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Nickel-Nitrogen-Modified Graphene: An Efficient Electrocatalyst for the Reduction of Carbon Dioxide to Carbon Monoxide

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Abstract

The electrochemical reduction of carbon dioxide (CO_2) has attracted considerable attention as an approach for maintaining the carbon cycle. Herein, we prepared nickel (Ni)-modified nitrogen (N)-doped graphene (Ni-N-Gr) as a selective electrocatalyst for the reduction of CO_2 to carbon monoxide (CO). The faradaic efficiency for CO formation by Ni-N-Gr reached 90% at -0.7 to -0.9 V versus RHE, whereas that for Ni metal and N-doped graphene was below 10%. The turnover frequency (TOF) for CO production on Ni-N-Gr came up to $\sim 2700 \text{ h}^{-1}$ at -0.7V vs RHE. Extended X-ray absorption fine structure and X-ray photoelectron spectroscopy analyses of Ni-N-Gr revealed that Ni-N coordination sites were doped into the graphene sheets and served as active centers for CO_2 reduction. Electrochemical characterizations further demonstrated that the suppression of the hydrogen evolution reaction was likely responsible for the high efficiency of CO_2 reduction under neutral and weakly acidic conditions.

Introduction

Carbon dioxide (CO₂) fixation has spurred huge interest as a practical method for removing CO₂ from the environment.¹ CO₂ can be reduced electrochemically under mild conditions;²⁻¹⁰ however, the hydrogen evolution reaction (HER) must be suppressed as it competes with CO₂ electroreduction under the range of operating potentials.^{11,12} Although copper (Cu) metal electrodes produce hydrocarbons with relatively high selectivity during CO₂ electroreduction, such electrodes exhibit over 20% faradaic efficiency (FE) for the HER.⁹

Numerous researchers have attempted to develop efficient electrocatalysts with high CO₂ reduction activity using organometallic complexes. For example, Shen *et al.* reported that a cobalt (Co) protoporphyrin immobilized on a pyrolytic graphite electrode efficiently catalyzed the reduction of CO₂ to CO and methane.¹³ Furthermore, covalent organic frameworks comprising Co porphyrins and Co based metal organic frameworks displayed the high FE for CO during CO₂ electroreduction.^{14,15} Among these catalysts, nickel-1,4,8,11-tetraazacyclotetradecane (Ni-cyclam) and its derivatives are widely attracted because these complexes reduce CO₂ to CO (90 %~ FE) with almost no H₂ evolution.¹⁶⁻¹⁹ The mechanism underlying the high selectivity of these materials for CO₂ reduction over HER can be explained as follows. In the case of Ni-cyclam, few protons bind to the Ni sites in neutral or weakly acidic solutions because the electrolyte pH is higher than the pK_a (approximately 1.8) of hydride complexes ([Ni(H)(cyclam)]²⁺), which is an essential intermediate for H₂ production^{18,19}. Thus, the deprotonated form is dominant in neutral or weakly acidic solutions, resulting in low HER activity and high FE for CO. However, as Ni-cyclam and its derivatives are homogeneous complexes, they are fragile and are difficult to separate and recycle. Thus, the synthesis of inorganic materials with Ni-N structures as heterogeneous CO₂-reduction catalysts is highly desirable.

Carbon-based materials due to robust property are alternative candidates to organometallic electrocatalysts. Metal-free carbon and M-N-carbon (M=Fe or Co)-based materials have been

well studied as efficient heterogeneous electrocatalysts for the oxygen reduction reaction (ORR) and displayed higher stability compared with that of the corresponding organometallic complexes.²⁰⁻²⁶ Recently, Varela *et al.* applied metal- (Fe, Mn) doped nitrogenated carbon materials as selective electrocatalysts for the reduction of CO₂ to CO.²⁷ Importantly, they observed that the CO selectivity was independent of the metal ions, and thus nitrogen moieties were considered to be the reaction center and determined the selectivity for CO₂ reduction. In contrast, taking into account the reaction mechanism of homogenous Ni-cyclam, Ni atoms coordinated by N atoms in carbon based materials are expected to serve as catalytic centers for CO₂ reduction. To date, however, Ni-N-doped carbon materials have not been reported, likely because Ni-N bonds are more susceptible to breakage under high-temperature heat treatment than Fe- and Co-N bonds.

Recently, the method about short-duration heat treatment of graphene oxide in the presence of metal complexes was developed for the synthesis of atomic metal- (Fe or Cu) and N modified graphene-based materials.^{28,29} It suppressed the breakage of M-N coordination bonds and resulted in the increased durability of catalysts. Based on this method, herein, Ni-N-modified graphene (Ni-N-Gr) was successfully synthesized through the heat treatment (900 °C) of Ni-pentaethylenhexamine and graphene oxides (GOs) within 1 min under an inert atmosphere (synthesis details shown in experimental section). Ni-N-Gr with atomic Ni-N structure displayed high electrocatalytic CO₂ reduction activity and CO formation selectivity, further the co-effect of Ni and N for CO₂ reduction selectivity on Ni-N-Gr system was firstly explored.

The synthesized Ni-N-Gr catalyst was structurally characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) analyses. High-resolution transmission electron microscopy (TEM) analysis revealed that no metal nano-particles (>1 nm) were formed on Ni-N-Gr (**Figure 1a** and Figure S1), and in the corresponding elemental maps (C, N, and

Ni) obtained by energy-dispersive X-ray EDX analysis (Figure 1b), Ni and N atoms were found to be uniformly dispersed on the graphene sheets. In addition, no clear peaks assignable to Ni species were observed in the XRD pattern of Ni-N-Gr (Figure S2), a result that is consistent with the HR-TEM findings.

The XPS spectrum of Ni-2p for Ni-N-Gr is shown in **Figure 2a**. The position of the Ni-2p_{3/2} peak (854.8 eV) of Ni-N-Gr revealed that the valence state of Ni was Ni²⁺,³⁰ and no peaks assignable to metallic Ni were detected.³¹ The Ni mass concentration was estimated to be 2.2 % by ICP (Table S1). The N-1s spectrum for Ni-N-Gr (Figure S3) could be deconvoluted into four distinct peaks: pyridine-like N at 398.5 eV (57.3 %), pyrrole-like N at 400.5 eV (27.5%), graphitic N at 401.5 eV (12.8%), and oxidized N at 404.5 eV (2.5%).²⁸ These results indicate that N atoms were doped into the graphene network. At the same time, N-doped graphene (N-Gr) was synthesized and corresponding N-1s spectrum was shown in Figure S3. The N/C ratios determined from the semiquantitative XPS analyses of Ni-N-Gr and N-Gr were 0.042 and 0.023, respectively (Table S2). We assumed that the difference in the N concentration between these two materials was due to suppression of the desorption of N atoms in Ni-N-Gr due to their coordination with Ni atoms. However, the ratios of N species in Ni-N-Gr and N-Gr were almost identical (Table S3). The same phenomenon was observed for the Fe-N doped graphene in our previous study. The coordination structure of Ni sites in Ni-N-Gr was directly confirmed using EXAFS. Figure 2b shows the Fourier-transformed k^3 -weighted EXAFS of Ni K-edges for Ni-N-Gr. A peak at 1.3 Å attributed to Ni-N was clearly observed,³² whereas the peak corresponding to Ni-Ni (2.2 Å) was absent.³³ Therefore, the first coordination sphere of the Ni atoms were N atoms in Ni/N-graphene. XPS and EXAFS results indicated that single Ni atom was formed and the Ni-N coordination structures were incorporated into the graphene matrix.

To examine the electrocatalytic CO₂ reduction activity of Ni-N-Gr, cyclic voltammograms (CVs) of Ni-N-Gr were obtained in Ar-deaerated phosphate buffer solution (PBS, pH 6.8) and CO₂-saturated KHCO₃ solutions (pH 6.8). As shown in **Figure 3a**, the cathodic current of Ni-

N-Gr markedly increased in the presence of CO₂. The onset potential for the reduction reaction in CO₂-saturated solution was -0.5 V vs RHE, whereas in the absence of CO₂, a current that was entirely attributable to the HER was observed from -0.6 V vs RHE. The increases of the onset potential and cathodic current in the presence of CO₂ in the electrolyte suggested that the CO₂ can be efficiently reduced by Ni-N-Gr catalyst. In contrast, in the case of nitrogen-doped graphene (N-Gr) and a Ni-metal electrode, the reduction current greatly decreased in the presence of CO₂ (Figures 3c and S4a).

Although the cathodic current generated by Ni-N-Gr increased in the presence of CO₂, CVs alone cannot provide conclusive evidence for CO₂ reduction. Thus, the CO₂ reduction products in the gas phase were quantitatively analyzed using gas chromatography/mass spectrometry (GC-MS) after long-term (1 h) electrolysis under the static condition (details shown in experimental section). The potential dependence of the faradaic efficiencies (FEs) for CO and H₂ for Ni-N-Gr in neutral solutions is shown in Figure 3b. Ni-N-Gr exhibited the highest activity for CO formation with a FE exceeding 90% at -0.7 to -0.9 V. At more negative potentials, however, the HER gradually became dominant. It should be noted here that the combined FEs for CO and H₂ formation were close to 100%, suggesting that liquid products were not significantly produced in a similar manner to the case of Ni-cyclam.^{16,17} In fact, we also conducted the high performance liquid chromatography (HPLC) measurements to detect liquid products. However, the amount of formaldehyde, methanol and formic acid were below the detection limit. The pH dependence of the FE for CO formation by Ni-N-Gr was also examined (Figure S5). CO₂ was reduced to CO in preference to protons in both neutral and weakly acidic solutions (pH 2.7), although the reduction of protons to hydrogen proceeded preferentially in highly acidic solutions (pH 0.7). In contrast, Figures S4b and 3d showed that the FEs for CO formation by N-Gr and the Ni metal electrode were negligible at all examined potential regions, respectively. In addition, the Tafel plots of Ni-N-Gr and N-Gr are shown in Figure S6. The Tafel slopes for Ni-N-Gr and N-Gr are 126 mV dec⁻¹ and 309 mV dec⁻¹,

respectively. These results indicate that the CO₂ reduction activity of Ni-N-Gr is much higher than that of N-Gr and Ni metal electrode.

Next, we attempted to identify the catalytic active sites of Ni-N-Gr. First, we replaced Ni with Cu to explore the effect of metal species. Cu-N modified graphene (Cu-N-Gr) was synthesized in a similar manner to Ni-N-Gr except for the use of CuCl₂ instead of NiCl₂. The XPS spectrum of N-1s revealed Cu-N-Gr contains four kinds of N species (Figure S7) and the ratios of N species were almost identical with that in Ni-N-Gr (Table S3). Although Cu metal electrodes are efficient for CO₂ reduction, the synthesized Cu-N-Gr exhibited poor CO₂ reduction activity (Figure S8). This is reasonable because that H₂ is known to become the main product of the CO₂ reduction on Cu nanoparticles below 2 nm.⁹ This result implies that the Ni atoms in Ni-N-Gr play a key role for the high activity in CO₂ reduction. Secondly, we decreased the content of Ni and N atoms in Ni-N-Gr to clarify the dependence of the electrocatalytic activity on the concentration of these foreign elements (denoted as Ni-N-Gr-1/5, for the detailed preparation see the experimental section). Although the Ni and N contents of Ni-N-Gr-1/5 decreased greatly compared with that of Ni-N-Gr (see Table S1 and Table S2), respectively, the FEs of CO for Ni-N-Gr and Ni-N-Gr-1/5 are almost identical (Figure S9). Therefore, although the N concentration of N-Gr (2.2 %) was lower than that of Ni-N-Gr (3.9 %), the low concentration of N atom in N-Gr is not the origin of its low FEs of CO. Taken together, above electrochemical results indicated that both Ni and N are necessary for the high catalytic activity. Therefore, considering the EXAFS, XPS and TEM results, it is most likely that atomic Ni coordinated with N in the graphene network is the active reaction center of our synthesized catalyst. The turnover frequencies for CO formation on per electroactive Ni atoms of Ni-N-Gr (TOFs; CO generation rate on per electrochemical active Ni atoms) reached up to 2700 h⁻¹ and 4600 h⁻¹ at -0.7 V and -0.8 V vs RHE in neutral solutions, respectively (for the detail calculations see the experimental section). As listed Table S4, Ni-N-Gr and Ni-N-Gr-1/5 have similar values of TOFs, suggesting that the active centers of both catalysts are the same. The

TOFs of Ni-N-Gr are comparable to those of the best porphyrin-based heterogeneous catalysts for CO₂ reduction (TOF for Co-porphyrin based COFs $\approx 2500 \text{ h}^{-1}$ at -0.67 V vs RHE) .^{13,14}

Meanwhile, as with our N-Gr, some N-doped carbon materials show that the FEs of CO were below 20 %.^{35,36} However, we recognize that CO₂ are effectively reduced to CO or formic acid on several metal-free N-doped carbon catalysts in the previous reports.^{27,37-39} Although the reason for this contradiction is unknown, soft X-ray absorption spectroscopy for elucidating electronic structures of N atoms is now under investigation.

Due to the similarity of the active centers of homogeneous Ni-cyclam and heterogeneous Ni-N-Gr catalysts, which contain single Ni atoms coordinated with N atoms, we can speculate why CO₂ was preferentially reduced over H⁺ by Ni-N-Gr in weakly acidic or neutral solutions. As mentioned in the introduction, proton adsorption behavior on Ni complexes is an important factor for the reduction of CO₂ to CO over proton reduction to H₂, which can be explained as follows.^{18,19} A protonated complex $[\text{Ni}(\text{H})\text{-L}]^+$ serves as an intermediate for HER, and the adsorbed proton blocks CO₂ adsorption. Thus, the adsorbed proton facilitates HER and obstructs CO₂ reduction. However, when the pK_a of $[\text{Ni}(\text{H})\text{-L}]^+$ is lower than an electrolyte pH, the deprotonation form (Ni-L) definitely dominates the protonated one, resulting that the CO₂ reduction reaction accelerates over HER. Although the reduction of CO₂ to CO also consumed proton, Song *et al.* demonstrated by the DFT calculation that the following pathway of the CO₂ reduction reaction was energetically favorable on Ni-cyclam : CO₂ first binds with an carbon atom to a Ni atom, and then the adsorbed CO₂ is protonated from water. Thus, the reduction of CO₂ to CO does not require the adsorbed hydrogen.¹⁹ For Ni-N-Gr, as H₂ was the main product at electrolyte pHs below 0.7 (Figure S5b), the suppression of proton adsorption at Ni sites of Ni-N-Gr may lead to a poor HER activity in weakly acidic and neutral solutions, as is observed for Ni-cyclam and its derivative. To confirm this speculation, we next examined the pH dependence of HER activity by Ni-N-Gr. Ni-N-Gr exhibited an HER onset potential of -0.6 V at pH 6.8, which is 300 mV more negative than that at pH 0.7 on the RHE scale (Figure

S10). For Ni foil, the onset potential for HER was -0.2 V vs RHE at pH 6.8. These results clearly demonstrate that the HER activity of Ni-N-Gr is much lower than that of bulk Ni, which is likely responsible for the high FE of CO in CO₂ saturated KHCO₃ solution. If we speculate that the pK_a of Ni-N-Gr locates at around 2.0 based on the reported pK_a value of Ni-cyclam (1.8),¹⁸ it is reasonable that the FEs of CO drastically changed between pH 2.7 and pH 0.7. However, the actual pK_a value of Ni-N-Gr is still unclear. Thus, further studies for identifying the pK_a value and the CO₂ reduction mechanism of Ni-N-Gr are now in progress in our laboratory.

Finally, the electrocatalytic durability of Ni-N-Gr was evaluated at -0.65 V (vs. RHE) for 5 h in CO₂ saturated KHCO₃ solution. The cathodic current and FE for CO and H₂ as a function of time are shown in **Figure 4**. As the cathodic current and FE for CO exhibited almost negligible decreases, it was demonstrated that the Ni-N-Gr catalyst produced a stable output of CO from CO₂ reduction. In addition, the Ni-2p_{3/2} XPS peak (855.1 eV) after the electrolysis at -0.7 V vs RHE for 1 h revealed that the Ni²⁺ valence state was still dominant (Figure S11), and the elemental contents scarcely changed (Table S1 and S2). Furthermore, the nanosheet morphology of Ni-N-Gr was well remained during the electrolysis as shown in the SEM images (Figure S12).

Conclusion

Novel Ni-N-modified graphene was successfully synthesized by the short-duration heat treatment of a Ni-N organometallic complex in the presence of GOs. The resultant carbon-based catalyst, Ni-N-Gr, efficiently catalyzed the electrochemical reduction of CO₂ to CO. XPS and EXAFS analyses revealed that heat treatment resulted in the introduction of Ni atoms coordinated with N atoms into the sp² networks of graphene, and that the Ni-N site was the active center for CO₂ reduction. The HER activity of Ni-N-Gr was much lower than that of Ni-metal electrode, a property that was likely responsible for the high efficiency of CO formation, as has been reported for the homogeneous Ni-based organometallic catalyst Ni-cyclam. Notably,

the present study is the first to describe the synthesis of a Ni-based heterogeneous catalyst with high activity for CO₂ electrochemical reduction and discover the influence of both N and metal for CO₂ reduction selectivity. This work provides atomic-level insight into the development of metal-bonded N-modified heterogeneous catalysts inspired by homogeneous catalysts for selective electrochemical reactions.

Experimental section

Ni-N-Gr was prepared as follows. Graphite oxides (GOs) were synthesized using a modified Hummers method.⁴⁰ For the synthesis, 5 mL pentaethylenhexamine (PEHA : 3.0 mmol) ethanol solution was added dropwise into 15 mL ethanol containing 2.0 mmol NiCl₂·6H₂O to form bright purple Ni-PEHA complexes. The Ni-PEHA complex solution (6.1 mL) was diluted with ethanol in a total volume of 20 mL, and 200 mg GOs was then dispersed into the solution using an ultrasonic bath. The resulting mixture was dried at 60 °C overnight, and the obtained residue was placed at the bottom of a half-closed quartz tube filled with Ar. This tube was quickly inserted into a muffle furnace at 900 °C for 45 s. After the heat treatment, the tube was quickly cooled to room temperature under Ar protection. The synthesized graphenes were then washed with 2 M H₂SO₄ at 65-70 °C for 3 h under stirring. Ni-N-Gr-1/5 was synthesized in the same method with that for Ni-N-Gr, with the exception that the amount of Ni-PEHA decreased to one-fifth.

N-Gr was prepared in a similar manner to that used for Ni-N-Gr, with the exception that Ni-sources, were not included in the preparation. Ni foil (Nilaco) was mechanically polished using 0.05-μm alumina paste before being used for electrochemical measurements.

Powder X-ray diffraction (XRD) patterns were measured on a Rigaku D/Max2500PC diffractometer with Cu Kα radiation ($\lambda=1.5418$ Å). XPS (Axis Ultra, Kratos Analytical Co.) spectra were obtained using monochromatic Al Kα X-rays at $h\nu = 1486.6$ eV. For XPS

component analysis, backgrounds of core-level spectra were subtracted based on the Shirley method. All the peak position was calibrated by the signal of C1s at 284.5 eV. N-1s spectra were fitted via Voigt functions (70% Gaussian and 30% Lorentzian). X-ray absorption measurements (XAFS) were performed using the hard X-ray beam line, BL01B01, at Spring-8, Japan. Transmission-yield spectra were measured using a double-crystal Si (111) monochromator. High-resolution TEM and EDX mappings were performed using a spherical aberration-corrected TEM system (JEOL ARM-200F). Scanning electron microscopy (SEM) was observed using a Hitachi S-5000 field emission scanning electron microscopy (FE-SEM) instrument. ICP was measured by Optima 8300 ICP-OES spectrometer (Perkin Elmer).

Electrochemical measurements were performed using a Hokuto Denko Electrochemical Station (Model HZ-5000) in a separated electrochemical cell at room temperature. Platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The working electrode was prepared as follows. A catalyst ink consisting of 3 mg graphene catalysts, 300 μL ethanol, and 28.5 μL nafion (5 wt.%, Du Pont, Corp.) was prepared in an ultrasonic bath. The resulting catalyst ink was dropped in 60 μL aliquots onto a glassy carbon plate (2 cm^2) to fabricate a catalyst layer with a loading weight of 0.3 mg cm^{-2} . Prior to the measurements, the electrolyte was saturated with CO_2 . The CO_2 reduction was carried out under the static condition without CO_2 flowing. After constant potential electrolysis for 1 h, the generated gas products were accumulated at the head of the cathodic part of an electrochemical cell. The accumulated gas products were quantitatively detected using a gas chromatography mass spectrometer (GCMS-QP 2010 Plus, Shimadzu, Japan) with micropacked ST MP-01 column (shincarbon-ST 80/100 mesh), and the representative chromatography chart of Ni-N-Gr at -0.7V vs RHE was shown in Figure S13. The calibration line of CO and H_2 was determined by standard CO and H_2 gas with different concentration.

In order to calculate electroactive Ni sites, the CV of Ni-N-Gr on glassy carbon was conducted in alkaline solution (0.1 M KOH) during the potential range of 0.5 ~ 1.3 V vs RHE.

As shown in Figure S14, the redox wave of $\text{Ni}^{2+}/\text{Ni}^{3+}$ was well-formed, and thus the electrochemically exposed active sites were estimated by the integrated $\text{Ni}^{2+}/\text{Ni}^{3+}$ peak area.

TOF was calculated as the following formula: (F : faraday constant, 96485 C/mol e^-).

$$\frac{\text{FE of CO} \times \text{Current}}{2F \times \text{active sites}}$$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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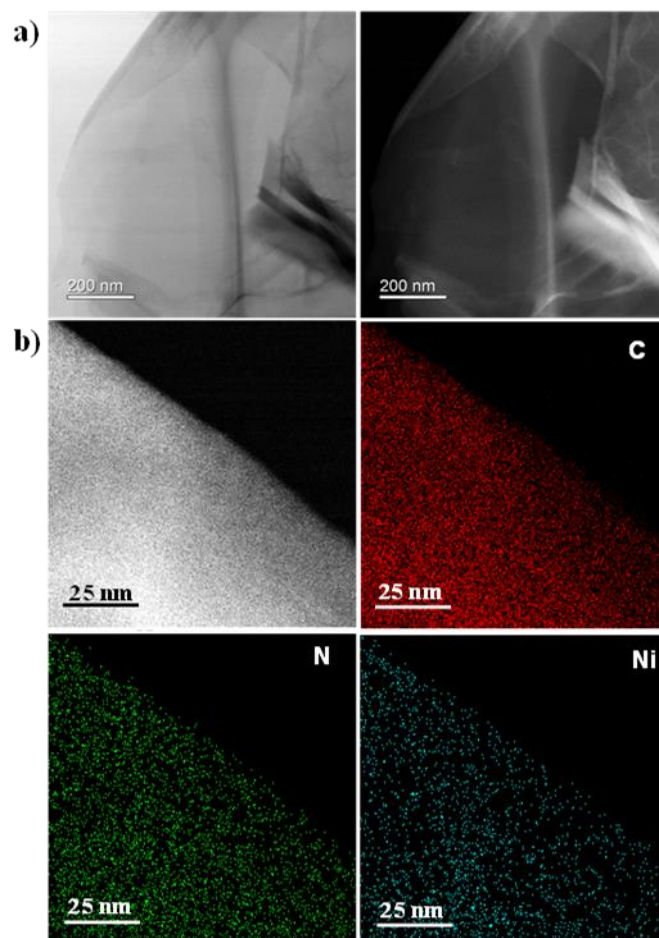


Figure 1. a) Representative TEM image of Ni-N-Gr (left) and corresponding high-angle annular dark-field scanning image (right), and b) high-resolution TEM image of Ni-N-Gr and corresponding EDX maps of C, N, and Ni, respectively.

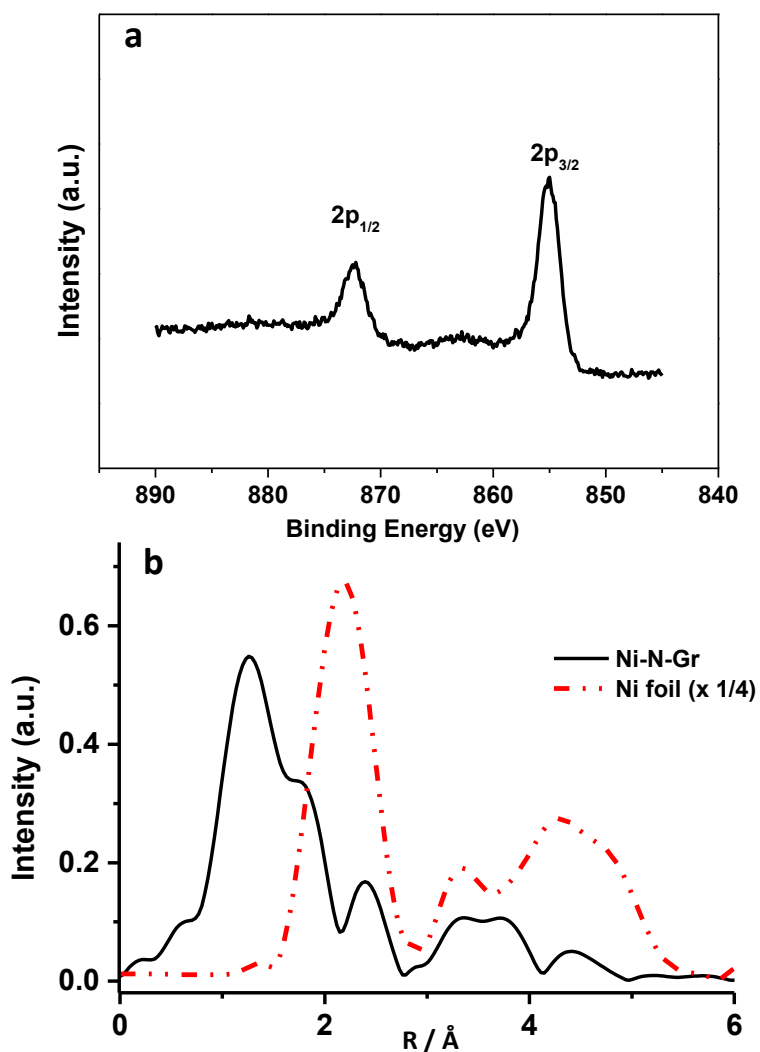


Figure 2. Ni-2p XPS spectrum of Ni-N-Gr (a) and k^3 -weighted Fourier transform EXAFS spectra at the Ni K-edge for Ni-N-Gr, Ni metal (b).

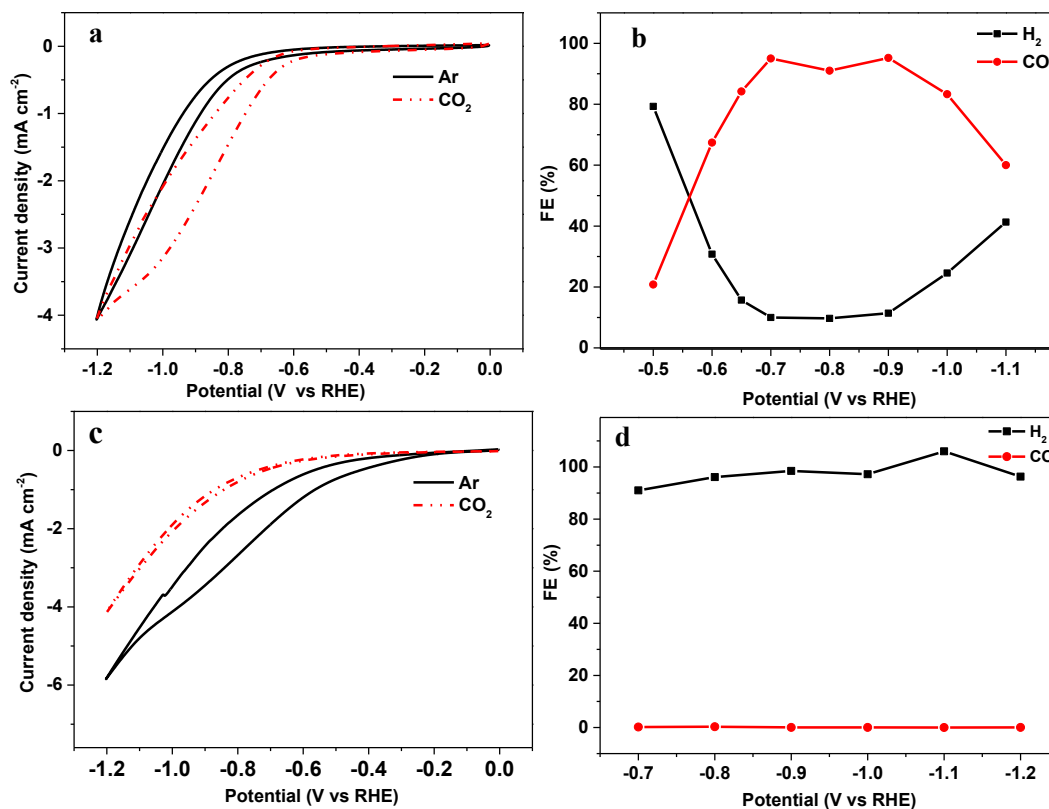


Figure 3. Cyclic voltammograms of Ni-N-Gr catalyst (a) and Ni foil (c) in CO₂-saturated 0.1 M KHCO₃ and Ar-saturated 0.1 M KH₂PO₄/K₂HPO₄ (pH=6.8) at 10 mVs⁻¹, and FEs for the reduction products generated by Ni-N-Gr catalyst (b) and Ni foil (d).

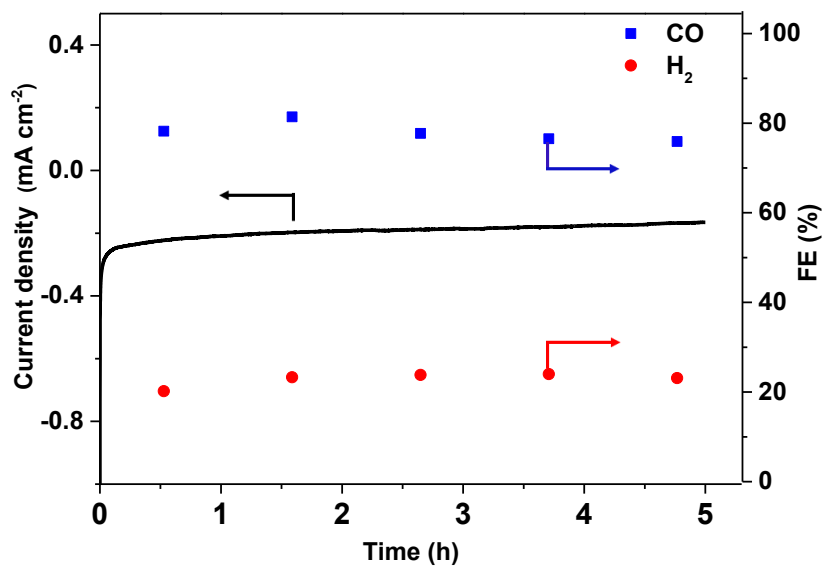
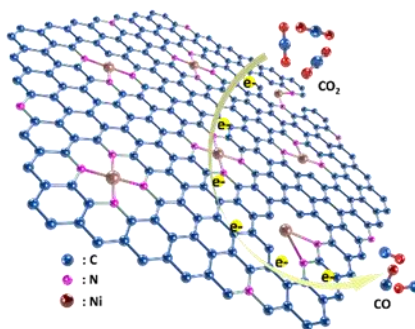


Figure 4. Chronoamperometric and FE results for the Ni-N-Gr catalyst in CO₂-saturated KHCO₃ (0.1 M) solution at -0.65 V_{RHE}.

Nickel-nitrogen-modified graphene (Ni-N-Gr) is fabricated and Ni-N coordination sites on Ni-N-Gr as active centers effectively reduce CO_2 to CO. The faradaic efficiency for CO formation reaches 90% at -0.7 to -0.9 V vs RHE, and the turnover frequency (TOF) for CO production comes up to $\sim 2700 \text{ h}^{-1}$ at -0.7 V vs RHE.



TOC figure