Supporting Information

Selective Nitrogen Doping in Graphene for Oxygen Reduction Reactions

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Experimental section

Materials. Nitrogen-doped graphene was grown on Cu foils (99.999%, 25 μm in thickness, Alfa Aesar) or Cu disks (99.99%, 5 mm in diameter, Niraco) using pyridine and julolidine as nitrogen-containing aromatic precursor molecules (Wako Pure Chemical). Prior to film growth, the Cu foils and Cu disks were annealed at 900 °C for 30 min in H_2 (flow rate: 300 sccm) to remove residual organics and oxides from the surface. Pyridine-based graphene was grown on the Cu surface by flowing saturated pyridine vapor gas with Ar (flow rate: 50 sccm) at the desired temperature (typically 400–600 °C) for 0.5–3 h. To prepare the julolidine-based graphene, julolidine powder was first heated at 100 °C, and then the julolidine-based graphene was grown on a Cu substrate at the desired temperature (typically 400–600 °C) for 0.5–4 h under flowing Ar gas (rate: 50 sccm).

At growth temperature in the range of 400–600 °C, no visible soot was observed inside wall of the furnace when saturated pyridine-Ar or julolidine-Ar vapor gases were introduced. The results imply that the temperature range could inhibit the pyrolysis of the precursor molecules.

Characterization. Raman spectra were recorded on a micro-Raman spectrophotometer (Thermo Fisher Scientific), equipped with a 532-nm laser. A laser power of <1 mW was used to avoid damage of the samples by laser-induced heating. Atomic force microscopy images were acquired in

tapping mode, in air, on a Veeco Digital Instruments Nanoscope IIIa. X-ray photoelectron spectroscopy was performed on a JEOL JPS-9200, using a monochromatic Al Kα X-ray source (1486.6 eV). Electrochemical measurements were carried out in a three-electrode cell with a Pt wire and Ag/AgCl (saturated KCl solution) as the counter and reference electrodes, respectively. The nitrogen-doped graphene, grown on the Cu disk, was used as the working electrode. The working electrode was supported onto a glassy carbon disk electrode, using a silver paste. The rim of the combined electrodes was carefully sealed with an acrylic resin. This process enables electrochemical measurements of the surface of the grown disk only.

Film transfer and morphology measurements. To assess film thickness and morphology by atomic force microscopy, grown samples on Cu foils were transferred to Si wafer substrate with 300 nm SiO_2 layer using PMMA coating and chemical etching technique as previously reported.[1,2] A protective thin film was deposited on the backside of the foils using 5 % polymethyl methacrylate (PMMA) dissolved in toluene. The frontside of the foil was etched away by floating the foils on 0.1 M $(NH_4)_2S_2O_8$ solution for 12 h at room temperature. After several washing by DI water, the PMMA-coated films were transferred to the SiO_2/Si substrate and completely dried in an oven at 60 ^oC for a few hours. Finally, the PMMA protective layers were removed by immersing the samples in a large volume of acetone at room temperature.

Oxygen reduction reaction (ORR) activity and measurements. The ORR studies were conducted in an O_2-saturated KOH aqueous solution (0.1 M) using a rotating disk electrode system (Hokuto). Prior to ORR measurements, the solution was bubbled with O_2 for 1 h.

The transferred electron numbers per oxygen molecule involved in the ORR were determined using the Koutechy–Levich equation as follows:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_K} + \frac{1}{B\omega^{0.5}}, \qquad \text{(Eq. S1)}$$

where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, B is the Levich constant, and ω is the electrode rotating rate. The transferred electron numbers per oxygen molecule can be calculated from the Levich constant as follows:

$$B = 0.62nFD^{2/3}\nu^{-1/6}C_0, \qquad \text{(Eq. S2)}$$

where n is the transferred electron numbers per oxygen molecule, F is the Faraday constant (F = 96 485 C mol^{-1}), D is the diffusion coefficient of O_2 in 0.1 M KOH (*i.e.*, 1.9×10^{-5} cm^2 s^{-1}), ν is the kinetic viscosity (0.01 cm^2 s^{-1}), and C_0 is the bulk concentration of oxygen (*i.e.*, 1.2×10^{-3} mol L^{-1}).

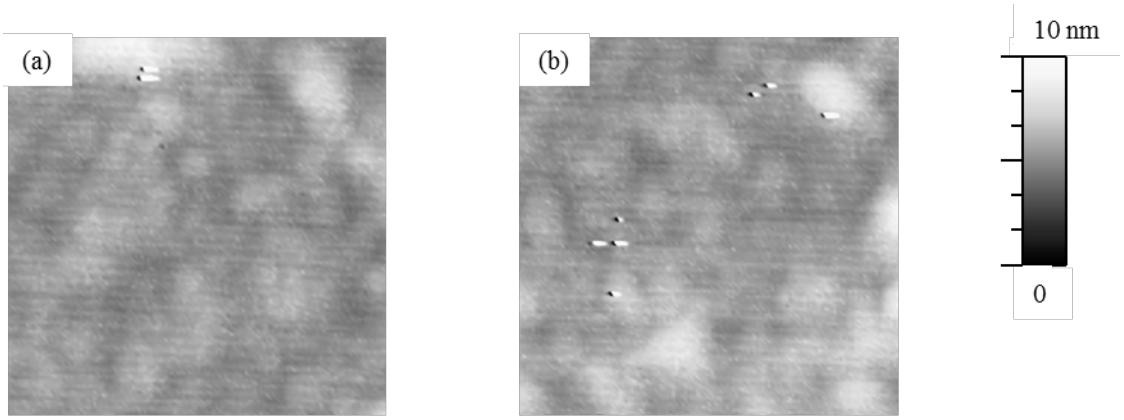

Fig. S1. Enlarged atomic force microscopy images of (a) pyridine-based graphene film and (b) julolidine-based graphene film.

	Pyridine made film (Py-NG)	Julolidine made film (Ju-NG)
N / C ratio	0.027	0.023

Table S1 relative nitrogen/carbon (N/C) ratio for Py-NG and Ju-NG

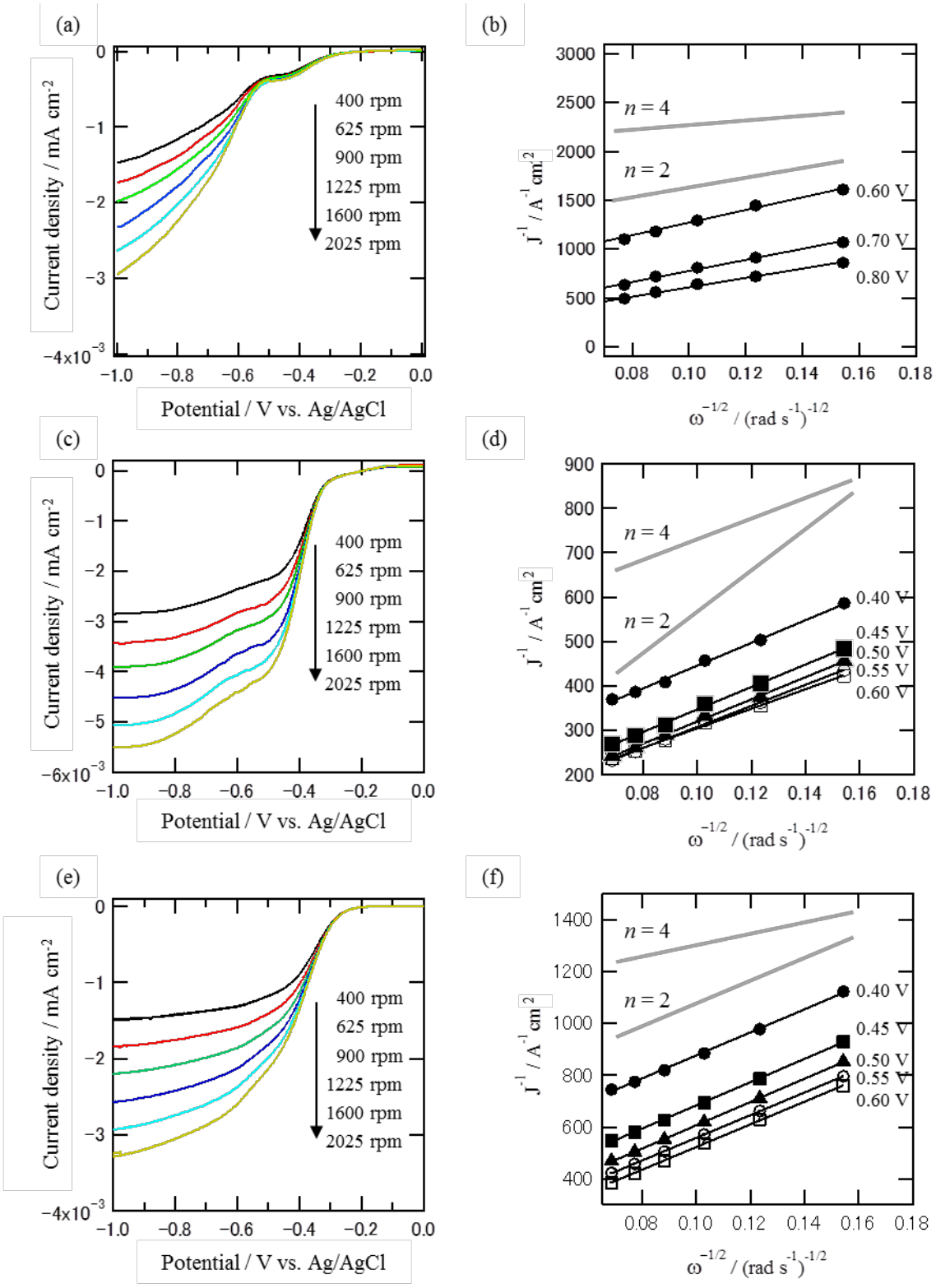
(a)
Current density / mA cm-2
400 rpm
625 rpm
900 rpm
1225 rpm
1600 rpm
2025 rpm
Potential / V vs. Ag/AgCl
(b)
n = 4
n = 2
0.60 V
0.70 V
0.80 V
j-1 / A-1 cm2
ω-1/2 / (rad s-1)-1/2
(c)
Current density / mA cm-2
400 rpm
625 rpm
900 rpm
1225 rpm
1600 rpm
2025 rpm
Potential / V vs. Ag/AgCl
(d)
n = 4
n = 2
0.40 V
0.45 V
0.50 V
0.55 V
0.60 V
j-1 / A-1 cm2
ω-1/2 / (rad s-1)-1/2
(e)
Current density / mA cm-2
400 rpm
625 rpm
900 rpm
1225 rpm
1600 rpm
2025 rpm
Potential / V vs. Ag/AgCl
(f)
n = 4
n = 2
0.40 V
0.45 V
0.50 V
0.55 V
0.60 V
j-1 / A-1 cm2
ω-1/2 / (rad s-1)-1/2

Fig. S2. Rotating disk electrode voltammetry curves of (a) pristine graphene, (c) pyridine-based graphene, and (e) julolidine-based graphene films. Koutechy–Levich plots of (b) pristine graphene, (d) pyridine-based graphene, and (f) julolidine-based graphene films.

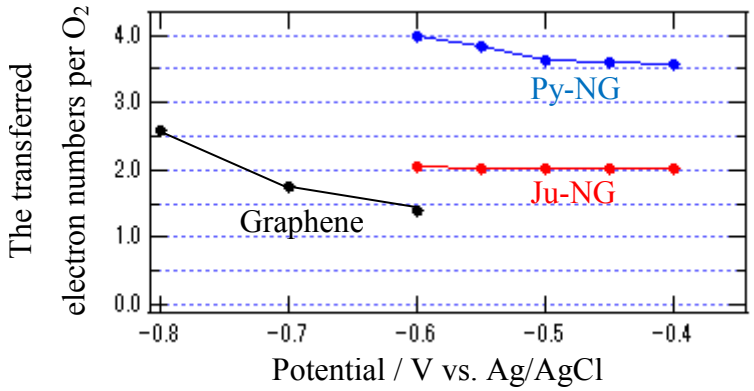

Fig. S3. Potential dependence on transferred electron numbers per O_2 for graphene, Py-NG, and Ju-NG.

References

S1. Z. Luo, S. Lim, Z. Tian, J. Shang, L. Lai, B. MacDonald, C. Fu, Z. Shen, T. Yu and J. Lin, *J. Mater. Chem*. 2011, **21**, 8038.

S2. Z. Luo, Y. Lu, D. W. Singer, M. E. Berck, L. A. Somers, B. R. Goldsmith and A. T. C. Johnson, *Chem. Mater.* 2011, **23**, 1441.