Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Nitrogen-Doped Graphenes as Efficient Electrocatalysts for Selective Reduction of Carbon Dioxide to Formate in Aqueous Solution

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Contents:

Materials.

All chemicals were purchased from commercial sources if not mentioned otherwise. Melamine, graphene oxide (dispersion in water), potassium bicarbonate (≥99.99%), nafion perfluorinated resin solution and isoproponal were purchased from Sigma Aldrich. Water was deionized and further purified by using a Milli-Q water purification system (Milli Q, Millipore, Barnstead, CA, USA). All reagents used as received without further purification.

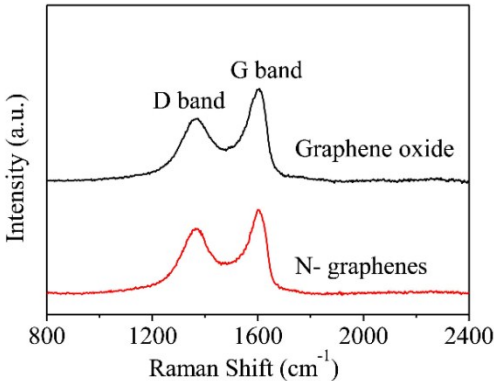

Figure S1. Raman spectra of as-received Graphene oxide and N-graphenes. The ratio of D band over G band increased and their peak positions negatively shifted. Both are the indicative of the successful nitrogen doping.

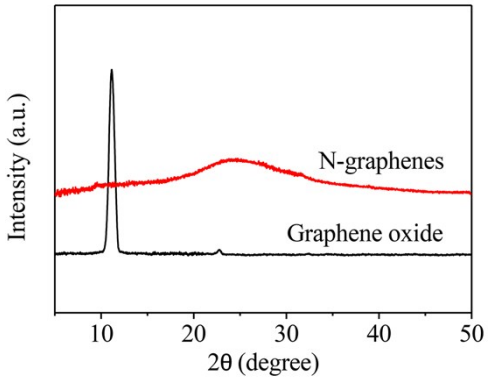

Figure S2. PXRD patterns of as-received Graphene oxide and N-graphenes.

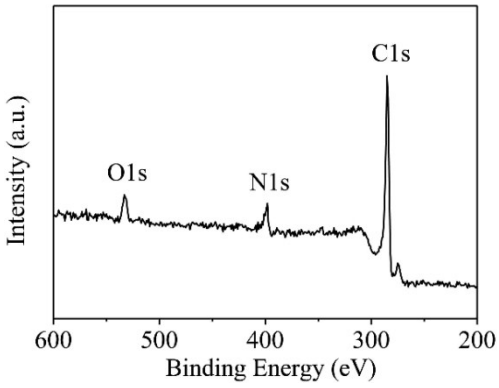

Figure S3. XPS survey spectrum for N-graphenes.

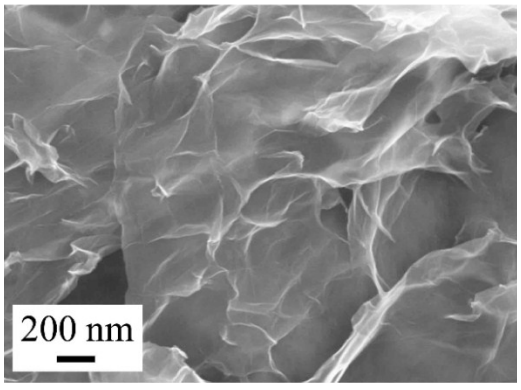

Figure S4. SEM images of N-graphenes/carbon paper after controlled potential electrolysis, reflecting that there was no noticeable change in the morphology of N-graphenes/carbon paper with respect to the initial sample.

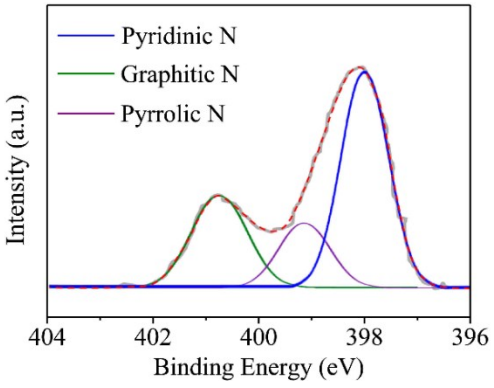

Figure S5. The XPS of N 1s for N-graphenes after long-term controlled potential electrolysis. The N 1s is deconvoluted into three peaks representing three different N functionalities.

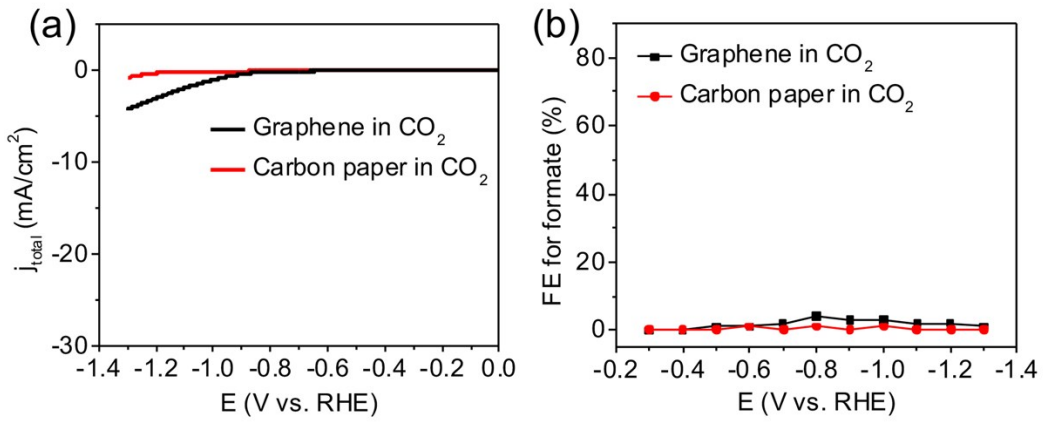

Figure S6. (a) 15 mV/s LSV scans for Graphene and Carbon paper in CO_2-saturated 0.5 M $KHCO_3$; (b) Dependence of FEs of formate on applied potential within electrocatalytic reduction of CO_2 for Graphene and Carbon paper.

Table S1. The summary of Tafel relationship for formate production on N-graphenes.

	Overpotential (η)	Transfer coefficient (α)
N-graphenes	$\eta = E\text{-}E_0 = b*\log i_0 - b*\log i_{formate}$ (1)	$\alpha = 2.3RT/bF$ (2)

Tafel plot data were collected in 0.5 M $KHCO_3/CO_2$ aqueous solution. The Tafel relationship for formate production can be derived as Equation 1 and 2,[S1] where E is the applied potential, E_0 is the equilibrium potential (−0.06 V vs RHE for the $CO_2/HCOO^-$ couple) in pH 7.3 aqueous solution, η is the overpotential for $CO_2/HCOO^-$ couple, b is the Tafel slope, α is transfer coefficient, i_0 is the exchange current density, and $i_{formate}$ is the partial current density for formate production within CO_2 reduction.

Reference

[S1] Gileadi, E. Electrode kinetics for chemists, chemical engineers, and materials scientists, Capstone, **1993**.