



Controlled synthesis of a Ni₂ dual-atom catalyst for synergistic CO₂ electroreduction

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ABSTRACT

Dual-atom catalysts (DACs) have drawn much attention recently by virtue of the synergistic effect within the dual-atom sites, while controlled synthesis of pure DACs remains a challenge. Herein, a uniform dual-atom Ni₂ catalyst (Ni₂-NCNT) was controllably synthesized using a dinuclear Ni complex as the precursor, in which directly bonded Ni₂ pairs are uniformly anchored on N-doped carbon nanotubes. Ni₂-NCNT exhibits extraordinary catalytic activity, selectivity and stability for electroreduction of CO₂ into CO, with a partial current density for CO (j_{CO}) of 76 mA cm⁻². The j_{CO} mass activity of Ni₂-NCNT is 2.3-times higher than that of corresponding Ni₁-NCNT single-atom catalyst. DFT calculations reveal that the synergistic coordination of *COOH at the Ni₂ dual-atom site can dramatically lower the reaction free energy for *COOH formation, thus promoting the CO₂ electroreduction.

1. Introduction

The energy shortage resulting from the limited fossil fuel resources and the climate change induced by the excessive CO₂ emission are critical problems restricting the sustainable development of human society [1–3]. Electrocatalytic CO₂ reduction is an attractive strategy to overcome these issues, enabling CO₂ to be utilized as a chemical feedstock and be converted into useful fuels or chemicals [4–14]. Large catalytic current and high Faradaic efficiency (FE) are required before CO₂ electroreduction comes to practical use. However, in aqueous electrolytes, hydrogen evolution reaction would proceed within a similar cathodic potential regime, which could substantially lower the selectivity towards CO₂ reduction along with the increase of current densities [15–18]. Few electrocatalysts with high FEs under large current densities have been reported, and the design and synthesis of electrocatalysts featuring both high current density and FE remains a major challenge [19–21]. In the last decade, single-atom catalysts (SACs) have attracted much attention because of their high atomic utilization and excellent catalytic activity in a wealth of reactions [22–28]. However, owing to the single-site nature, they are generally not as competent for complex multi-step reactions such as CO₂ reduction reaction (CO₂RR) [29–32].

It has been found that the coordination environment of active sites plays a vital role for electrocatalytic activity and selectivity of CO₂ reduction via changing the reaction energy barriers [19,23,33] and the electrochemical route [11,28]. Dual-atom catalysts (DACs), with an

additional metal active center introduced near the single-atom site, have drawn much attention recently by virtue of the synergistic effect within the dual-atom sites [33–45], which can change the adsorption configuration of reactants and intermediates, thereby reducing the reaction free energies [33]. As a result, DACs usually exhibit higher catalytic performance compared with corresponding SACs. Moreover, DACs offer a unique perspective for revealing the structure–performance relationship at the atomic level [46–48]. Therefore, it is highly desirable to develop new strategies for controlled synthesis of highly pure DACs, which, however, still remains a great challenge. Thus far, only a few strategies (such as atomic layer deposition [49–51] and wet chemical reduction [52–57]) have been reported. The routine method of synthesizing DACs is to increase the probability of pairing between metal atoms by simply elevating their concentration. However, the controllable synthesis of highly pure DACs via the above routine method is rather difficult, because it is inevitable to form a mixture of SAC and DAC, and metal atoms are also prone to agglomerate [46]. Therefore, it is highly desirable to develop a controllable strategy for the fabrication of pure DACs to accurately understand the synergy mechanism.

Herein, a highly pure Ni₂ DAC of Ni₂-NCNT was controllably synthesized via pyrolysis a mixture of a dinuclear complex Ni₂(ppyzc)₂ with carbon nanotubes (CNTs) and dicyandiamide under 600 °C (H₂ppyzc = 8-quinoline-1*H*-pyrazole-3-carboxamide). The dinuclear complex precursor effectively fixes the Ni₂ dual-atom sites during pyrolysis process, thus rendering this synthesis method highly reproducible. The obtained Ni₂-NCNT can take advantage of the synergy between two adjacent Ni

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atoms as active centers to exhibit outstanding CO₂RR catalytic performance, with a high FE for CO above 90% over a wide potential range from -0.8 V to -1.2 V vs. RHE, a large partial current density for CO (76 mA cm⁻² at -1.40 V vs. RHE), and a high electrocatalytic stability. Density functional theory (DFT) calculations reveal that the Ni₂ site in Ni₂-NCNT can significantly lower the reaction free energy of *COOH intermediate for promoting the CO₂ electroreduction.

2. Experimental section

2.1. Materials

Purified water (18.25 MΩ·cm) used in all the experiments was produced from a Water Purifier (UPR-II-10T). All chemicals used were of the highest purity available from commercial sources without any further purification.

2.2. Synthesis of H₂qpyzc (8-quinoline-1H-pyrazole-3-carboxamide)

Triphenyl phosphite (1.55 g, 5 mmol), tetrabutyl ammonium bromide (1.61 g, 5 mmol), 1H pyrazole-3-carboxylic acid (0.56 g, 5 mmol) and 8-aminoquinoline (0.72 g, 5 mmol) were heated at 120 °C for 1 h under careful stirring. Then cold MeOH (10 mL) was added to the viscous reaction mixture and stirred for 30 min. A light-yellow precipitate formed, and was filtered off and then washed with cold MeOH. Yield: 774 mg, 65%.

2.3. Synthesis of H₂qpyrc (N-(quinolin-8-yl)-1H-pyrrole-2-carboxamide)

The ligand was obtained with a synthesis method similar to that for H₂qpyzc; 1H pyrrole-2-carboxylic acid (0.56 g, 5 mmol) was used as the starting material instead of 1H pyrazole-3-carboxylic acid. Yield: 714 mg, 60%.

2.4. Synthesis of Ni₂-NCNT

CNT (40 mg), H₂qpyzc (1.25 mg) were dispersed in EtOH (20 mL), and the solution was agitated with sonication for 10 min. The MeOH solution (5 mL) containing Ni(CH₃COO)₂·4H₂O (2.5 mg) was then added into the above system, and the mixture was refluxed for 4 h under vigorous stirring. The samples with dinuclear complexes loaded on CNT were obtained after centrifugation, and then washed and dried in vacuum at 40 °C. A small porcelain boat containing dicyandiamide (200 mg) was placed in a larger magnetic boat along with the dried black powder. Then, the boat was heated at 600 °C under Ar atmosphere for 2 h at a rate of 5 °C min⁻¹. The obtained product was dispersed in hydrochloric acid (0.1 M, 20 mL) and stirred for 10 h, and then washed with H₂O and EtOH. Ni₁-NCNT was dried in vacuum at 40 °C for 12 h.

2.5. Synthesis of Ni₁-NCNT

The Ni₁-NCNT was obtained with a synthesis method similar to that for Ni₂-NCNT. H₂qpyrc (1.25 mg) was used as the starting material instead of H₂qpyzc. The samples with mononuclear complexes loaded on CNT were obtained after rotary evaporation and dried in vacuum at 40 °C. Other reactants and synthesis procedure were the same as that for Ni₂-NCNT.

2.6. Synthesis of NCNT

A small porcelain boat containing dicyandiamide (200 mg) was placed in a larger magnetic boat along with the dried CNT (40 mg). Then, the boat was heated at 600 °C under Ar atmosphere for 2 h at a rate of 5 °C min⁻¹. The obtained product was washed with H₂O and EtOH. NCNT was dried in vacuum at 40 °C for 12 h.

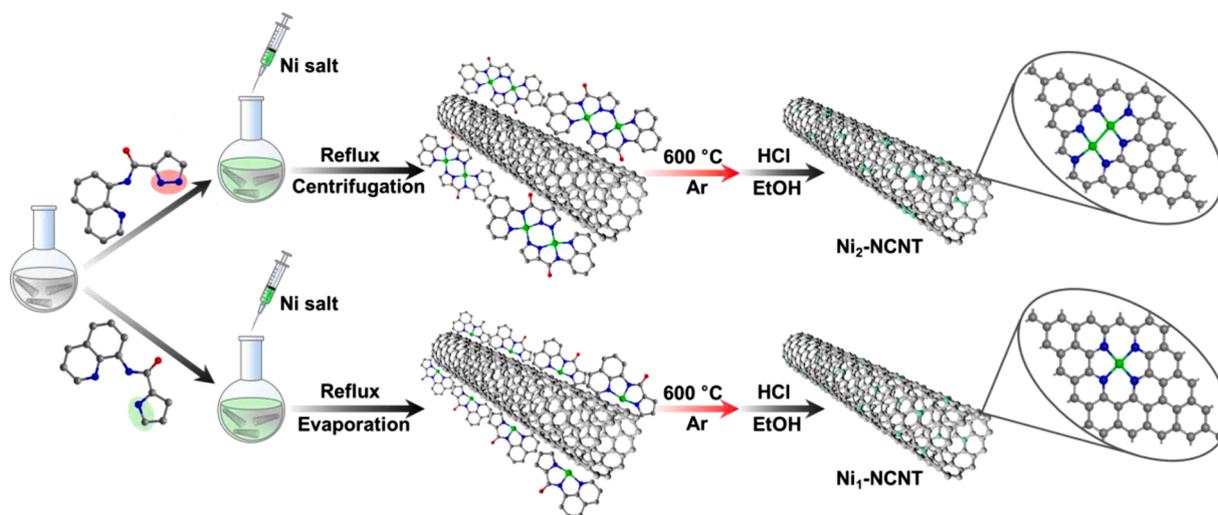
3. Results and discussion

3.1. Synthesis and structural characterization

Dinuclear complexes have well defined molecular structures, and thus could ideally serve as the precursor for the synthesis of DACs. Under proper conditions, the coordination bonds between metal centers and the organic ligand could effectively stabilize the diatomic metal pair, and thus prevent the metal atoms from agglomeration during the pyrolysis process, which could enable the precise and controllable synthesis of DACs. In this work, the organic ligands H₂qpyzc and H₂qpyrc were synthesized according to the reported methods (H₂qpyzc = 8-quinoline-1H-pyrazole-3-carboxamide, H₂qpyrc = N-(quinolin-8-yl)-1H-pyrrole-2-carboxamide) [58], and their structures were confirmed via ¹H nuclear magnetic resonance (NMR) analysis (Figs. S1 and S2). Fig. S3 illustrates the molecular structure of the dinuclear complex Ni₂(qpyzc)₂, and Fig. S4 shows the powder X-ray diffraction (XRD) pattern of the synthesized Ni₂(qpyzc)₂. Owing to the poor solubility of Ni₂(qpyzc)₂, it is rather difficult to use the conventional method of physical mixing to ensure the Ni₂(qpyzc)₂ molecules to be evenly distributed on the surface of CNTs. Therefore, we adopted the strategy of in situ synthesis. As shown in Scheme 1, by adjusting the ligands (H₂qpyzc or H₂qpyrc), the dinuclear or mononuclear complex was in situ generated on CNTs, respectively, and the corresponding DAC or SAC was obtained after pyrolysis. First, the solid powders of the ligand and CNTs were dispersed in ethanol, and the resulting suspension was subsequently heated to 60 °C. Ni(CH₃COO)₂·4H₂O (dissolved in methanol) was added into the above suspension, and the mixture was refluxed for 4 h. The dinuclear Ni complexes formed in situ could be readily anchored onto the CNTs, resulting in a more even distribution. The solid mixture was collected via centrifugation and washed with water and ethanol. The in situ formed dinuclear complexes on CNTs were verified via XRD. As shown in Fig. S5, diffraction peaks belonging to dinuclear complex and CNTs could be found with a Ni₂(qpyzc)₂/CNT feeding ratio ≥ 8%; as the content of the complex decreases, the peaks of dinuclear complex become less prominent. Upon heating Ni₂(qpyzc)₂/CNT composite to 600 °C in Ar atmosphere, the N-coordinated Ni₂ dual-atom sites were formed on CNTs with dicyandiamide used as a nitrogen source. Finally, dilute hydrochloric acid and ethanol were used to remove the nanoparticles and organic impurities that could have formed. For comparison, the SAC counterpart (denoted as Ni₁-NCNT) was synthesized in a similar way using H₂qpyrc to instead of H₂qpyzc, and N-doped carbon nanotubes (denoted as NCNT) were also synthesized via direct pyrolysis of CNTs with dicyandiamide as the nitrogen source under 600 °C.

In the Raman spectra of NCNT, Ni₁-NCNT and Ni₂-NCNT (Fig. S6a), the peaks located at 1336 and 1570 cm⁻¹ are assigned to chaotic sp³ carbon (D band) and graphitic sp² carbon (G band), respectively, confirming the formation of graphitized structures and carbon defects in these catalysts. From the value of I_D/I_G, it can be seen that Ni₁-NCNT and Ni₂-NCNT are more defect-rich than NCNT, which probably results from the Ni doping. The XRD patterns of NCNT, Ni₁-NCNT and Ni₂-NCNT show peaks at 25.5° and 42.7°, which are assigned to the (002) and (100) planes of graphitic carbon, respectively, and the peaks corresponding to Ni nanoparticles are not found (Fig. S6b). N₂ adsorption analysis shows the Brunauer–Emmett–Teller (BET) surface areas of Ni₁-NCNT and Ni₂-NCNT are comparable (Fig. S7a). Both Ni₁-NCNT and Ni₂-NCNT show almost identical CO₂ adsorption capacities, which are significantly higher than that for NCNT due to the Ni doping (Fig. S7b).

The microscopic structures of Ni₁-NCNT and Ni₂-NCNT were examined via high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The HRTEM and SEM images reveal that the carbon supports of Ni₁-NCNT and Ni₂-NCNT inherited the morphology of CNTs (Figs. 1a, c, S9a and S9d). In addition, elemental mapping shows an even distribution of C, N, Ni elements over the CNTs for Ni₁-NCNT and Ni₂-NCNT (Fig. S8c and



Scheme 1. Schematic illustration for the synthesis procedures of Ni₂-NCNT DAC and Ni-NCNT SAC.

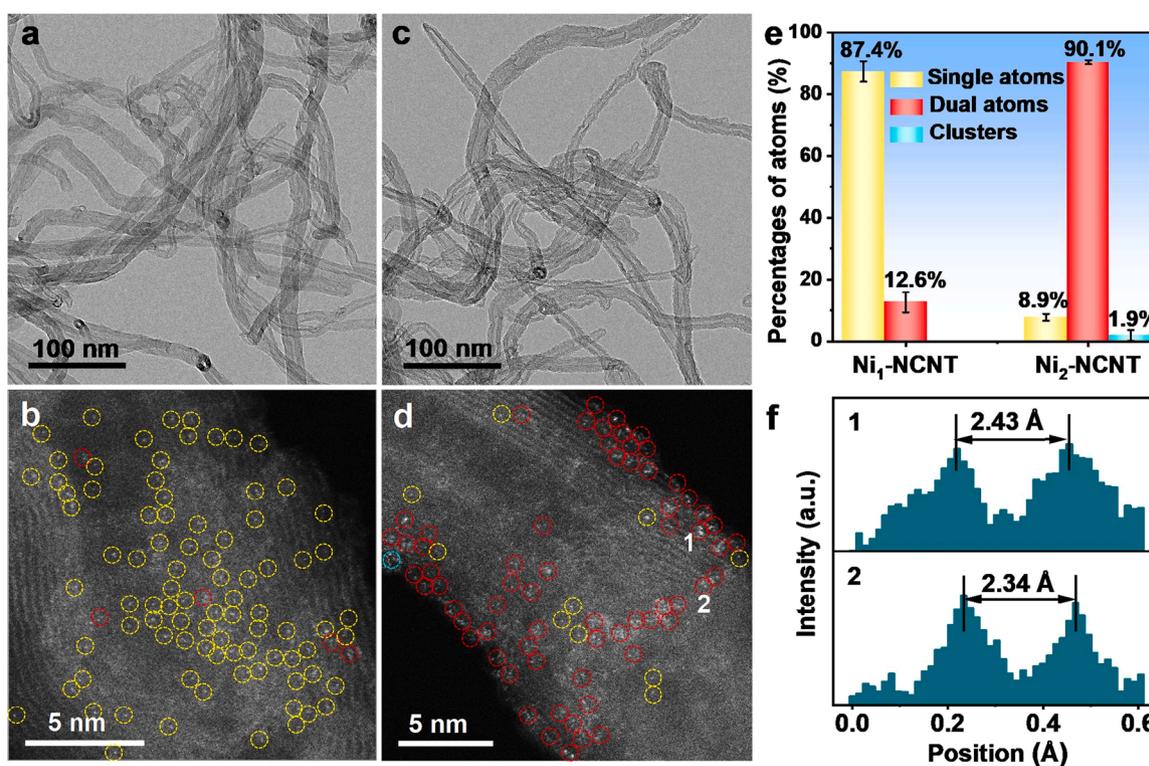


Fig. 1. (a, c) TEM images of Ni₁-NCNT (a) and Ni₂-NCNT (c). (b, d) High-resolution HAADF-STEM images of Ni₁-NCNT (b) and Ni₂-NCNT (d), with single-atoms, dual-atoms and nanoclusters highlighted with yellow, red, and blue circles, respectively. (e) The percentages of single-atoms, dual atoms and nanoclusters in 1b and 1d. (f) Intensity profiles at the areas 1 and 2 in 1d.

S8f). The atomic-resolution HAADF-STEM images confirm the existence of rich isolated Ni single atoms in Ni₁-NCNT (Figs. 1b, S9a and S9b) and Ni₂ dual-atoms in Ni₂-NCNT (Fig. 1d, S9c and S9d). As shown in Figs. 1b, S9a and S9b, the Ni atoms in Ni₁-NCNT are mainly isolated single-atoms accompanied with a small number of dual-atoms, with the percentage of single-atoms and dual-atoms being 87.4% and 12.6%, respectively, after counting the numbers of single-atoms and dual-atoms in above three individual images (Fig. 1e). By counting the numbers of single-atoms, dual-atoms and nanoclusters in Fig. 1d, S9c and S9d, we found that 90.1% of the Ni atoms are in pairs in Ni₂-NCNT (Fig. 1e), much higher than those of DACs synthesized using metal salts as a precursors [59], demonstrating that our strategy can successfully achieve the controlled

synthesis of pure DACs. As shown in Fig. 1f, the intensity profiles at areas 1 and 2 indicate that the distance between the adjacent Ni atoms is approximately 2.4 Å.

X-ray photoelectron spectroscopy (XPS) was conducted to probe the electronic state and coordination environment of Ni atom in Ni₁-NCNT and Ni₂-NCNT. As shown in Fig. S10, the binding energies of Ni 2p_{3/2} (855.5 eV) in both Ni₁-NCNT and Ni₂-NCNT are higher than that of Ni⁰ (853.5 eV) [60], and lower than that of Ni²⁺ (855.9 eV) [61], indicating the valence state of Ni in both Ni₁-NCNT and Ni₂-NCNT are between 0 and +2. The high-resolution N 1s spectra can be deconvoluted into four subpeaks at ~398.9, 399.5, 400.4, and 401.4 eV, corresponding to pyridinic N, Ni-N (pyridinic), pyrrolic N, and graphitic N, respectively

(Fig. S11) [13,62–64]. No subpeak at ~ 399.5 eV was found in NCNT, demonstrating that the subpeaks at 399.5 eV in Ni₁-NCNT and Ni₂-NCNT are ascribed to Ni–N. In addition, the high-resolution C 1s spectra show almost identical profiles for Ni₁-NCNT, Ni₂-NCNT and NCNT (Fig. S12), suggesting no coordination between Ni and C in Ni₁-NCNT and Ni₂-NCNT.

X-ray absorption fine structure (XAFS) spectroscopy was conducted to investigate the electronic and structural information of Ni atoms in Ni₁-NCNT and Ni₂-NCNT. The energies of the pre-edges in the X-ray absorption near-edge structure (XANES) spectra for Ni₁-NCNT and Ni₂-NCNT are higher than that for Ni foil and lower than those for phthalocyanine nickel (NiPc) and NiO (Fig. 2a, Fig. S13), further indicating the valence states of Ni atoms in Ni₁-NCNT and Ni₂-NCNT are between 0 and +2. The identifiable pre-edge peaks *a* and *b* in Fig. 2a are attributed to the Ni 1s \rightarrow 3d and 1s \rightarrow 4p_z transitions, respectively [65]. As shown in Fig. 2b, the main peaks are located at ~ 1.43 Å in Ni₁-NCNT and 1.36 Å in Ni₂-NCNT, which are close to the distance of Ni–N bond in NiPc (1.51 Å), and thus could be assigned to the Ni–N bonds. In addition, the peak at 2.30 Å in Ni₂-NCNT is close to that of the Ni–Ni bond (2.18 Å) in Ni foil, and this distance is also close to the Ni–Ni distance observed in the HAADF-STEM image of Ni₂-NCNT (Fig. 1 f), indicating the existence of Ni–Ni coordination in Ni₂-NCNT. A small peak around 2.30 Å is also observed in the Ni K-edge FT-EXAFS profile of Ni₁-NCNT (Fig. 2b and e), which can be ascribed to the Ni–Ni bonds due to the existence of 12.6% dual-atoms in Ni₁-NCNT (Fig. 1 e). The coordination number of Ni–N is 3.7 ± 0.6 for Ni₁-NCNT, whereas the coordination numbers of Ni–N and Ni–Ni are 2.9 ± 0.6 and 1.1 ± 0.4 for Ni₂-NCNT, respectively (Table S1). To identify the coordination structure around Ni atom, Fourier-transform extended X-ray fine structure (FT-EXAFS) spectra were recorded for Ni₁-NCNT, Ni₂-NCNT and the reference samples (Fig. 2c, 2d, and S14, S15). The spectra of Ni₁-NCNT and Ni₂-NCNT were fitted in R space on the basis of optimized structural models of the SAC (Ni–N₄) and DAC (Ni₂–N₃) (the inset shown in Fig. 2c

and d), and the fitting curves agree well with the experimental results. To further clarify the coordination structures for the Ni species, EXAFS wavelet transform analysis was carried out (Figs. 2e, and S16). Compared with Ni₁-NCNT, Ni₂-NCNT shows not only the signals of Ni–N coordination but also the signals of Ni–Ni coordination, further confirming that the coordination structure of Ni₂-NCNT is Ni₂–N₃ and that of Ni₁-NCNT is Ni–N₄.

3.2. Electrocatalytic CO₂ reduction

The electrocatalytic CO₂ reduction performances were assessed with a standard three-electrode system in CO₂-saturated 0.5 M KHCO₃ electrolyte. We firstly investigated the electrocatalytic activity for CO₂ reduction of a physical mixture of Ni₂(ppyzc)₂ and CNTs (Fig. S17), the results reveal that H₂ is the only product, indicating the physical mixture of Ni₂(ppyzc)₂ and CNT do not display the electrocatalytic activity for CO₂ reduction. As a key point in the synthesis process, the loading of complex precursor may affect the catalytic activities of DACs. Low concentration of the precursor can evenly distribute on the surface of CNTs during the in situ synthesis process, forming DACs with good dispersion after subsequent pyrolysis. High concentration of the precursor will lead to the aggregation of the complexes through intermolecular π - π stacking, and eventually the generation of nanoparticles in the subsequent pyrolysis process, thus decrease the selectivity for CO₂ electroreduction. In this regard, the feed ratio of ligand H₂ppyzc, nickel acetate and CNT was varied to prepare diatomic Ni₂ catalysts with different Ni loadings. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) revealed that the final Ni contents are 0.37, 0.61, 1.04, 1.85 and 1.87 wt% for 2%-Ni₂-NCNT, 4%-Ni₂-NCNT, 8%-Ni₂-NCNT, 12%-Ni₂-NCNT and 24%-Ni₂-NCNT catalysts (the percentages denote the mass ratios of the Ni₂(ppyzc)₂ precursor to CNT), respectively (Table S2). As shown in the XRD patterns (Fig. S18), although the Ni content increases, there are no discernible peaks

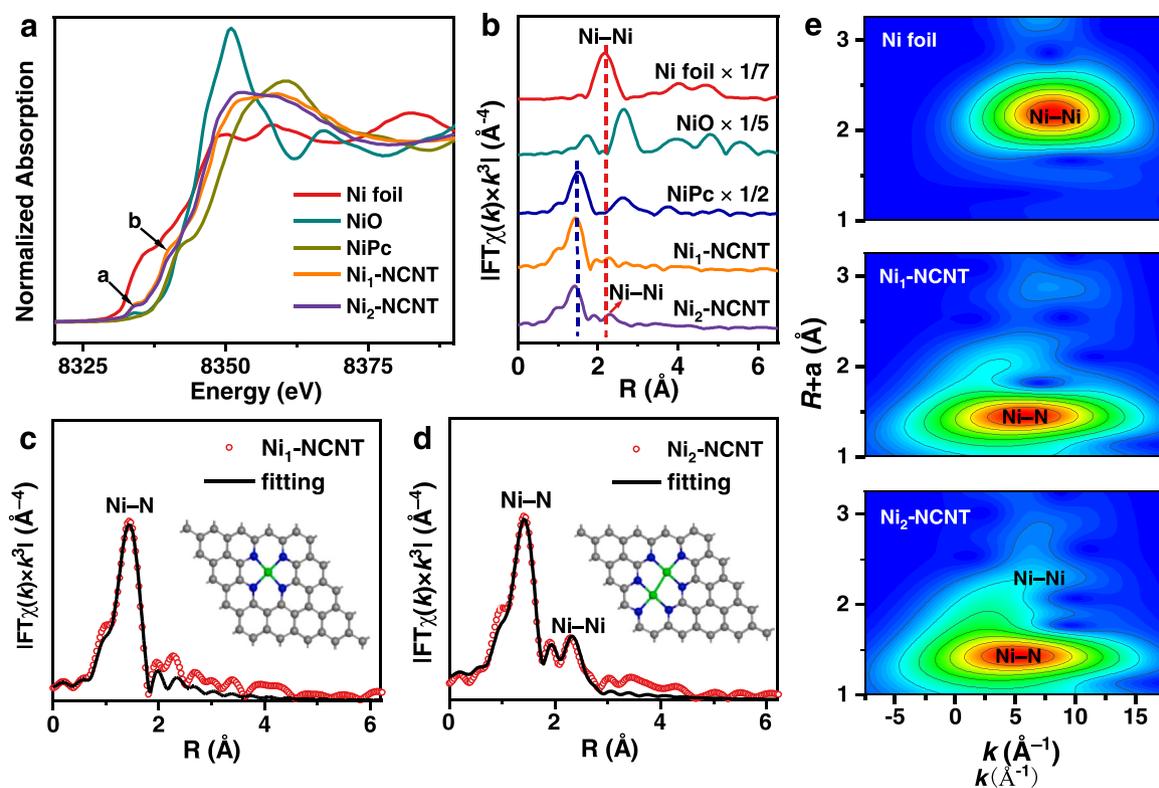


Fig. 2. (a) Ni K-edge XANES spectra of the samples. (b) Ni K-edge FT-EXAFS profiles of the samples. (c) Ni K-edge EXAFS fitting curves of Ni₁-NCNT in the R space, the inset showing the optimized structural model of SACs (Ni–N₄). (d) Ni K-edge EXAFS fitting curves of Ni₂-NCNT in the R space, the inset showing the optimized structural model of DAC (Ni₂–N₃). (e) Wavelet transforms of k^2 -weighted EXAFS.

characteristic of metallic Ni nanoparticles for these samples after acid washing. The final Ni loadings and catalytic activities of 12%-Ni₂-NCNT and 24%-Ni₂-NCNT are very close, indicating that the loading of diatomic Ni₂ pairs was almost saturated when the ratio reached 12%, and further increased Ni loading in 24%-Ni₂-NCNT mainly forms Ni nanoparticles, which were removed by acid washing. In the performance tests, 4%-Ni₂-NCNT exhibits the best catalytic activity. A higher or lower mass ratio of Ni₂(ppyzc)₂/CNT would result in lower the activity of final Ni₂-NCNT catalyst (Fig. S19). 2%-Ni₂-NCNT shows inferior activity, probably owing to the lower Ni content; higher Ni contents would lead to partial agglomeration of Ni atoms to generate Ni nanoparticles (Fig. S20), resulting in a lower activity and selectivity for CO₂ electroreduction.

Pyrolysis temperature is another important parameter during the synthesis, and it could affect the controllable synthesis of diatomic catalysts and thus their catalytic activities. Thermogravimetric analysis (TGA) shows that the distinct weight loss of Ni₂(ppyzc)₂ starts at the temperature around 500 °C, and the weight loss could be ascribed to the decomposition of Ni₂(ppyzc)₂ (Fig. S21). Therefore, the pyrolysis temperatures were set at 500, 550, 600, 650, 700, 800, and 900 °C, respectively, and distinct XRD peaks of crystalline Ni (PDF # 04-0850) emerge when the pyrolysis temperature reaches over 800 °C (Fig. S22), revealing that higher temperature would induce agglomeration of Ni atoms. The DAC displays the highest electrocatalytic performance when the pyrolysis temperature was set at 600 °C (Fig. S23), and a higher pyrolysis temperature would cause the decrease in the CO partial current density (*j*_{CO}) and FE of the catalyst, particularly when Ni nanoparticles are present on CNTs. On the basis of the above experimental results, we obtained the best electrocatalytic CO₂RR of Ni₂-NCNT when the mass ratio of Ni₂(ppyzc)₂/CNT was 4% (0.61 wt% of Ni loading) and the pyrolysis temperature was 600 °C.

Then we compared the electrocatalytic CO₂ reduction performance of Ni₂-NCNT (0.61 wt% of Ni content, Table S2), Ni₁-NCNT (0.66 wt% of Ni content) and NCNT. CO and H₂ are the only gas products according to the analysis of gas chromatography (GC). Moreover, no significant liquid products were detected via ¹H NMR spectroscopy (Fig. S24). The electrochemical performance was first assessed via linear sweep voltammetry (LSV) at the scan rate of 2 mV s⁻¹; Ni₂-NCNT delivers a higher catalytic current density than Ni₁-NCNT and NCNT (Fig. 3a, Fig. S25).

The control potential electrolysis and GC analysis revealed that Ni₁-NCNT shows lower FE_{CO} (87–90%) in the potential range from -0.8 V to -1.1 V vs. RHE, whereas Ni₂-NCNT exhibits higher FE_{CO} (90–97%) over a wider potential range from -0.8 V to -1.2 V vs. RHE (Fig. 3b). For FE_{CO} > 80%, the potential range for Ni₂-NCNT is from -0.7 to -1.4 V vs. RHE, in contrast to from -0.8 to -1.1 V for Ni₁-NCNT. The maximum FE_{CO} for Ni₂-NCNT is 97%, in contrast to 89% (for Ni₁-NCNT) and 0.6% (for NCNT) under the same potential (-0.9 V vs. RHE). The significant difference in FE_{CO} between Ni₂-NCNT and Ni₁-NCNT indicates that dual-atom site can effectively inhibit HER and thus give superior electrocatalytic activity for CO₂ reduction.

The difference in *j*_{CO} between DACs and SACs is more pronounced. A large catalytic current density of 76.2 mA cm⁻² was obtained for Ni₂-NCNT at -1.4 V vs. RHE, which is much higher than that of Ni₁-NCNT (32.7 mA cm⁻²) and NCNT (0.4 mA cm⁻²) (Fig. 3c). As shown in Fig. S26, after iR correction, Ni₂-NCNT DAC also displays much higher *j*_{CO} (82.0 mA cm⁻²) than Ni₁-NCNT SAC (*j*_{CO} = 42 mA cm⁻²) at -1.1 V vs. RHE. These *j*_{CO} values are higher than those of most reported electrocatalysts for CO₂-to-CO conversion (Table S3), revealing that Ni₂-NCNT is one of the best electrocatalysts reported thus far for CO₂ reduction.

The charge-transfer resistance was evaluated via electrochemical impedance spectroscopy (EIS), and Ni₂-NCNT shows a better charge transfer efficiency than Ni₁-NCNT and NCNT (Fig. S27a). The Tafel slope value for Ni₂-NCNT (117 mV dec⁻¹) is significantly lower than that of Ni₁-NCNT (189 mV dec⁻¹), demonstrating a better kinetics for CO₂ reduction (Fig. S27b). Furthermore, the double-layer capacitance (*C*_{dl}) values for Ni₂-NCNT (5.7 mF cm⁻²) and Ni₁-NCNT (5.9 mF cm⁻²) are quite similar (Fig. S28), demonstrating that the higher catalytic activity of Ni₂-NCNT does not stem from a larger electrochemical active surface area (ECSA). SCN⁻ anion is commonly used as a poisoning agent for the catalytic sites [66]. As shown in Fig. S29, the current density of Ni₂-NCNT is dramatically lowered after the addition of SCN⁻, indicating the Ni₂ dual-atom site is the primary active site for CO₂ electroreduction. In order to compare the catalytic activities of Ni₂-NCNT and Ni₁-NCNT more directly, their current densities were normalized to A mg_{Ni}⁻¹, and more pronounced differences in catalytic activities are shown in Fig. 3d. The *j*_{CO} mass activity of Ni₂-NCNT (25.0 A mg_{Ni}⁻¹) is 2.3-times higher than that of Ni₁-NCNT (10.9 A mg_{Ni}⁻¹), confirming that the enhanced

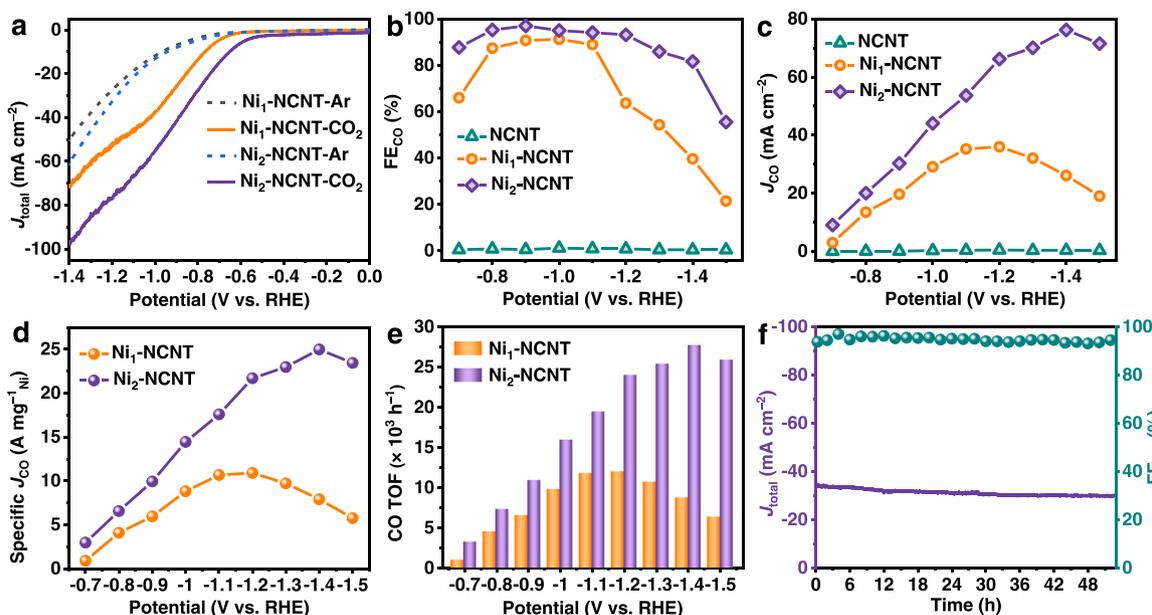


Fig. 3. (a) LSV curves in Ar- or CO₂-saturated 0.5 M KHCO₃ electrolyte. (b, c) FE_{CO} (b) and CO partial current density (c) for NCNT, Ni₁-NCNT and Ni₂-NCNT catalysts. (d) The specific current densities of CO normalized by the mass of Ni for Ni₁-NCNT and Ni₂-NCNT. (e) TOFs for Ni₁-NCNT and Ni₂-NCNT at different potentials. (f) Chrono-amperometry curve and FE_{CO} for Ni₂-NCNT at -0.9 V vs. RHE. All the data were measured without the iR correction.

catalytic activity of Ni₂-NCNT originates from its dual-atom synergistic effect rather than the different Ni loading. The turnover frequencies (TOFs) for CO₂ reduction were calculated to evaluate the intrinsic activity of single Ni sites, and Ni₂-NCNT gives a high TOF value of $2.75 \times 10^4 \text{ h}^{-1}$ at -1.4 V , much higher than that of Ni₁-NCNT ($1.19 \times 10^4 \text{ h}^{-1}$ at -1.2 V) (Fig. 3e). In addition, Ni₂-NCNT exhibits a good stability, with the Faraday efficiency remaining constant within 52 h continuous electrolysis (Fig. 3f). The results of XPS measurements demonstrate that the valence states of Ni atoms before and after the catalysis are the same (Fig. S30), further demonstrating the good stability of Ni₂-NCNT. To further evaluate the intrinsic electrocatalytic activity of Ni₂-NCNT, electrocatalytic CO₂ reduction activity and selectivity were investigated in a flow cell with 1.0 M KHCO₃ electrolyte (Fig. S31). As shown in Fig. S31, the CO Faraday efficiency (FE_{CO}) of Ni₂-NCNT maintains over 93.4% even at a high current density of 250 mA cm⁻², this value is much higher than that of reported Ni₂ DAC (with a FE_{CO} of ~86% at a current density of 200 mA cm⁻²) [46], further demonstrating the outstanding activity and selectivity of as-prepared Ni₂-NCNT DAC for electrocatalytic CO₂ reduction.

3.3. Diatomic synergistic mechanism

In order to further unveil the mechanism of CO₂RR and the activity difference between Ni₂-NCNT and Ni₁-NCNT, the density functional theory (DFT) calculations were performed. Two optimized DAC models of Ni₂-N₄ and Ni₂-N₃ (Ni₂-NCNT), as well as two related SAC models of Ni-N₄ (Ni₁-NCNT) and Ni-N₃ were constructed for comparison (Fig. 4a, and S32, S33). As shown in Fig. 4b, the CO₂ electroreduction to CO involves four elementary steps: (1) CO₂ + * → *CO₂ (* = catalytic site); (2) *CO₂ + H⁺ + e⁻ → *COOH; (3) *COOH + H⁺ + e⁻ → *CO + H₂O; (4) *CO → CO + *. The calculated Gibbs free energy diagrams for these four steps are shown in Fig. 4c. For CO₂ adsorption and proton-coupled electron transfer (PCET) steps, Ni-N₄, Ni₂-N₄, Ni₂-N₃ and Ni-N₃ exhibit the free energy changes (ΔG) of 1.65 eV, 1.64 eV, 0.76 eV and -0.06 eV, respectively, in which Ni-N₃ shows the most favorable ΔG for the formation of adsorbed *COOH intermediate. Subsequently, the *COOH intermediate undergoes the second PCET, forming a water molecule and *CO, and the free energy change for this step over the four

model catalysts are all downhill. Finally, the *CO desorbs from the catalysts and releases the active site. For Ni-N₃ and Ni₂-N₃, the *CO desorption step is endothermic with a free energy change of 1.26 eV and 0.21 eV, respectively. While for Ni-N₄ and Ni₂-N₄, the *CO desorption step is spontaneous with a free energy change of -0.62 eV and -0.56 eV, respectively. According to our calculations, the formation of the *COOH intermediate is regarded as the rate-determining step (RDS) for Ni-N₄, Ni₂-N₄ and Ni₂-N₃, whereas the desorption of the *CO intermediate is the RDS for Ni-N₃. Among the four model catalysts, the Ni₂-N₃ exhibits the superior CO₂ reduction activity with a free energy change of 0.76 eV in the rate-determining step, the synergistic effect between two Ni atoms in Ni₂-N₃ can stabilize the *COOH intermediate and obviously lower the free energy change in the RDS compared with that of Ni-N₄ SAC (1.65 eV). Therefore, the Ni₂-N₃ exhibits the best electrocatalytic activity for CO₂ reduction, which is consistent with the experimental results.

4. Conclusions

In summary, we have developed an effective strategy for controlled synthesis of a Ni₂ dual-atom catalyst as well as a Ni₁ single-atom catalyst by modulating the ligands of the precursors. The effects of precursor concentration and pyrolysis temperature on controlled synthesis and catalytic activity of Ni₂-NCNT DAC were investigated. Excessively high concentration of the dinuclear complex precursor and high pyrolysis temperature would lead to the agglomeration of Ni atoms, thus lowering the CO₂ reduction catalytic activity and selectivity. The optimized Ni₂-NCNT DAC with diatomic synergy exhibits excellent electrocatalytic activity and stability for electrocatalytic CO₂ reduction, achieving a high current density of 76 mA cm⁻² and a high Faradaic efficiency of 97%. DFT calculations confirm that the diatomic Ni₂-N₃ structure of Ni₂-NCNT can enhance the catalytic activity by lowering the reaction free energy via the formation of a bridged *COOH intermediate at Ni₂ catalytic site. Our work not only provides an ideal strategy for precise and controlled synthesis of DACs, but also clarifies the intrinsic origin of the superior activity of dual-atom Ni₂ electrocatalyst toward CO₂RR.

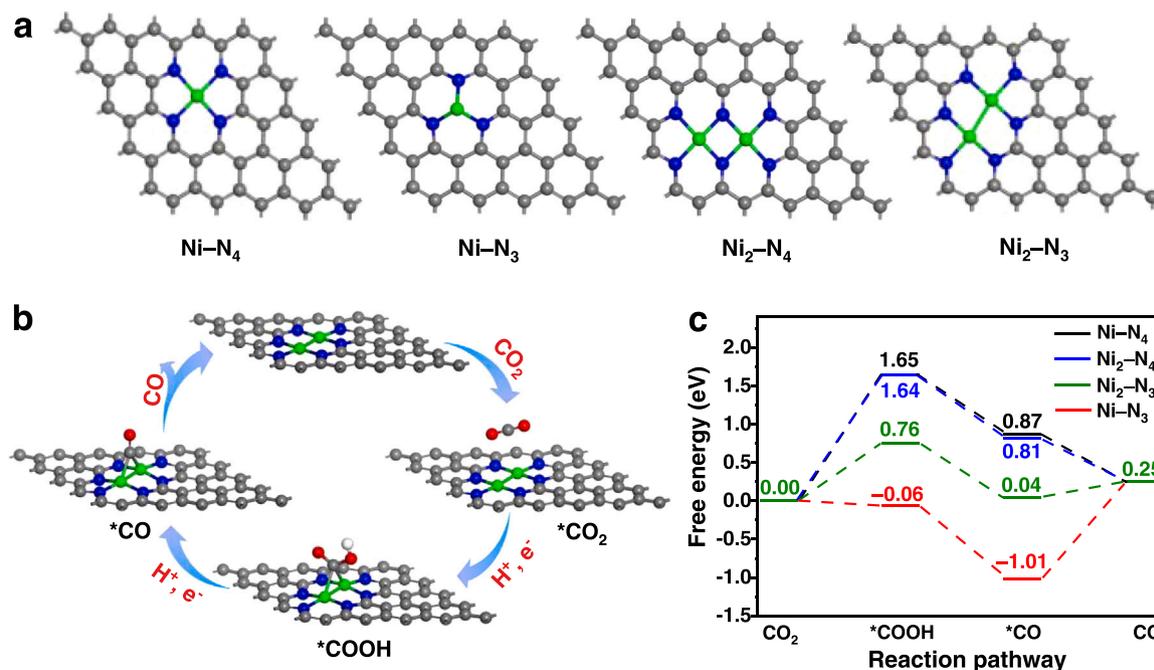


Fig. 4. (a) The structural models of Ni-N₄ (Ni₁-NCNT) and Ni-N₃ SACs, as well as Ni₂-N₄ and Ni₂-N₃ (Ni₂-NCNT) DACs. (b) The proposed reaction pathways of Ni₂-N₃ (Ni₂-NCNT) for CO₂ electroreduction to CO. (c) Calculated free energy diagram for the conversion of CO₂ to CO.

CRediT authorship contribution statement

Xiang-Ming Liang: Writing – original draft. **Hong-Juan Wang:** Investigation. **Chao Zhang:** Writing – review & editing. **Di-Chang Zhong:** Formal analysis. **Tong-Bu Lu:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.122073](https://doi.org/10.1016/j.apcatb.2022.122073).

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