C₃N₄ [24,25], which provided rich nitrogen sources to react with carboxyl/hydroxy of carbon intermediates and substitute carbon atoms, leading to the formation of the M–N complexes and other C–N and O–N groups.

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