Controlled Assembly of Cu Nanoparticles on Pyridinic-N Rich Graphene for Electrochemical Reduction of CO₂ to Ethylene

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Abstract: Monodisperse Cu nanoparticles (NPs) assembled on a pyridinic-N rich graphene (p-NG) support show a Cu NP mass- and size-dependent catalysis for the selective electrochemical reduction of CO₂ to ethylene (C₂H₄). For the 7 nm Cu NPs assembled on the p-NG with the p-NG/Cu mass ratio of 1:1, the C₂H₄ formation Faradaic efficiency and hydrocarbon selectivity reach 19% and 79% respectively at -0.9 V (vs reversible hydrogen electrode). The p-NG itself can catalyze the CO₂ reduction to formate, but in the composite p-NG-Cu structure, the pyridinic-N functions as a CO₂ and proton absorber, facilitating hydrogenation and carbon-carbon coupling reactions on Cu for the formation of C₂H₄. The work demonstrates a new strategy to improve Cu NP catalytic activity and selectivity for the electrochemical reduction of CO₂ for sustainable chemistry and energy applications.

Keywords: Cu nanoparticles, Self-assembly, Graphene, Nitrogen doping, CO₂ reduction, Electrocatalysis.

Graphical Abstract

1 Introduction

The electrochemical reduction of CO₂ is a promising green approach to convert CO₂ into a reusable form of carbons. Unlike the conventional thermal catalysis method where high pressure and high temperature are needed to initiate the reaction, the electrochemical reduction reaction can proceed in ambient environments and the reaction can in principle achieve much higher selectivity [1-6]. In reality, however, the multi-electron reduction of CO₂, combined with hydrogenation and carbon-carbon (C-C) coupling reactions required for the formation of hydrocarbons, makes it extremely difficult to control a specific reaction pathway toward a targeted hydrocarbon product. Recent studies have indicated that when a right catalyst is used, certain degree of selectivity can be achieved, as demonstrated in the electrochemical reduction of CO₂ to CO on Au[7] (or Ag[8]) or to formate on In[9] (or Sn[10], or Pb[11]). To convert CO₂ to hydrocarbons, especially to C-C hydrocarbons, Cu has to be involved in the catalyst formulations [12-15]. Despite the extensive efforts devoted to both experimental and theoretical studies, the Cu-based catalysts studied for the CO₂ reduction tend to yield a diversity of hydrocarbon products [15-17] and a practical approach to increase Cu catalytic selectivity towards a hydrocarbon molecule is still actively sought-after.

Recent synthetic advances allow monodisperse nanoparticles (NPs) routinely prepared with the desired dimension controls [18]. Consequently, catalytic properties of these NPs can now be better studied to identify catalytically active sites for possible catalysis optimization. For example, the preparation of monodisperse Au NPs enables identification of NP edges as the active sites for the CO₂ conversion to CO [19], which leads to the further tuning and optimization of the Au NP catalysis by developing monodisperse ultrathin (2 nm wide) Au nanowires as the most efficient catalyst for the conversion [20]. When hydrocarbons are the

targeted products, nanostructured Cu should be explored as the catalyst. Earlier studies show that a Cu NP-covered Cu electrode can show a better CO₂ reduction selectivity towards hydrocarbons than an electropolished or an argon-sputtered nanostructured Cu surface [13]. Cu NPs prepared by reducing a micrometer thick Cu₂O film yields a mixture of formate, CO and C₂ hydrocarbons at much lower overpotentials than the untreated counterpart [14]. The reduction catalysis on the Cu NPs is also dependent on NP sizes, surface Cu coordination sites and the adsorption strength of the hydrocarbon products [15]. With the NP control and possible catalysis optimization in mind, in this work, we prepared monodisperse Cu NPs and studied their catalysis for electrochemical reduction of CO₂ in 0.5 M KHCO₃. The Cu NPs deposited on conventional carbon support (or graphene oxide, GO) showed moderate activity to hydrocarbons. But when assembled on the N-doped graphene (NG), they exhibited both N-doping and Cu NP-dependent reduction activity/selectivity. The 7 nm Cu NPs assembled on the pyridinic-N rich G (p-NG) showed the best reduction activity and selectivity to ethylene (C₂H₄): among formate, ethylene, ethane and methane detected, C₂H₄ was present as a major product (19% Faradaic efficiency and 79% ethylene selectivity) at -0.9 V vs. RHE (reversible hydrogen electrode). Our work demonstrates a promising approach to improve Cu NP catalysis for electrochemical reduction of CO₂ to C₂H₄.

2 Experimental Section

2.1 Synthesis of p-NG

2.0 g melamine and 0.4 g single-layered graphene oxide (Graphene supermarket) were mixed in 400 mL deionized water and stirred at room temperature for 48 h. Water was evaporated at 60°C and in a N₂ atmosphere. The solid product was first annealed at 350°C for 0.5 h and then at 900°C for 1 h. After cooled down to room temperature, the powder was ready for further use.

2.2 Synthesis of Cu NPs

In a four-neck flask, a mixture of 0.122 g copper(I) acetate, 0.139 g tetradecylphosphonic acid and 10 mL trioctylamine was stirred and degassed at 130°C under an Ar atmosphere for 30 min. The solution was heated to 180°C and maintained at this temperature for 30 min. The solution was then heated to 250°C in 5 min and held at this temperature for 10 min before cooled down to room temperature. The product was precipitated by adding ethanol and collected by centrifugation (8500 rpm, 8 min). The final product, 7 nm Cu NPs, was dispersed in hexane for further use. To synthesize 13 nm Cu NPs, 0.278 g tetradecylphosphonic acid was used and other processes were the same as those used in the synthesis of 7 nm Cu NPs.

2.3 Preparation of Catalyst and Working Electrode

To prepare p-NG-Cu, 30 mg p-NG was first dispersed in 10 ml isopropanol + 20 ml hexane under ultrasonication for 30 min, and then 30 mg of Cu NPs dispersed in hexane was added dropwise into the dispersion. The mixture was kept sonicated for 1 h. The catalyst was separated by centrifugation and washed with ethanol and DI water. To remove the surfactant, the as-obtained p-NG-Cu catalyst was suspended in 60 mL n-butylamine and stirred for three days under N₂ atmosphere at ambient temperature. The mixture was separated by centrifugation and washed with ethanol and DI water to obtain the final catalyst. The Cu mass loadings in p-NG-Cu-7 at different p-NG/Cu mass ratios were measured to be 39% (1:2), 35% (1:1), 23% (2:1), and 12% (4:1) as analyzed by ICP-AES. The Cu mass loadings in p-NG-Cu-13 were measured to be 39% (1:1), 28% (2:1), and 12% (4:1). GO-Cu (or C-Cu) (mass ratio of 1:1) was prepared similarly. The Cu mass loading in GO-Cu (or C-Cu) was measured to be 36% (or 38%).

To prepare the working electrode, 20 mg of the catalyst was ground with 3 mg of polyvinylidene fluoride (PVDF, as a catalyst binder) and a few drops of N-methyl-2-pyrrolidone

(NMP, as the solvent) to produce catalyst paste. The paste was then painted directly onto the carbon paper ($\sim 0.7\text{ cm} \times 0.7\text{ cm}$) and dried overnight at 60°C in a vacuum-oven.

2.4 Electrochemical Reduction of CO_2

The electrochemical reduction of CO_2 was conducted in a gas-tight two chamber reaction vessel separated by an anion exchange membrane (Nafion[®] 212, Ion Power) on an EC-Lab VSP Ultimate electrochemical workstation (**Figure S1 in Supporting Information**). The experiment was performed in an aqueous 0.5 M KHCO_3 . Micro Ag/AgCl electrode (4.0 M KCl , Pine instrument) was calibrated and used as reference electrode. All potentials were later converted to the RHE scale. A 99.9% platinum wire was used as a counter electrode.

To start the experiment, the reaction system was purged with Ar for 10 min to remove air. The 0.5 M KHCO_3 solution was then saturated with CO_2 via 30 min bubbling of CO_2 ($\text{pH} = 7.3$). In the cathodic compartment, CO_2 gas flow was controlled at 40 ml/min and the solution was stirred at 1000 rpm . The gas product was introduced directly to the gas sample loop of gas chromatograph (Agilent 7890A) for gas analysis. The gas phase composition was analyzed by GC every 30 min with different potential applied. Liquid products were characterized by ^1H NMR on Bruker DRX 400 Avance and 600 Avance MHz spectrometers. ^1H chemical shifts were referenced to residual protic solvent signals. The faradaic efficiency (FE) for the formation of a hydrocarbon was calculated as described [18].

3 Results and Discussion

3.1 Catalyst Synthesis and Characterization

Monodisperse Cu NPs were synthesized by reductive decomposition of copper(I) acetate, CuAc, in trioctylamine and tetradecylphosphonic acid (TDPA) at 250°C [21]. In the synthesis, mixing 1

mmol CuAc with 0.5 mmol TDPA gave 7 nm Cu and reacting 1 mmol CuAc with 1 mmol TDPA produced 13 nm Cu NPs. **Figure 1A&B** show the transmission electron microscopy (TEM) image of the 7 nm (7.4 ± 0.4 nm) (**Figure 1A**) and 13 nm (13.1 ± 0.6 nm) Cu NPs (**Figure 1B**). The representative Cu NPs were further characterized by HRTEM (**Figure 1C&D**). The HRTEM images show the lattice fringes with the inter-fringe distance of 0.21 nm, corresponding to the (111) plane of the face-centered cubic (fcc) Cu. The multiple crystal domains and the surface disordering observed from the images also indicate the as-synthesized NPs are in polycrystalline and the surface Cu may have been oxidized.

NG was synthesized by high-temperature (900°C) pyrolysis of GO and an N-precursor to control N-doping amount and N-binding modes (**Supporting Information**) [22, 23]. We tested three different kinds of N-precursors, ethylenediamine (EDA), melamine (MA), and polyaniline (PANI) and found the GO + MA combination was especially effective for the production of pyridinic-N with the highest pyridinic-N/graphitic-N ratio among three samples (**Figure S2 and S3** in **Supporting Information**). The powder product (**Figure S2B** in **Supporting Information**) was dispersible in isopropanol and could be deposited on the carbon-coated copper grid for TEM image (**Figure S2C** in **Supporting Information**). Both SEM and TEM images show that graphitic sheets are formed after the pyrolysis reaction. The pyridine-rich-binding modes in p-NG was characterized by high resolution N 1s X-ray photoelectron spectroscopy (XPS) (**Figure S2D** in **Supporting Information**). The pyridinic N (~2.9 wt%) is at 398.3 eV while the graphitic N (~1.6 wt%) at 400.8 eV and the pyrrolic N (~0.9 wt%) at 399.3 eV [22]. The XPS analysis further shows (**Table S1** and **Figure S4** in **Supporting Information**) that the p-NG contains C, N, O elements, and the N mass content is calculated to be 5.4 wt%. NG's prepared from the

pyrolysis of GO + EDA and GO + PANI did not yield high ratio of pyridinic-N in the NG structure (**Figure S3 in Supporting Information**).

The Cu NPs were assembled on the p-NG (at a mass ratio of 1:1) by mixing the hexane dispersion of Cu NPs and the solution of NG sheets in hexane + isopropanol (v:v 2:1) under sonication, and the p-NG-Cu was activated by n-butylamine/ethanol/water washing (see the **Supporting Information**). TEM images (**Figure 2**) indicate that the NPs are well dispersed on the p-NG surface. X-ray diffraction (XRD) patterns of the p-NG-Cu NPs (**Figure S5 in Supporting Information**) show much broader (111) peak than that expected from the single crystalline Cu NPs and the presence of Cu₂O phase, further confirming the HRTEM analysis that the NPs are in polycrystalline structure and the surface Cu is oxidized. TEM images of the 7 nm Cu NPs deposited on p-NG at different mass ratios are given in **Figure S6A-C in Supporting Information**. The Cu NPs were also deposited on the conventional carbon support (Ketjen EC-300J), denoted as C-Cu (**Figure S6D in Supporting Information**) or pristine GO, denoted as GO-Cu (**Figure S6E**), and were used as controls. The NP sample (20 mg p-NG-Cu) was grounded with PVDF and NMP and then painted directly onto the carbon paper for electrochemical studies (**Experimental Section**).

3.2 Electrochemical Reduction of CO₂

The redox properties of the 7 nm Cu NPs in the p-NG-Cu, denoted as p-NG-Cu-7, was first studied by cyclic voltammetry (CV) in the Ar-saturated 0.5 M KHCO₃. From the cyclic voltammogram (**Figure 3A**), we can see that the p-NG-Cu-7 shows one anodic peak at 0.80 V due to the oxidation of Cu and two cathodic peaks that correspond to the reduction of CuO to Cu₂O (at 0.46 V) and Cu₂O to Cu (at 0.15 V) [13]. The linear sweep voltammetry (LSV) scans in the Ar- or CO₂-saturated 0.5 M KHCO₃ were measured and compared (**Figure 3B**). The higher

current observed in the CO₂-saturated 0.5 M KHCO₃ indicates that the presence of Cu NPs on p-NG promotes CO₂ reduction and conversion.

The reaction products collected at a constant reduction potential were analyzed and their formation FE's were summarized in **Figure 4A** (for the p-NG-Cu-7 catalyst) and **Figure 5** (for the C-Cu-7 and GO-Cu-7 catalysts). The electrolysis produces H₂ and hydrocarbons but no CO in the studied potential range. In potential range from -0.8 to -1.1 V, the C-Cu-7 catalyst generates C₂H₄ (maximum FE 6.3% at -1.1 V) and C₂H₆ (maximum FE 3.6% at -1.1 V), the GO-Cu-7 gives CH₄ (maximum FE 3.9% at -1.1 V) and C₂H₄ (maximum FE 7.5% at -1.1 V). When reducing CO₂ on p-NG-Cu-7 at -0.8 V, formate (FE 62%) and C₂H₄ (FE 1.4%) are initially detected (**Figure 4B**). At more negative potentials, C₂H₄ is predominately formed and the formate generation is suppressed. The FE for the C₂H₄ formation reaches 19% at -0.9 V, where other hydrocarbons (3.8% formate, 0.9% CH₄ and 0.6% C₂H₆) are also observed but the total FE is less than 5.3% (**Figure 4C**). Among all hydrocarbons produced on the p-NG-Cu-7 at -0.9 V, C₂H₄ selectivity is 79%. When normalized against the Cu mass (obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES)), the p-NG-Cu-7 has a C₂H₄ formation mass activity of 2.9 A/g_{Cu}, much higher than that from the GO-Cu-7 and C-Cu-7 (**Figure 4D**). Our p-NG-Cu-7 is also very different from all other Cu-based catalysts and achieves much higher selectivity on formate at -0.8 V and C₂H₄ from -0.9 V to -1.1 V (**Figure 4E**). These results demonstrate that the p-NG as a support enhances significantly the Cu NP catalyst selectivity toward C₂H₄ at -0.9 V or more negative potentials.

To understand the p-NG effect on Cu NP catalysis for the CO₂ reduction, we studied the pure p-NG as the catalyst for the CO₂ reduction. LSV scans in the Ar- or CO₂- saturated 0.5 M KHCO₃ solution were measured and compared (**Figure S7 in Supporting Information**). When

analyzing the reduction products, we found that the presence of p-NG led to the formation of formate and H₂ (As a comparison, the reduction in the presence of GO only yielded H₂). FE's for the formate formation at different reduction potentials were plotted in **Figure 6A**. The p-NG catalyst has an onset potential of -0.7 V (10% FE) and a maximal formate formation FE of 65% at -0.90 V (100% selectivity). Its reduction mass activity at a given reduction potential was also calculated and plotted (**Figure 6B**), in which we can see that its mass activity increases linearly with the reduction potentials, reaching 7.7 A/g at -0.9 V and 19.0 A/g at -1.2 V. When the potential was set at -0.9 V, the FE for the formate formation was quickly increased, reaching 65% level within ~ 0.5 h. The FE value was stabilized at ~60% in the 12 h electrolysis period (**Figure 6C**). NG's prepared without high enough amount of pyridinic-N in the NG network (GO + EDA and GO + PANI) had much lower FE's (< 25%) and mass activity (< 1.3 A/g) for the formate formation in the same reduction potential range studied (**Figure S8 in Supporting Information**). These results suggest that pyridinic-N favors the CO₂ activation and reduction to formate.

3.3 Possible Reduction Mechanisms

Pyridinic-N is formed when N replaces C at the terminal end of the C₆-ring in the graphitic plane, leaving a localized electron pair pointing 120° away from two N-C σ bonds and perpendicular to the graphitic π -network. In contrast, both graphitic and pyrrolic N have their p-electrons fully conjugated with the graphitic π -network and do not have such a localized electron pair. As a result, the p-NG should have a stronger Lewis basicity for its binding to proton and CO₂, facilitating CO₂ interaction with the catalyst and reduction. The CO₂ activation and reduction on the p-NG was studied by Tafel plot. The applied reduction potential is linear to the logarithm of the formate formation current density (**Figure 6D**). The slope of 106 mV/dec is close to the 118

mV/dec expected for rate-limiting single-electron transfer process [24]. This indicates that the first step one-electron reduction of CO₂ to CO₂^{•-} anion radical is the rate-determining step and the presence of more pyridinic-N's in the p-NG structure facilitates CO₂ adsorption and one-electron reduction that is followed by protonation to give COOH* (asterisk denotes a surface-bound species) [25]. The COOH* can undergo a second protonation on the C-end to yield formic acid (formate in the KHCO₃ solution), or on the O-end followed by dehydration to give CO [26]. We did not detect CO in the reduction reaction, indicating that the p-NG promotes COOH* protonation on C, not on OH, for selective formation of HCOOH.

When Cu NPs are attached to p-NG, the COOH* formed around p-NG may be subject to next step protonation and dehydration to CO* on Cu, which would be further protonated to CH_xO* (x = 1-3) and finally converted to hydrocarbons, including C₂H₄ [26-30]. The possible reaction steps leading to the formation of C₂H₄ have been proposed previously and are summarized below:

where the asterisk (*) denotes either a surface-bound species or a vacant catalytically active site. To form C₂H₄, the COOH* generated at step 1 should first be converted to CO* via reductive protonation and dehydration (step 2). The adsorbed CO undergoes further hydrogenations, giving CH_xO* (step 3), which are the essential intermediates for the formation hydrocarbons. C₂H₄ is formed by C-C coupling via the proposed step 4 and/or 4' [27]. For the p-NG-Cu-7 catalyst, the

enhanced catalysis for the formation of C_2H_4 at -0.9 V at the expense of formate formation arises likely from the synergistic effect between p-NG and Cu NPs: the presence of Lewis base in the p-NG structure helps to concentrate more proton/hydrogen around Cu, thus facilitating the conversion of $COOH^*$ to CO^* , CH_xO^* and C-C coupling to C_2H_4 .

3.4 p-NG/Cu Mass Ratio and NP Size Effects

The synergistic effect observed above was further supported by the reduction catalysis of the p-NG-Cu-7 of different mass ratios of 1:2, 2:1, and 4:1 (**Figure 7**). Compared with the same p-NG-Cu with 1:1 ratio, these catalysts were active for the formation of formate at -0.8 V, but their activity towards C_2H_4 was decreased (maximum FE ~10%). For the p-NG-Cu-7 (1:2), Cu NPs are not well dispersed on p-NG (**Figure S6A in Supporting Information**) due probably to the overloading of the NPs. The aggregation of Cu NPs may lower their surface area and weaken the p-NG-Cu interaction. For the p-NG-Cu-7 (4:1), the amount of Cu NPs is not enough to cover the p-N-binding sites. Therefore, the catalytic activity towards formate is affected only slightly but the activity towards C_2H_4 is reduced. From these experiments, we can see that the p-NG-Cu-7 (1:1) is the optimal composite for catalytic reduction of CO_2 to C_2H_4 (**Figure 7D**). The synergistic effect between p-NG and Cu is maximized at -0.9 V where the formation of formate is greatly suppressed while C_2H_4 formation is enhanced.

We also tested the p-NG-Cu-13 (13 nm Cu NPs) on the CO_2 reduction reaction (**Figure S9 in Supporting Information**). In this case, the synergistic effect between p-NG and 13 nm Cu NPs is observed more obviously on p-NG-Cu-13 (2:1) catalyst (**Figure 8A,B**), from which the generation of formate is suppressed from -0.9 V to -1.1 V while the formation of C_2H_4 is enhanced compared to that on C-Cu-13 (**Figure 8D**). However, compared with p-NG-Cu-7 (1:1), the maximum FE for C_2H_4 formation on p-NG-Cu-13 (2:1) catalyst (13%) is lower and appears

at more negative potential (-1.1 V) (**Figure 8B**). We attribute this lower activity/selectivity of the 13 nm Cu NPs to their larger size and reduced p-NG-Cu interactions. To show the synergistic effect, the Cu NPs need to bind to (or stay close to) the p-N-binding sites. Due to the limited pore (void) area present around each p-N unit in the NG structure, larger Cu NPs may limit their ability to reach the p-N sites and therefore reduce their catalysis synergy with the p-N sites. On the other hand, if more p-N sites are made available in such as p-NG-Cu-13 (4:1) (**Figure 8C**), the catalytic role of the p-NG is evident and formate is selectively formed. This further proves that 13 nm Cu NPs are prone to attach to the general G plane, not the p-N sites. As a control, the C-Cu-13 is only slightly active for the C_2H_4 formation but is not active at all for the formate formation (**Figure 8D**).

4 Conclusions

In summary, we have reported a new approach to enhance Cu NP catalysis for electrochemical reduction of CO_2 to C_2H_4 in 0.5 M $KHCO_3$ by assembling Cu NPs on p-NG. Monodisperse Cu NPs are prepared by reductive decomposition of CuAc in trioctylamine and tetradecylphosphonic acid at 250°C, and p-NG is synthesized by high-temperature (900°C) pyrolysis of graphene oxide and melamine. The electrochemical reduction of CO_2 on the pure p-NG yields formate (65% FE and 100% hydrocarbon selectivity at -0.9 V). When monodisperse 7 nm Cu NPs are assembled on the p-NG at the mass ratio of 1:1, the p-NG-Cu catalyzes the reduction of CO_2 to formate (62% FE, 97% hydrocarbon selectivity) at -0.8 V but to C_2H_4 (19% FE, 2.9 A/g_{Cu} mass activity, and 79% hydrocarbon selectivity over other hydrocarbons) at -0.9 V, achieving much superior selectivity towards C_2H_4 than any other Cu-catalysts reported previously. Our data show that the combination of p-N in the p-NG and Cu NPs of a proper size (7 nm in this work) facilitates CO_2 reduction, hydrogenation and C-C coupling for the formation

of C₂H₄. The reported synthesis and assembly offers a general approach to a new class of p-NG-NP catalysts for the electrochemical reduction of CO₂ with much enhanced activity and selectivity.

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Appendix A. Supporting Information

Experimental details, Figure S1-S9. This material can be found in the online version at

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Figure 1. TEM images of monodisperse 7 nm (A) and 13 nm Cu NPs (B). HRTEM images of a representative 7 nm (C) and 13 nm Cu NP (D).

Figure 2. TEM images of (A) p-NG-Cu-7 and (B) p-NG-Cu-13 catalysts after Cu NP assembly on the p-NG and n-butylamine/ethanol/water washing to remove capping agents for electrochemical reduction of CO₂.

Figure 3. (A) Cyclic voltammogram of the p-NG-Cu-7 (1:1) in Ar-saturated 0.5 M KHCO_3 aqueous solution, scan rate = 100 mV/s. (B) LSV scans in the presence of the p-NG-Cu-7 (1:1) catalyst in Ar- or CO_2 -saturated 0.5 M KHCO_3 aqueous solution, scan rate = 5 mV/s.

Figure 4. (A) Reduction potential dependent FE's of the p-NG-Cu-7 catalyzed electrochemical reduction of CO_2 to various hydrocarbons. (B, C) Product selectivity of the hydrocarbons generated from the p-NG-Cu-7 catalyzed reduction at (B) -0.8 V and (C) -0.9 V. (D) Comparison of mass activity of the p-NG-Cu-7, C-Cu-7, and GO-Cu-7 catalyzed reduction of CO_2 to C_2H_4 at various reduction potentials. (E) Selectivity of C_2H_4 and all other hydrocarbons generated from the p-NG-Cu-7 catalyzed reduction of CO_2 at various potentials.

Figure 5. FE of (A) C-Cu-7 (1:1) and (B) GO-Cu-7 (1:1) catalysts for electrochemical reduction of CO₂ to various hydrocarbons.

Figure 6. (A) FE of p-NG and pristine GO for their electrochemical reduction of CO₂. (B) Reduction potential dependent mass activity of the p-NG for formate production. (C) Reduction time dependent FE for the formation of formate at -0.9 V. (D) The Tafel plot for the electrocatalysis of the p-NG. The experimental data are fitted linearly with the slope at 106 mV/dec.

Figure 7. (A-C) Reduction potential dependent FE's for electrochemical reduction of CO₂ measured on p-NG-Cu-7 catalysts with different p-NG/Cu mass ratios. (D) Dependence of FE for C₂H₄ formation at -0.9 V on the p-NG/Cu mass ratio of p-NG-Cu-7 catalysts.

Figure 8. (A-C) Reduction potential dependent FE's for electrochemical reduction of CO₂ measured on p-NG-Cu-13 catalysts with different p-NG/Cu mass ratios. (D) FE of C-Cu-13 catalyst for electrochemical reduction of CO₂ to various hydrocarbons.