Pyridinic-N-Doped Graphene Paper from Perforated Graphene Oxide for Efficient Oxygen Reduction

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ABSTRACT: We report a simple approach to fabricate a pyridinic-N-doped graphene film (N-pGF) without high-temperature heat treatment from perforated graphene oxide (pGO). pGO is produced by a short etching treatment with hydrogen peroxide. GO perforation predominated in a short etching time (∼1 h), inducing larger holes and defects compared to pristine GO. The pGO is advantageous to the formation of a pyridinic N-doped graphene because of strong NH$_3$ adsorption on vacancies with oxygen functional groups during the nitrogen-doping process, and the pyridinic-N-doped graphene exhibits good electrocatalytic activity for oxygen reduction reaction (ORR). Using rotating-disk electrode measurements, we confirm that N-pGF undergoes a four-electron-transfer process during the ORR in alkaline and acidic media by possessing sufficient diffusion pathways and readily available ORR active sites for efficient mass transport. A comparison between Pt/N-pGF and commercial Pt/C shows that Pt/N-pGF has superior performance, based on its more positive onset potential and higher limiting diffusion current at ∼0.5 V.

INTRODUCTION

With increasing demand for environmentally friendly and renewable energy, the generation and storage of clean energy have become a major concern.1–3 Electrocatalysts are important components of promising clean energy technologies such as fuel cells, metal–air batteries, and renewable energy.4–11 The oxygen reduction reaction (ORR) is a key step for clean energy technologies. Various materials including metal oxides,3,4,7,9 heteroatom-doped carbon nanotubes,12–16 few-layer graphene nanosheets,14,15,17–22 and graphene nanoribbons15,24 have been used to promote the ORR in alkaline solutions. To improve their electrocatalytic ORR performance, similar atomic-sized N atoms are used to dope the carbon networks of graphene-based materials, with the resultant lone pair electronic structure, facilitating reductive O$_2$ adsorption.17,25,26 Thus, N-doped graphene is a promising alternative to high-cost Pt, which is currently the best ORR catalyst.

The hybridization of the nitrogen atoms in graphitic networks is a central factor that determines the unique electrocatalytic activity of N-doped graphene for the ORR. Recent studies have shown that the electrocatalytic activity of N-doped graphene depends on the presence of pyridinic N (N bonded to two carbon atoms) or graphitic N (N bonded to three carbon atoms).26–28 Pyridinic N atoms especially facilitate electron transfer from the electronic bands of carbon in the graphitic lattice to the antibonding orbitals of O$_2$.12,20,30 Very recently, Guo et al. reported that the ORR active sites are carbon atoms next to pyridinic N by designing model graphite catalysts consisting of pyridinic-N-dominated highly oriented pyrolytic graphite (HOPG) and graphitic N-dominated HOPG.20 The development of facile methods for the synthesis of pyridinic-N-doped graphene rich in ORR active sites is a major research topic in the field of high-performance ORR catalysts, which necessarily includes the important feature of favorable reactants’ and products’ access to the active sites. However, most of the reported methods for N-doping have required the heat treatment of between 600 and 1100 °C11,17–19 or have high cost,18 which have drawbacks for large-scale production.

Here, we report a facile and scalable approach without high-temperature heat treatment to the large-scale production of N-doped graphene, which has pyridinic-N-dominated catalytic
sites for ORR. The pyridinic-N-doped graphene film (N-pGF) was prepared from perforated graphene oxide (pGO) at low temperature below 100 °C, which provided high ORR active sites and sufficient diffusion pathways. Electrochemical measurements showed that the pyridinic N endowed the material with a high degree of electrocatalytic activity.

**RESULT AND DISCUSSION**

Graphene etching treatments with H₂O₂ eventually cause graphene to fracture into small pieces, and the etching reaction time determines the lateral size and perforated structure of the graphene fragments. The control GO that did not undergo H₂O₂ treatment shows typical AFM images, with a measured thickness of ~1.2 nm and no aggregation. On the other hand, GO-1 and GO-2.5 aggregated to form large films, as shown in Figure 1C,D, respectively. The GO-1 and GO-2.5 films exhibited the morphology of dense, uniform, and self-assembled structures. Moreover, GO-1 and GO-2.5 were well-connected with one another, forming large and homogeneous ~1.4 nm thick monolayer films. This result indicates that the materials containing more oxygen functional groups tend to cluster together by an enhanced wettability and hydrogen bonding capability. Additionally, the self-assembled nanostructures of GO-1 and GO-2.5 show a clear phase contrast between GO-1 or GO-2.5 flakes and an empty region on the SiO₂ substrate (Figure S1). The AFM phase image of GO-2.5 shows many small, bright spots that correspond to the nano-sized holes (or vacancies) formed in the self-assembled GO-2.5 with lateral sizes of less than 100 nm (Figure S1B). The result shows that GO-2.5 is broken into small fragments as the H₂O₂ treatment time increases. The bright lines and small spots in the phase image of the GO-1 film also indicate nano-sized holes (or vacancies) and the two-dimensional nanocapillaries (Figure S1A). Although some small GO flakes were present after H₂O₂ etching, most of the GO-1 sample had large lateral sizes (~500 nm) on account of the short etching reaction time. GO-1 was further characterized...
by transmission electron microscopy (TEM) and scanning electron microscopy (SEM); a comparison of the TEM images of control GO and GO-1 is shown in Figure 2A, B. The TEM image of the GO-1 flakes shows nano-sized pores in the basal plane; no pores are evident on the control GO that did not undergo H2O2 treatment. It is well-known that H2O2 is a strong oxidizing agent that generates nano-sized holes (or vacancies) by the attack of H2O2 to sp2-hybridized domains around the initial defect sites of GO. The cross-sectional SEM image of the GO-1 paper shows that more pores and a large thickness of ∼3.1 nm were obtained relative to the tightly packed control GO paper (∼1.8 nm thickness) (Figure 2C). The increase in the thickness of the self-assembled GO-1 paper may be due to the additional number of oxygen-containing functional groups after H2O2 etching.

We next prepared N-doped graphene solutions by simultaneous N-doping and reduction of the control GO, GO-1 (pGO), and GO-2.5 (GO nanofragments, GOnf) in the presence of N2H4/NH3 for 1 h. This N-doping method in N2H4 and NH3 is one of the most widely used methods in liquid-phase environments and is the most successful approach to obtain a flat N-doped graphene at low temperature from the pGO during N-doping and reduction reactions. Films of these N-doped materials were then obtained by filtration (Figure S2).

Figure 3. (A) XRD, (B) FTIR, and (C) Raman spectra of N-GF (black line), N-pGF (red line), and N-GnfF (blue line).
N-pGF, the νCH and νC=O bands at 2950 and 1725–1650 cm⁻¹, respectively, are predominant in the perforated graphene structure. The νCH peaks are attributed to the stretching vibration of aliphatic CH groups of the vacancies and edges induced by the etching treatment. The C=O stretching mode is sensitive to its surrounding environment including conjugation, hydrogen bonding, and ring strain. The νC=O modes at the vacancies and edges in N-pGF were observed at 1650–1695 cm⁻¹ (unsaturated and amide C=O at vacancies) and 1724 cm⁻¹ (ketones at edges), whereas that of N-GnfF was observed at 1724 cm⁻¹ for the edge ketones. Additionally, the strong νC–N band at 1251 cm⁻¹ was assigned to aromatic amide groups, and aromatic CH out-of-plane bending vibrations appeared between 900 and 600 cm⁻¹. Thus, the oxygen-functionalized groups of N-pGF and N-GnfF increasingly determine the interlayer distance of the graphene nanoflakes, which is consistent with the XRD data.

Figure 3C shows the Raman spectra of N-GF, N-pGF, and N-GnfF. The Raman spectra of all graphene materials typically exhibit two bands D and G, located at ~1348–1352 and ~1585–1592 cm⁻¹, respectively. The D band corresponds to the sp³-hybridized carbon atoms at the vacancies and edges of graphene flakes, whereas the G band corresponds to the E₂g vibrational mode of the sp²-hybridized carbon atoms in the hexagonal structure. The N-GF samples, which did not undergo H₂O₂ treatment, showed bands similar to the D band at 1385 cm⁻¹ and the G band at 1592 cm⁻¹, with a D to G band intensity ratio (I_D/I_G) of 1.02. By comparison, the I_D/I_G values of the H₂O₂-treated N-pGF and N-GnfF were 1.08 and 1.18, respectively, which is higher than that of N-GF. Higher I_D/I_G ratios are associated with a more disordered carbon network. Thus, these results indicate that N-pGF and N-GnfF had more vacancies or edges than N-GF.

We used X-ray photoelectron spectroscopy (XPS) to investigate the chemical environments of N-GF, N-pGF, and N-GnfF. The survey spectra of all samples showed principal peaks corresponding to carbon (C 1s at ~284 eV), oxygen (O 1s at ~530 eV), and nitrogen (N 1s at ~398 eV) (Figure. S3). The O/C atomic ratios of N-GF, N-pGF, and N-GnfF were 0.15, 0.19, and 0.30, respectively, demonstrating that N-GnfF had a relatively higher level of oxidation than either N-GF or N-pGF (Figure. S3C). The deconvoluted high-resolution C 1s and N 1s spectra are shown in Figure 4. The C 1s peak can be divided into five subpeaks: C–C (284.4 eV), C–N (285.4 eV), C–N/C–OH (286.4 eV), C=O (287.9 eV), and O=C–OH (289.2 eV). The C 1s spectra of the N-doped graphene samples are dominated by the peak corresponding to sp²-hybridized graphite-like carbon at 284.4 eV (Figure 4A–D). The area of these peaks indicates that N-GF consists of 59.9% sp²-hybridized C atoms; by comparison, the sp²-hybridized C fraction decreased to 48.4% for N-pGF and 41.7% for N-GnfF. Additionally, the C–N/C–OH content in N-GnfF was 15.4%, whereas N-GF and N-pGF contained a much smaller amount (1.5–3.5%). Collectively, the high OH content in N-GnfF, as confirmed by FTIR spectroscopy, and these XPS results suggest an enrichment of hydroxyl groups in N-GnfF.

The N 1s XPS spectrum was also used to determine the N-bonding configurations. The high-resolution N 1s peaks were fitted into three types of N bonding at 398.4, 399.2, and 401.3 eV, corresponding to pyridinic, pyrrolic, and graphitic N, respectively (Figure 4E–H). Analysis of the fitted N 1s peaks showed that the predominant types were pyridinic, pyrrolic, and pyridinic N; the pyridinic-N contents are 2.1, 3.9 and 1.7% for N-GF, N-pGF, and N-GnfF, respectively. N-pGF had a higher content of pyridinic N than N-GF and N-GnfF, which may result from structural defects such as vacancies and edges, as well as a large number of active sites. Li et al. used ab initio molecular dynamic simulations to show that NH₃ molecules are well-trapped by the vacancies of defective graphene and that pyridinic N is formed in the vicinity of double vacancies by a doping process. This previous report suggests that the vacancies of defective pGO are beneficial to the formation of pyridinic N. On increasing the N-doping reaction time from 1 to 10 h (N-pGF-10), the total N amount increased from 4.78 to 6.63%. A distinct higher-energy peak corresponding to graphitic N appeared at 401.3 eV, indicating that a lengthy N-doping
reaction favors the formation of graphitic N (Figure 4H). The pyridinic-N and graphitic-N contents of N-pGF-10 were 4.1 and 2.5%, respectively; the pyrrolic/pyridinic N accounted for only a small portion of the total N content.

Thus, the strongly oxidizing free radicals generated by H2O2 can induce graphene perforation by the electrophilic attack and oxidation of sp2-hybridized carbon atoms. During the etching reaction at 85−90 °C, the perforation of graphene predominated in the short etching time of ∼1 h, and as the etching reaction was further increased to 1.5 h, fractured GOnf with high OH functionality were formed rather than increased perforation. A pyridinic-N-doped graphene tends to be produced on vacancies of the pGO during the nitrogen-doping process. A schematic representation for the formation of N-pGF, N-pGF-10, and N-GnfF is illustrated in Figure S4.

Finally, the electrochemical ORR activity of N-pGF and N-GnF was examined using cyclic voltammetry (CV) in N2- and O2-saturated alkaline media. A clear oxygen reduction peak with increasing current was observed in the O2-saturated electrolyte solution but not in the N2-saturated solution (Figure S5). Figure 5A shows a comparison of the CV curves of N-pGF, N-GnF, N-GF, and bare glassy carbon (GC) in an O2-saturated 0.1 M KOH electrolyte. As seen, N-pGF has a much higher current density and more positive peak potential compared with the other samples, suggesting an enhanced electrocatalytic ORR activity. We also compared the ORR capability of N-pGF with that of N-pGF-10, which had a higher N content. Despite the higher N content in N-pGF-10, it exhibited a decreased current density with no peak potential shift and its CV curve resembled that of N-GnF. This finding is supported by its corresponding XRD results (Figure S6). We further established the activity of N-pGF using linear sweep voltammetry (LSV) with a rotating-disk electrode (RDE) by comparing our material with a reference sample of commercial 20% Pt/C under the same conditions. The LSV curves of N-GF, N-pGF, N-pGF-10, N-GnF, and Pt/C were obtained in an O2-saturated 0.1 M KOH electrolyte at 1600 rpm and 10 mV s−1 (Figure 5B). The onset potentials were determined from the intersection between the baseline and the signal current. The onset potentials of N-GF, N-pGF, N-pGF-10, and N-GnF were −0.17, −0.12, −0.19, and −0.23 V (vs Ag/AgCl), respectively, which followed the order of N-pGF > N-GF > N-pGF-10 > N-GnF (Figure 5C). N-pGF, which possesses a relatively high pyridinic N and very low pyrrolic and graphitic-N contents, showed the lowest onset potential and the highest limiting diffusion current, suggesting that it has excellent electrocatalytic activity for the ORR. Relative to Pt/C, N-pGF showed a small downshift of 64 mV in the half-wave potential (E1/2) and a higher limiting diffusion current at −0.5 V. Relative to N-pGF, N-pGF-10 showed a more negative onset potential and a lower limiting current, which is noteworthy because N-pGF-10 possesses the most graphitic-N functionality (Table S1). These results confirm the low contribution of graphitic and pyrrolic N to the ORR. Moreover, these results are consistent with a recent report that pyridinic N is much more active than graphitic N in a model HOPG ORR catalyst.26

Figure 5D−F shows the electrochemical activity of N-pGF for the ORR process at different rotational rates and a
The calculated electron-transfer number \( n \) was calculated to be 3.9 (±0.2) from −0.3 to −0.7 V (vs Ag/AgCl). The calculated \( j_k \) value shows a current density of 20.8 mA cm\(^{-2}\) at −0.5 V. The Tafel slope is 39.7 mV/dec and is comparable to that of Pt/C (34.5 mV/dec) (inset of Figure 5A). These results suggest that the ORR kinetics of N-pGF gives rise to a facile 4\(e^-\) transfer and are similar to those of Pt/C. The N-pGF exhibits good electrocatalytical activity in an alkaline electrolyte for ORR and shows higher ORR catalytic performance than the N graphene synthesized at high temperature of 800 °C or much better ORR activity than the electrochemical synthesized N graphene at room temperature (Table S1).

To evaluate the ORR activity of N-doped graphene samples in acidic solution, we obtained the linear sweep voltammograms in an O\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) electrolyte at 1600 rpm 10 mV s\(^{-1}\) (Figure S7A). The ORR onset potentials were 0.018, 0.045, −0.110, and 0.009 V for N-GF, N-pGF, N-GnfF, and N-pGF-10, respectively. N-pGF showed the lowest onset potential and the highest limiting diffusion current. LSV curves at different rotation rates (400–2000 rpm) are shown in Figure S7B, and the corresponding K–L plots at various applied potentials are shown in Figure S7C. The diffusion current density values increased with the increasing rotation rate, while the onset potentials were almost independent of the rotation rate. The K–L plots show good linearity. From the linear fitted K–L plots, the calculated electron-transfer number is 3.6–4.2. The ORR activity of N-pGF is coincident with the results in alkaline solution.

To examine the stability and the crossover effect of methanol tolerance, the chronoamperometric responses on ORR at N-pGF and Pt/C electrodes were obtained at a constant potential of −0.6 V in O\(_2\)-saturated 0.1 M KOH and 0.5 M H\(_2\)SO\(_4\) (Figure 6A–D). In a 0.1 M KOH electrolyte, N-pGF shows higher stability (94.6%) than Pt/C (91%). Under a 0.5 M H\(_2\)SO\(_4\) electrolyte, N-pGF and Pt/C exhibit similar stability before 1.5 h. After 4 h, N-pGF retains 89.3% current density. After addition of methanol, the ORR current for the N-pGF electrode was slightly changed in both alkaline and acidic electrolytes, while Pt/C exhibited a distinct drop (Figure 6C,D). N-pGF is a durable catalyst with high methanol tolerance for ORR.

The excellent ORR activity of N-pGF is reflected by the influence of pyridinic-N-doping-induced charge redistribution. Pyridinic N with lone pair electrons can accept electrons from the adjacent carbon atoms, which is favorable for the adsorption of O\(_2\) or OOH and ultimately facilitates the reduction of OH to form H\(_2\)O. On the basis of the K–L analysis, N-pGF shows similar electron-transfer numbers of 3.9 (±0.2) at different potentials and a small Tafel slope of 39.7 mV/dec at low}
overpotentials. These results are consistent with those of the reported N-doped graphene,19,26 which suggest the four-electron ORR pathway of N-pGF in the direct four-electron mechanism or sequential 2 + 2 electron mechanism with OOH⁻ formation. The catalytic activity of N-doped graphene is highly related to the pyridinic-N-bonding configuration.

We also compared the LSV curves for the ORR with 20% Pt/N-pGF and commercial 20% Pt/C in O₂-saturated 0.1 M KOH at 10 mV s⁻¹ and 1600 rpm (Figure 6F). As seen, Pt/N-pGF exhibited much better performance than the commercial Pt/C in terms of the onset potential and limiting diffusion current, showing a positive shift of 30 mV in the onset potential and 1.3 times higher limiting diffusion current at ~0.5 V. The electron-transfer numbers (n) calculated from the K–L plots for Pt/C and Pt/N-pGF were 3.4 ± 0.2 and 4.0 ± 0.3 between ~0.2 and ~0.6 V (vs Ag/AgCl), respectively (Figure S8). The high performance of Pt/N-pGF can be attributed to a fast ORR and an abundance of electrocatalytic active sites in N-pGF, which are present because of its perforated structure and pyridinic-N functionality.

## CONCLUSIONS

In summary, we report a facile and straightforward approach without high-temperature heat treatment to prepare perforated pyridinic-N-doped graphene with high active sites and effective diffusion pathways for a fast ORR. Under the etching time of GO and the N-doping reaction time of 1 h, a pyridinic-N-doped graphene film was produced by pGO, which showed a higher pyridinic-N content (3.9%) than that of either N-GF (2.1%) or N-GnfF (1.7%). When the N-doping reaction time of pGO was increased from 1 h to 10 h (N-pGF-10), the total N content increased from 4.78 to 6.63%. The N 1s XPS spectrum of N-pGF-10 showed a distinct graphitic-N peak at 401.3 eV, indicating that a lengthy N-doping reaction favors the formation of graphitic N. Despite N-pGF-10 having the most graphitic-N functionality, it showed a smaller contribution to the ORR performance than N-pGF. By comparison, N-pGF, which had predominantly pyridinic-N functionality, showed enhanced electrocatalytic activity and four-electron transfer, suggesting that pyridinic N caused the high electrocatalytic activity. A comparison between 20% Pt/N-pGF and commercial 20% Pt/C showed that the performance of Pt/N-pGF was superior in terms of its onset potential and limiting diffusion current. These results provide an easily scalable method for the preparation of N-doped graphene catalysts that are rich in ORR active sites, which would be invaluable to applications in the areas of catalysts, sensors, and nano-electronics.

## EXPERIMENTAL SECTION

### Materials and Characterization

GO (>7 μm, Standard Graphene Co. Ltd. South Korea), hydrogen peroxide (H₂O₂, 30 wt % in H₂O, Sigma-Aldrich), hydrazine (35 wt % in H₂O, Aldrich), and ammonium hydroxide solution (28% NH₃ in H₂O, purity >99.99%, Sigma-Aldrich) were used as received. Deionized (DI) water with a resistivity of 18 MΩ cm was used for all experiments.

XRD patterns were collected using a high-power microarea X-ray diffractometer ( Rigaku, D/Max-2500) using Cu Kα radiation. XPS elemental analysis was carried out using a K-Alpha XPS analyzer with monochromatic Al Kα X-ray sources (Thermo Scientific, Waltham, MA, USA). The XPS spectra were fitted using a Gaussian–Lorentzian peak shape after baseline correction. Raman spectra were obtained at 514 nm using a HORIBA Jobin Yvon LabRAM-HR instrument (HORIBA Scientific, Edison, NJ, USA). The silicon peak at 520 cm⁻¹ was used to calibrate the absolute peak position. FTIR spectra were obtained using a Nicolet iS50 FT-IR spectrometer (ThermoFisher Scientific) equipped with a DLaTGS attenuated total reflection accessory. AFM measurements were performed with a Digital Instruments Dimension (D3100, Veeco). Samples were prepared for AFM imaging by sonication at 2000 rpm (100 μL of 1 mg/mL GO, pGO, and GOnf was spin-coated onto a 1 × 1 cm SiO₂/Si substrate) and dried under vacuum for 15 h. TEM images were recorded using a JEOL JEM 2100F transmission electron microscope using a Cu grid coated with a lacey carbon film. TEM samples were prepared by drop-casting a very dilute dispersion on a substrate and drying under ambient conditions. CV and LSV analyses were carried out in a standard three-electrode system using a BAS electrochemical analyzer (BAS 100B, USA) coupled with a Pine Modulated Speed Rotator system. A GC electrode (geometric area: 0.2 cm²) was used as the working electrode and was polished to a mirror finish with 0.3 and 0.05 μm alumina. Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. All N-doped graphene samples were dispersed by sonication in a mixture of DI water and dimethylformamide (DMF) (1 mg/mL) containing 10 wt % Nafion to form a homogeneous graphene ink. From these dispersions, 15 μL was drop-casted onto the GC electrode and allowed to dry at 23–25 °C. Finally, this electrode was further dried in vacuum. CVs were obtained between −1.0 and 0.2 V (vs Ag/AgCl) at 50 mV s⁻¹ in an O₂-saturated and N₂-saturated 0.1 M KOH aqueous electrolyte. LSV was performed to determine the ORR activity using a RDE in an O₂-saturated 0.1 M KOH electrolyte at 10 mV s⁻¹ with a rotational rate of 400, 800, 1200, 1600, or 2000 rpm. For comparison, commercial 20 wt % Pt on graphitized carbon (Pt/C, 20 wt % Pt on Vulcan XC 72, Aldrich) was also measured.

### Preparation of pGO

The pGO materials were prepared according to the following procedure: GO powder was dispersed in DI water and sonicated for 1 h to obtain a homogeneous suspension (2.2 mg/mL) containing 10 wt % Nafion to form a homogeneous graphene ink. From these dispersions, 15 μL was drop-casted onto the GC electrode and allowed to dry at 23–25 °C. Finally, this electrode was further dried in vacuum. CVs were obtained between −1.0 and 0.2 V (vs Ag/AgCl) at 50 mV s⁻¹ in an O₂-saturated and N₂-saturated 0.1 M KOH aqueous electrolyte. LSV was performed to determine the ORR activity using a RDE in an O₂-saturated 0.1 M KOH electrolyte at 10 mV s⁻¹ with a rotational rate of 400, 800, 1200, 1600, or 2000 rpm. For comparison, commercial 20 wt % Pt on graphitized carbon (Pt/C, 20 wt % Pt on Vulcan XC 72, Aldrich) was also measured.

### Preparation of N-Doped Graphene Films (N-GF, N-GnfF, N-pGF, and N-pGF-10)

N-pGF, N-GnfF, and N-GF were prepared by the simultaneous N-doping and reduction of pGO, GOnf, and control GO in the presence of N₂H₄/NH₃ for 1 h. The pGO and GOnf dispersions (0.2 mg/mL, 100 mL) were each mixed with ammonium hydroxide (350 μL, 28% NH₃) and hydrazine (50 μL, 35 wt %) solution in a round-bottom flask with a Teflon cap and then reacted in a water bath at 95 °C for 1 h without stirring. After cooling to 60 °C, the reaction mixture was filtered with an Anodisc membrane filter (aluminum oxide membrane, 0.02 μm) and washed with DI water and methanol. The resultant films were obtained in the...
form of a black freestanding film (Figure S2). N-pGF-10 was prepared from pGO by a simultaneous N-doping and reduction reaction for 10 h under the same conditions as N-pGF.

**Electrochemical Measurements.** To maintain the as-is structure of N-pGF, the working electrode was carefully prepared so that the N-pGF form was not broken into particles. N-pGF was dispersed in a mixture of DI water and DMF (1 mg/mL) containing 10 μL Nafion solution (10 wt %) with mild sonication for 1 min to form a uniform graphene ink. From the dispersion, 15 μL was drop-casted onto a GC electrode or a RDE and allowed to dry at 23–25 °C. Finally, this electrode was further dried in a vacuum desiccator overnight. All N-doped graphene and commercial 20 wt % Pt on graphitized carbon (Pt/C, 20 wt % Pt on Vulcan XC 72, Aldrich) electrodes were prepared in the same conditions as N-pGF. CVs were obtained between −1.0 and 0.2 V (vs Ag/AgCl) at 50 mV s⁻¹ in an O₂-saturated and N₂-saturated 0.1 M KOH or 0.5 M H₂SO₄ aqueous electrolyte. LSV was performed to determine the ORR activity using a RDE in an O₂-saturated 0.1 M KOH or 0.5 M H₂SO₄ electrolyte at 10 mV s⁻¹ with a rotational rate of 400, 800, 1200, 1600, or 2000 rpm. For comparison, commercial 20 wt % Pt/C was also measured. Stability and methanol tolerance tests on N-pGF and Pt/C were conducted by chronoamperometry at a constant potential of −0.6 V (vs Ag/AgCl) in an O₂-saturated 0.1 M KOH or 0.5 M H₂SO₄ electrolyte.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00400.

Photographs of freestanding films of N-doped graphene materials (N-GF, N-pGF, and N-GnFF); AFM analyses of pGO and GO/n on a SiO₂/Si substrate; XPS survey spectra and elemental composition of N-doped graphene materials; schematic representation for the formation of N-doped graphene; CV of N-pGF and N-GnFF under N₂ and O₂-saturated 0.1 M KOH solution; XRD spectrum of N-GF, N-pGF, and N-pGF-10; LSV and K–L plot of N-pGF in 0.5 M H₂SO₄; LSV and K–L plot of Pt/C and Pt/N-pGF with various rotation rates; and comparison of our samples and the reported N-doped graphene (PDF).

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**Notes**

The authors declare no competing financial interest.

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