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Supporting Information

Highly Selective Electrochemical Reduction of CO_2 to Formate on Metal-Free Nitrogen-Doped PC61BM

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Experimental section

Preparation of N-doped PC61BM (N-C61). The commercially available [6, 6]-Phenyl-C61-Butyric Acid Methyl Ester (PC61BM, 99%, denoted as C61) powder was purchased from Sigma-Aldrich, and without any further pretreatment before used. In a typical preparation of N-C61 electrocatalyst, 50 mg of PC61BM powder (C precursor) was mixed with 2.0 g of urea (N precursor) and then grounded together in an agate mortar for about 30 min to form a homogeneous precursor. Subsequently, the obtained homogeneous powder was pyrolyzed at six different temperatures of 500, 600, 700, 800, 900, and 1000 °C for 1 h in the tube furnace under a high purity argon (99.999%) atmosphere (gas flow rate of 150 sccm, heating rate of 2 °C min^{-1}). These six kinds of N-C61 electrocatalysts are denoted as N-C61-500, N-C61-600, N-C61-700, N-C61-800, N-C61-900, and N-C61-1000, respectively.

Preparation of working electrodes. The substrate electrode was fabricated by carbon cloth (1×1 cm), which was sonicated in hydrochloric acid (5 M), acetone and deionized water for 15 min, respectively. Typically, N-C61 powder (2.0 mg) was dispersed in Nafion perfluorinated resin solution (5 wt.%, 50 μL) and isopropanol (250 μL) by ultrasonication for 30 min to form the homogeneous catalyst ink. Subsequently, the catalyst ink was sprayed onto the carbon cloth substrate electrode, and then the obtained composite electrodes were vacuum dried for 12 h (45 °C). Finally, the working electrode with a uniform catalyst loading of 1 ± 0.1 mg cm^{-1} was achieved. The pristine C61 working electrode was prepared by the same procedures as the N-C61/ carbon cloth composite electrodes.

Electrochemical experiments. All the electrochemical experiments were carried out in a gas-tight H-cell, which was separated by a Nafion N117 membrane. N-C61/carbon cloth and pristine C61/carbon cloth composite electrodes were used as the working electrodes. The Ag/AgCl (saturated KCl) and Pt plate (1×1cm) served as the reference and counter electrodes, respectively. Electrochemical data were recorded on a CHI660E electrochemical workstation. Before each experiment, CO_2 (99.999%) was continuously bubbled into the cathodic compartment of the H-cell for 30 minutes to eliminate O_2 from electrolyte and saturate the electrolyte with CO_2. The current density (j) was normalized to the geometrical area of the working electrode (1 cm^2). The electrochemical experiments were measured at room temperature (25 ± 3 °C), and all potentials reported in this paper are referenced to reversible hydrogen electrode (RHE, $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.0591 \times pH$). The pH of CO_2-saturated 0.5 M $KHCO_3$

electrolyte is 7.33 in this paper.

Cyclic voltammetry (CV) was carried out in CO_2-s aturated or N_2-saturated 0.5 M $KHCO_3$ electrolyte with a scan rate of 50 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was recorded at -1.0 V in CO_2-saturated 0.5 M $KHCO_3$ electrolyte with an amplitude of 5 mV. The frequency range is from 0.1 Hz to 100000 Hz. Tafel plot (overpotential versus log j_{HCOO^-}) was derived from the controlled potential electrolysis results (Figure 4c). Electroreduction of CO_2 was investigated for 30 min at each applied potential by the controlled potential electrolysis method. Prior to each new electrocatalyst test, 50 cycles of CV were used to activate the electrodes.

Characterization and analysis. Scanning electron microscopy (SEM) images were obtained from the Hitachi S-4800 high-resolution electron microscope. Transmission electron microscopy (TEM) were performed on a Tecnai G2 20 transmission electron microscopy operated at 200 kV. X-ray photoelectron spectroscopy (XPS) were recorded on a PHI Quantera SXM spectrometer. All the binding energy corresponds to the standard C1s peak at 284.8 eV in this experiment. Raman spectra were collected by a Renishaw inVia Raman microscope with a REM Laser at wavelength of 532 nm.

The concentration of gaseous samples was measured by gas chromatography (GC, Inficon S3 Micro 3000 GC), which is equipped with the flame ionization detector (FID) and the thermal conductivity detector (TCD) detectors. Gases were collected by air bags during the electrolysis process firstly and then injected into the GC by a gas-tight syringe (1 ml). The hydrogen concentration was analyzed by the TCD detector.

Liquid phase products were quantified by a high performance liquid chromatography (HPLC, Agilent 1200) with Aminex HPX-87H Ion Exclusion columns.

Faradaic efficiency (η) of fomate production was achieved by the formula:

$$\eta = 2nF / Q$$

where η is Faradaic efficiency of formate; 2 represents the number of electrons required to form formate from CO_2; n represents the total number of moles of formate formation, which was measured by HPLC; F represents Faraday constant (96485); and the Q corresponds to the amount of cumulative charge in the process of CO_2 reduction, which was provided by the electrochemical workstation.

Supplementary Figures

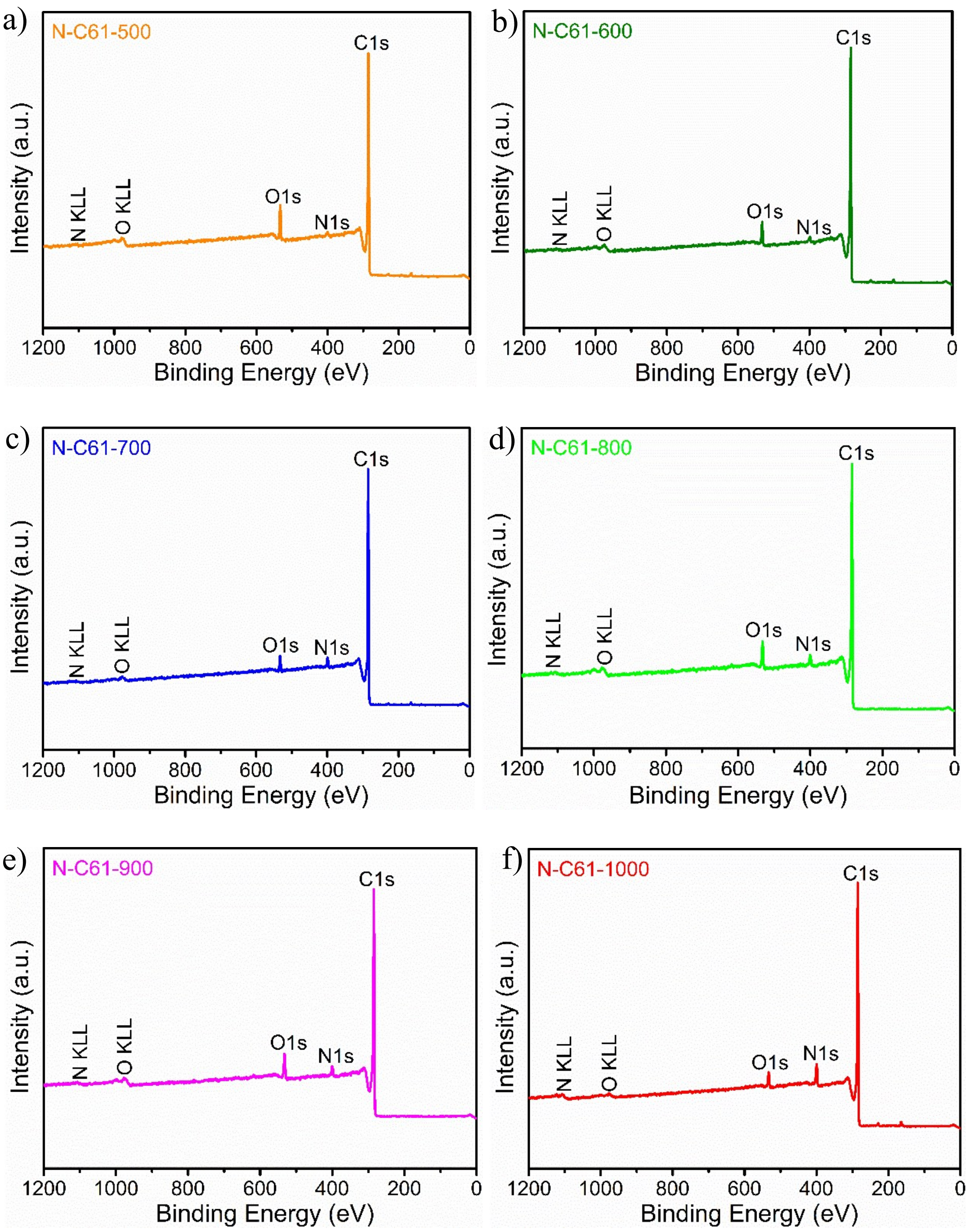

Figure S1. The survey XPS spectra for N-C61 electrocatalysts. N-C61-500 (a). N-C61-600 (b). N-C61-700 (c). N-C61-800 (d). N-C61-900 (e). N-C61-1000 (f).

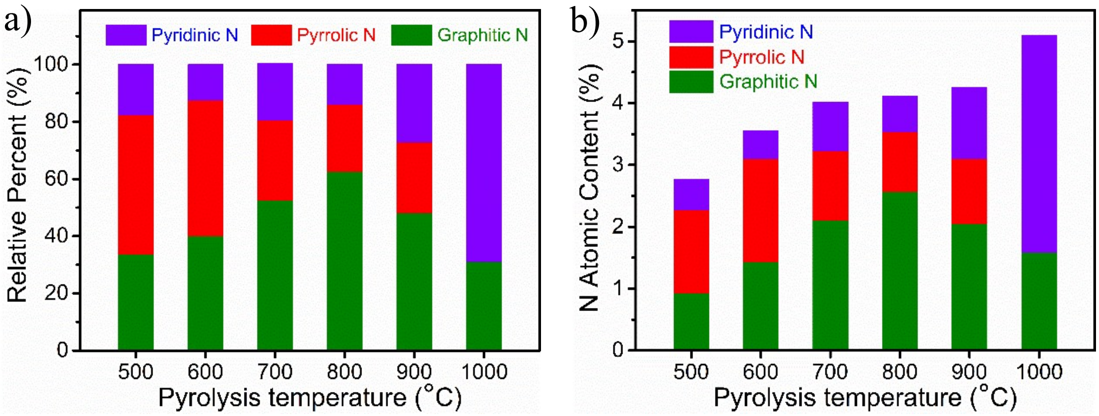

Figure S2. Relative percentage (a) and atomic content (b) of the three types N-defects in N-C61 electrocatalysts at different pyrolysis temperature.

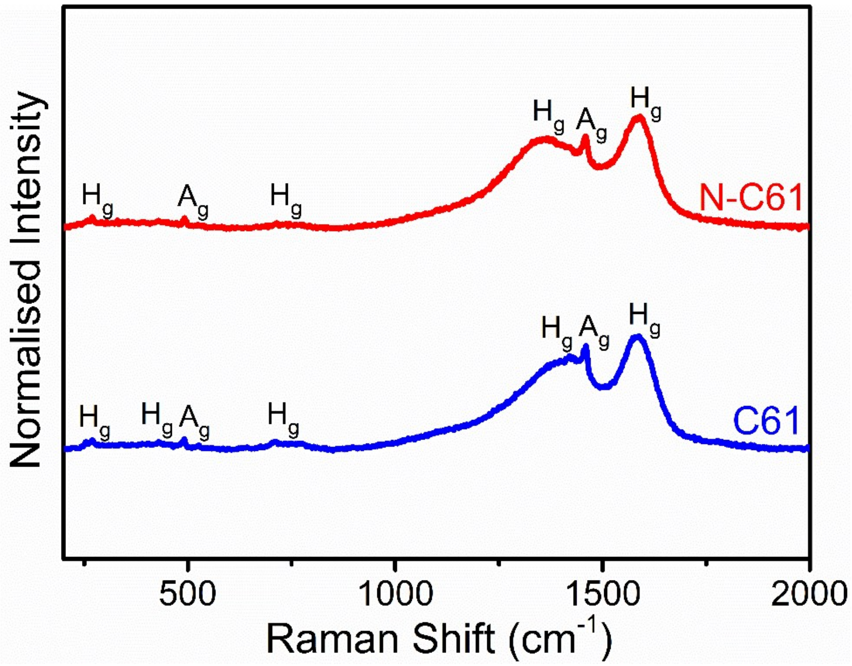

Figure S3. Raman spectra of pristine C61 and N-C61-800 electrocatalysts.

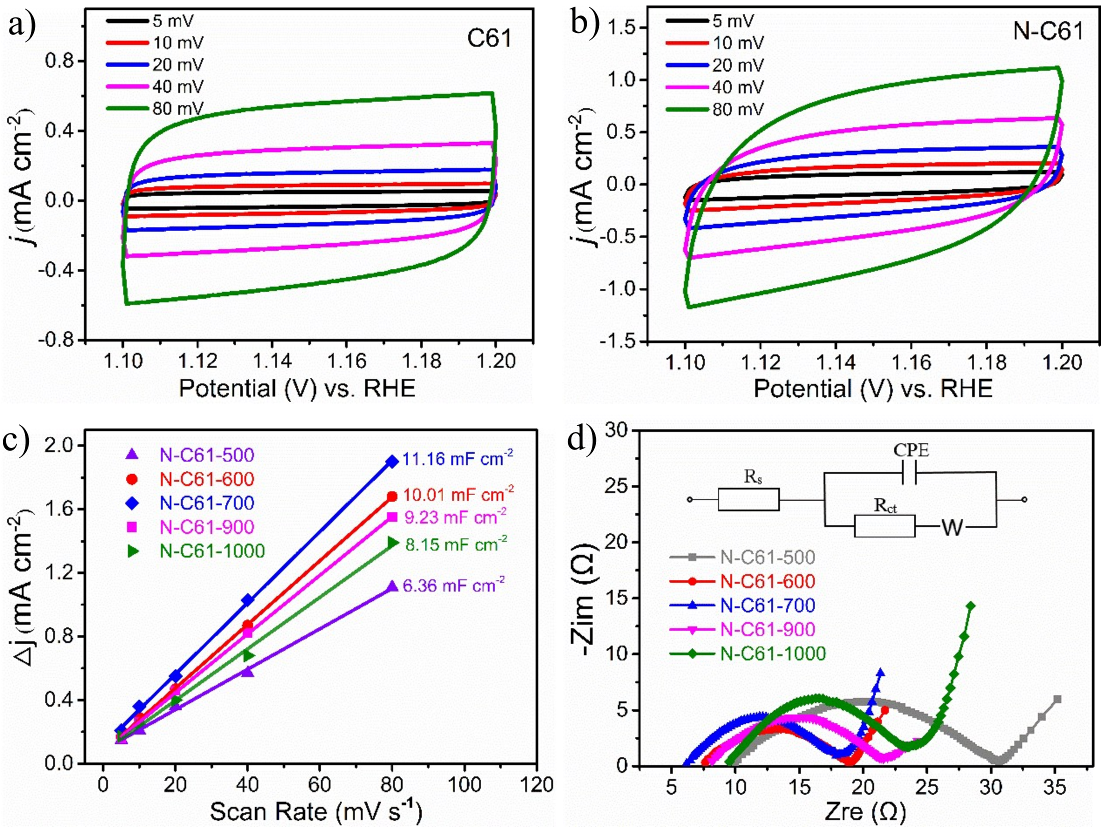

Figure S4. CVs at the range of 1.1 to 1.2 V with different scan rates (5, 10, 20, 40 and 80 mV·s^{-1}) of C61 (a), N-C61-800 (b). Variations of ΔJ (Ja- Jc) for N-C61-500, N-C61-600, N-C61-700, N-C61-900, and N-C61-1000 with the scan rates (c). The Nyquist diagrams and fitting equivalent circuit of the N-C61-500, N-C61-600, N-C61-700, N-C61-900, and N-C61-1000 (d).

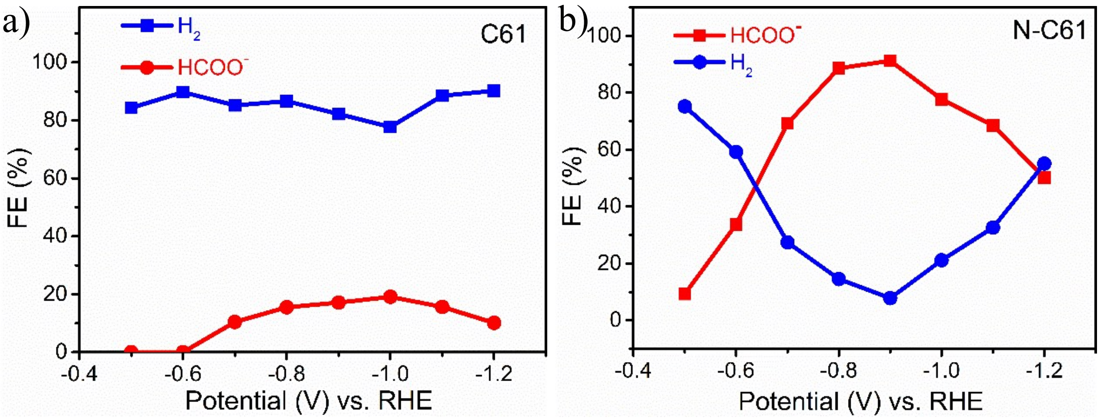

Figure S5. FEs of all reduction products (formate and H_2) versus the electrolysis potentials for the C61 (a) and N-C61-800 (b).

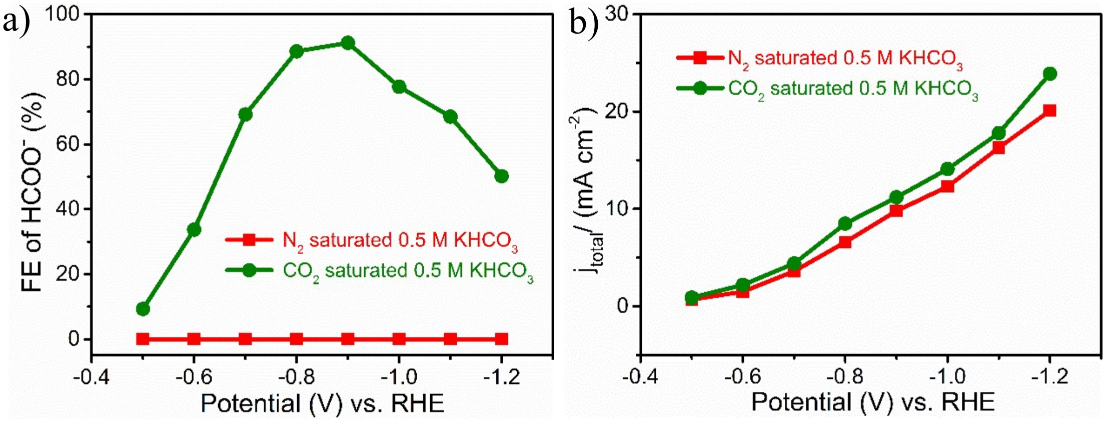

Figure S6. Comparison of the formate FE (a) and total current density (b) for N-C61-800 in the N_2 and CO_2 saturated 0.5 M $KHCO_3$, respectively.

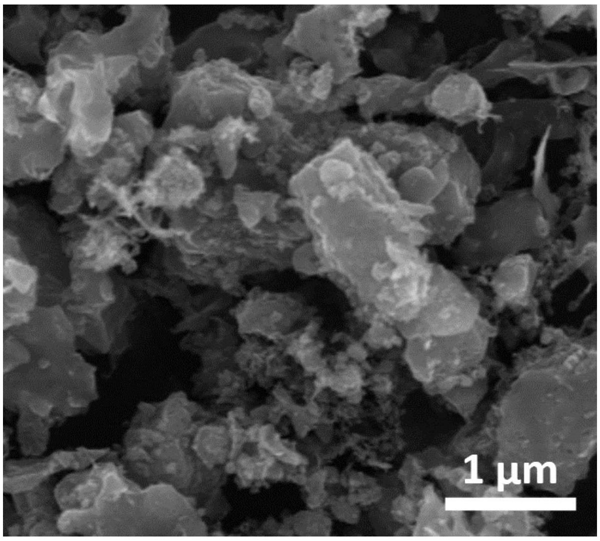

Figure S7. SEM image of N-C61-800 after long-term electrolysis experiments.

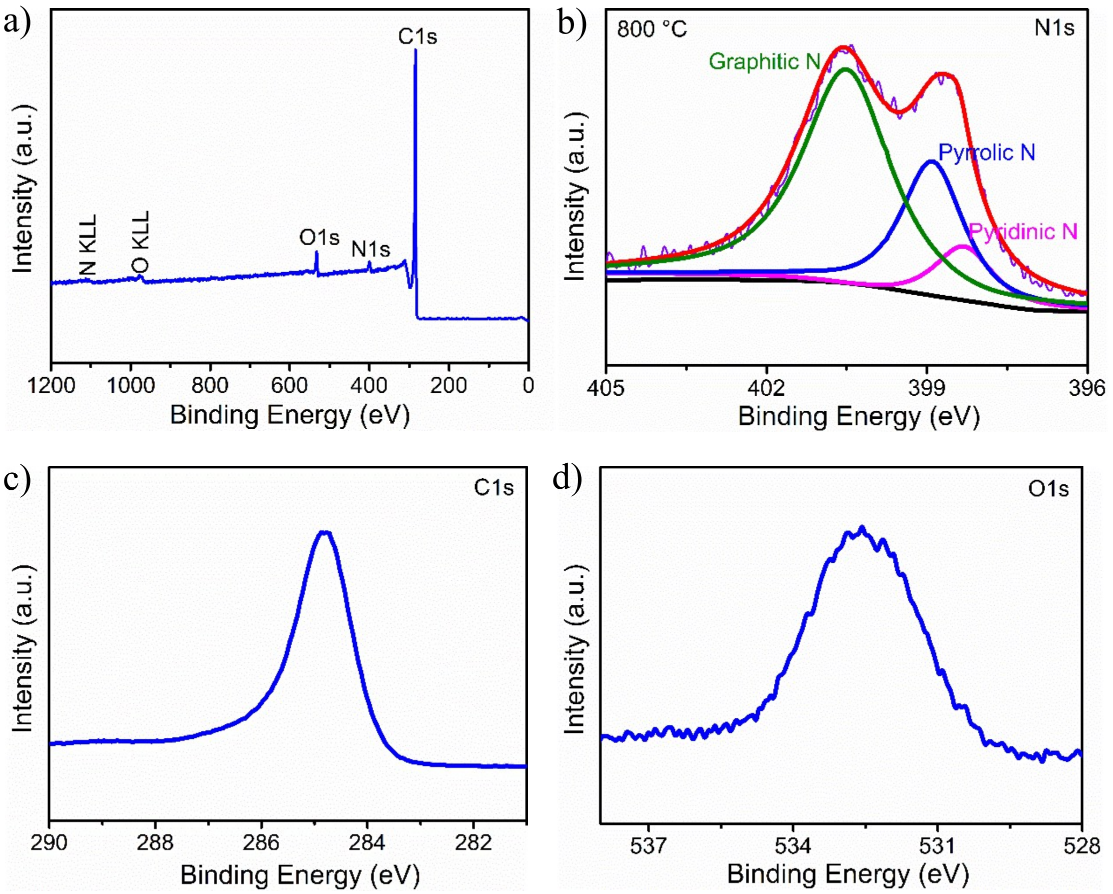

Figure S8. The XPS spectra for N-C61-800 after long-term electrolysis experiments. Survey XPS spectrum (a). High-resolution N1s spectrum, the respective atomic content of graphitic, pyrrolic, and pyridinic N is 2.39%, 1.11%, and 0.46% (b). C1s peak (c). O1s peak (d).

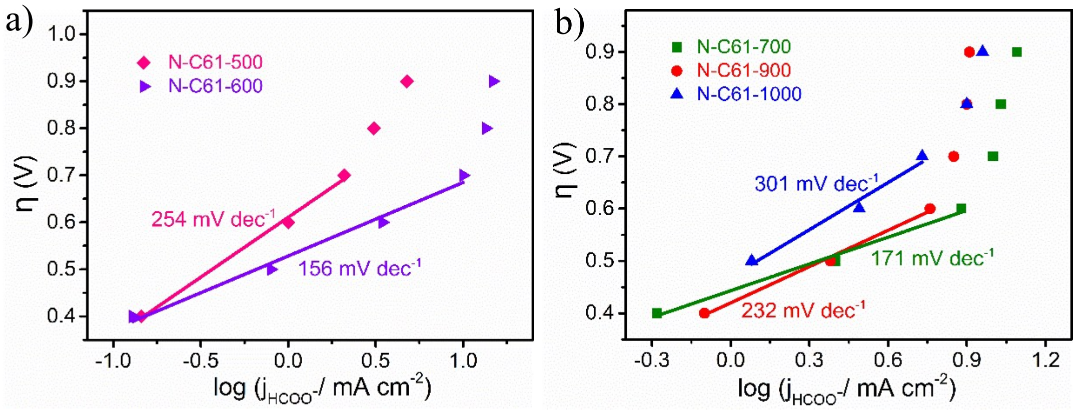

Figure S9. Tafel plots for N-C61-500 and N-C61-600 (a), N-C61-700, N-C61-900, and N-C61-1000 (b).

Supplementary Tables

Table S1. The fitting values of EIS equivalent circuit

Electrocatalysts	R_s /Ω	R_{ct} /Ω
C61	10.1	15.8
N- C61-500	10.0	22.1
N- C61-600	7.6	12.3
N- C61-700	6.3	11.6
N- C61-800	7.1	9.2
N- C61-900	8.2	14.3
N- C61-1000	9.5	15.4

Table S2. Comparison of electrocatalytic activity for electrochemical reduction of CO_2 to formate on prevalent metal-free electrocatalysts.

Electrocatalyst	Applied potential vs. RHE	FEs of Formate (%)	Current density (mA cm^{-2})	Refs.
B-graphene	–0.73 V	66	2.0	1
N-graphene	–0.84 V	73	7.5	2
HNCM/CNT	–0.80 V	81	11.0	3
PEI-NCNT	–1.13 V	87	9.5	4
N-C61-800	–0.90 V	91	11.6	This work

References

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