

Catalyst-free synthesis of iodine-doped graphene via a facile thermal anneal process and its use for electrocatalytic oxygen reduction in an alkaline medium

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Supporting Information

Experimental Section

Electrode preparation Glassy carbon (GC) electrodes (3 mm diameter, CH instrument Inc.) were polished with a 0.05 and 0.3 μm alumina slurry (CH Instrument Inc.) on a microcloth, and subsequently rinsed with ultrapure water and ethanol. The electrodes were then sonicated in ultrapure water for 5 min to remove any bound particles, rinsed thoroughly with ultrapure water and dried under a gentle nitrogen stream. To prepare the working electrode, a 1 mg graphene sample was ultrasonically dispersed in 1 mL ethanol, then 2 μL of the resulting suspension was dropped onto the GC surface and dried at room temperature. For comparison, a commercially available Pt/C-modified GCE (20 wt% Pt supported on carbon black, fuel cell grade from Alfa) was prepared in the same way.

Synthesis of the I-graphene Graphene oxide (GO) was purchased from Tianjin Plannano Co. Ltd. I-graphenes were prepared by annealing graphene oxide (GO) and iodine at 500–1100 $^{\circ}\text{C}$. The anneal treatment was carried out in a tube furnace with high purity argon as protective ambient. Detailed procedure is as follows: GO and I_2 were firstly ultrasonically dispersed in ethanol for about 30 min. The resulting suspension was spread onto an evaporating dish and dried at 30 $^{\circ}\text{C}$, forming a uniform solid mixture. The mixtures were placed into a quartz tube with argon atmosphere and annealed at 500-1100 $^{\circ}\text{C}$ for 30 min. After that, the sample was cooled to room temperature under Ar ambient and collected from the quartz tube. The contents and bonding configurations of sulfur in these I-graphenes can be adjusted through varying the mass ratio of GO and BDS as well as the annealing temperatures. For comparison, the GO without any dopants was treated under the same condition. The resulting materials are denoted graphene-500, I-graphene-500, graphene-700, I-graphene-700, graphene-900, I-graphene-900, graphene-1100, and I-graphene-1100, respectively. Moreover, the GO (or graphene-900) was also mixed with I_2 by ultrasonical dispersion in ethanol. Their mixtures were denoted GO+ I_2 and graphene-900+ I_2 , respectively.

Electrochemical measurements All electrochemical measurements, including cyclic voltammograms (CV), rotating-disk electrode voltammograms and chronoamperometry, were performed at room temperature in 0.1 M KOH solutions, which were purged with high purity nitrogen or oxygen for at least 30 min prior to each measurement.

Characterizations of physical parameters X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ultra-high vacuum setup, equipped with a monochromatic Al K α X-ray source and a high resolution Gamdata-Scienta SES 2002 analyzer. Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) images were recorded with a JEOL-3010 instrument. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. The nitrogen adsorption/desorption data were recorded at the liquid nitrogen temperature (77K) using a Micromeritics ASAP 2020M apparatus. Before the measurements, the samples were evacuated for 10 h at 300 °C.

Table S1 Physical parameters, electrochemical properties and corresponding experimental data

for various graphenes and a Pt/C catalyst.

Samples	Mass ratio Of I ₂ and GO	Specific surface area (m ² /g)	I content (wt.%)	I ₃ ⁻ (at.%)	I ₅ ⁻ (at.%)	Peak Potential (V) and current (μA)	Kinetic current density, (mA cm ⁻²)	Number of electron transfer, n
I-graphene-500	1:1	440	1.21	43.6	56.4	-0.35, 85	3.87	2.16
I-graphene-700	1:1	438	1.13	50.4	49.6	-0.32, 123	5.64	3.01
I-graphene-900	1:1	435	1.05	61.4	38.6	-0.29, 216	9.21	3.86
I-graphene-1100	1:1	443	0.83	62.1	37.9	-0.30, 189	8.01	3.51
Pt/C		102				-0.23, 112	4.52	3.90

S1. Rotating-disk voltammetry measurements

To further study the ORR electrochemical procedures of I-graphene-900, we performed rotating-disk electrode (RDE). The RDE current-potential curves at various rotating speeds are shown in Figure S1. The limited diffusion currents are dependent on the rotating rates. The number of electrons involved in the ORR can be calculated from the Koutecky-Levich (K-L) equation:

$$(1) J^{-1} = J_L^{-1} + J_K^{-1} = (B\omega^{1/2})^{-1} + J_K^{-1}$$

$$(2) B = 0.62nFC_0(D_0)^{2/3}v^{-1/6}$$

$$(3) B = nFkC_0$$

$$(4) J_K^{-1} = J^{-1} - (0.62nFC_0(D_0)^{2/3}v^{-1/6}\omega^{1/2})^{-1}$$

Where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotation speed), n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant ($F = 96485 \text{ C} \cdot \text{mol}^{-1}$), C_0 is the bulk concentration of O_2 , ($C_0 = 1.2 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$), v is the kinematic viscosity of the electrolyte ($v = 0.01 \text{ cm}^2 \cdot \text{s}^{-1}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$). According to Equations (1) and (2), the number of electrons transferred (n) can be calculated to be 3.86 at -0.30 V , which indicates that the I-graphene-900 lead to a four-electron-transfer reaction to reduce directly oxygen into OH^- . The calculated J_K value is 9.21 mA cm^{-2} at -0.30 V from equation (4).

In our experiment, from Figure S1a, it can be found that the oxygen reduction current density for I-graphene-900 electrode increases as the rotation speed increased in the potential range from -0.26 to -0.80 V , but keeps steady in the potential range from 0 to -0.25 V , which suggests that the currents at the potentials (0 to -0.25 V) are a kinetic control. The Koutecky-Levich plots (J^{-1} vs. $\omega^{-1/2}$) at different electrode potentials displayed good linearity (Figure S1b), and the slopes remained approximately constant over the potential range from -0.26 to -0.8 V , which suggest that the electron transfer numbers are similar for oxygen reduction at different electrode potentials. Moreover, we also noted the Levich plot (from -0.26 to -0.80 V) does not intercept the i^{-1} axis at the origin (Figure S1c), proving that the currents at the potentials are a combined kinetic-diffusion control.

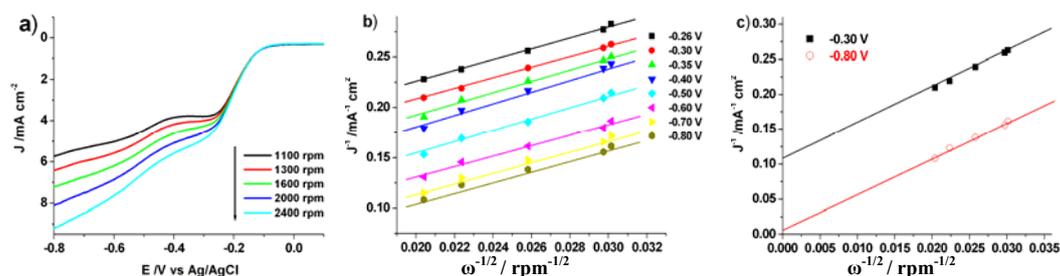


Figure S1 (a) Rotating-disk voltammograms recorded for the I-Graphene-900 electrode in an O_2 -saturated 0.1M solution of KOH at a scan rate of 10 mV s^{-1} and different rotation rates. (b, c) Koutecky-Levich plot of J^{-1} versus $\omega^{-1/2}$ at different electrode potentials and the experimental data were obtained from (Figure S1a).

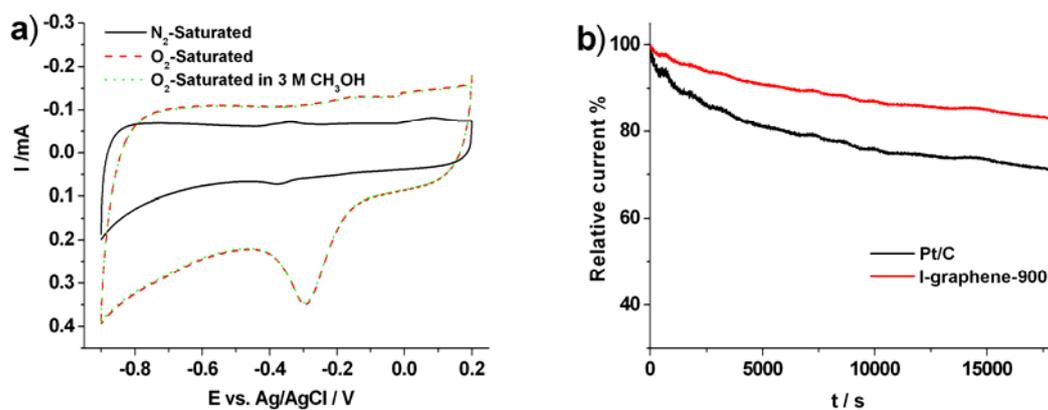


Figure S2 (a) Cyclic voltammograms for I-Graphene-900 for oxygen reduction in a 0.1M KOH solution, saturated with N_2 or O_2 , in a 0.1 M KOH O_2 -saturated solution upon the addition of CH_3OH (3M) saturated with O_2 ; (b) Chronoamperometric responses of I-graphene-900 and Pt/C-modified GC electrodes at -0.30 V in an O_2 -saturated 0.1M KOH solution.

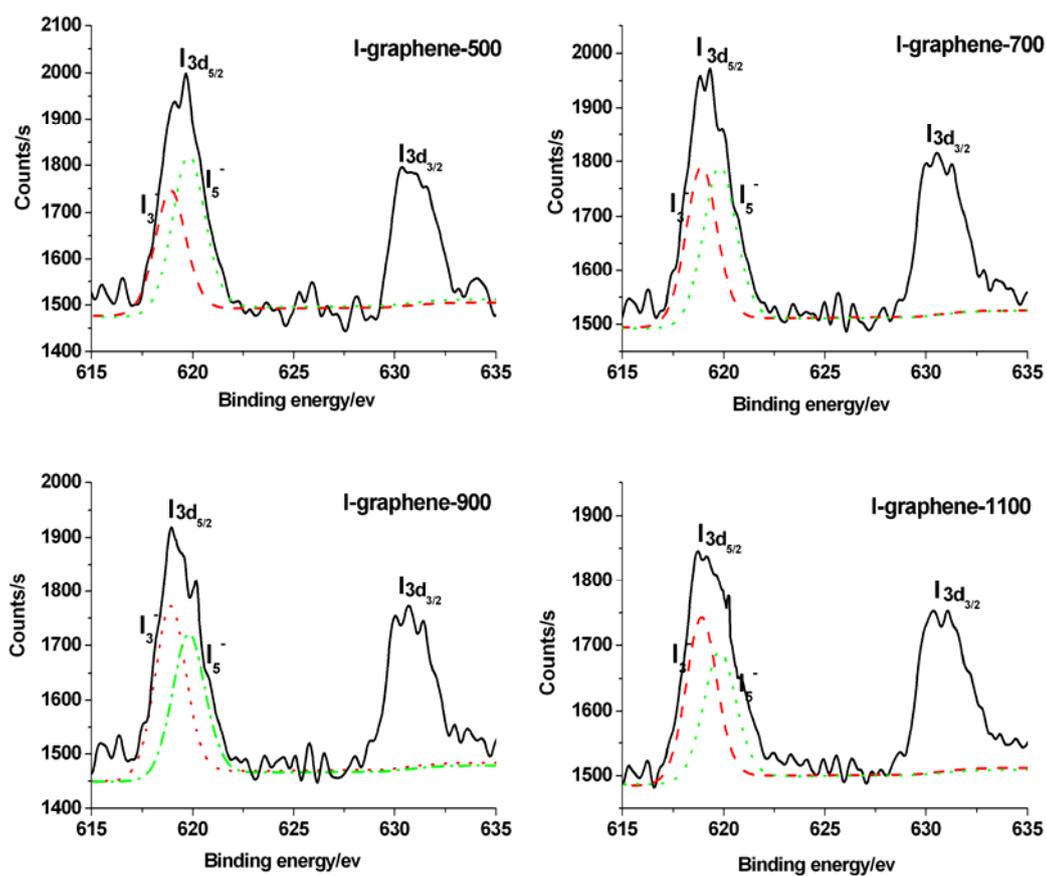


Figure S3 High-resolution XPS spectra of I-graphene-500, I-graphene-700, I-graphene-900 and I-graphene-1100. The signals fit into two energy components centered around 618.6 and 620.2 eV, which are correspond to I_3^- and I_5^- , respectively.

As a control experiment, we investigated the effect of I₂ content on the ORR activity. The contents of iodine in these I-graphenes can be adjusted by varying the mass ratios of GO and iodine. Figure S4 show the CV and LSV measurement curves for these graphene samples obtained from different mass ratios of GO and iodine at 900°C. From Figure S4a, it can be found that the doped graphene obtained from the mass ratios of GO and iodine of 4:4 shows the highest peak current and most positive ORR peak potential of all the graphene samples. The results of LSV measurement in Figure S4b also support the CV observations. All the observations strongly indicate that the I-graphene obtained from the mass ratios of GO and iodine of 4:4 holds the most outstanding ORR activity amongst the graphene samples. The possible explanation for the phenomenon may be as follows: When the mass ratios of iodine and GO increase from 1:4 to 4:4, this improved ORR performance may be due to that more dopant in the samples would contribute more sites and thus more active activity. With the further increase of dopant content, the onset potential of ORR is shifted to the negative direction, and the current density decreased significantly. This is because more dopants adsorbed on the graphene would increase resistance and block the more active for sites for ORR.

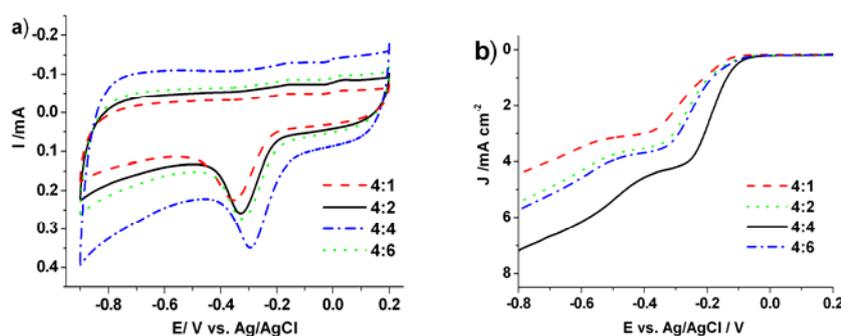


Figure S4 Cyclic voltammograms (a) and LSV (a rotation rate of 1600 rpm) (b) curves for various graphenes on a glass carbon rotating disk electrode saturated in O₂