Supporting Information

Three Dimensional Nitrogen-Doped Graphene Hydrogels with in-situ Deposited Cobalt Phosphate Nanoclusters for Efficient Oxygen Evolution in Neutral Electrolyte

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I. Experimental Section

1. Material Synthesis

Catalytic electrode preparation. Graphene oxide (GO) was prepared using commercial graphite as outlined by Hummer's method¹. This graphene oxide was exfoliated by ultrasonication for approximately 30 min to make up a uniform dispersion in deionised water of concentration ~ 2 mg/mL. The nitrogen doped graphene (N-Graphene) hydrogels were prepared via a single step hydrothermal process. To prepare the N-graphene hydrogels, 7 samples (2mL each) of graphene oxide dispersion were prepared. Into each sample, a varying amount of nitrogen precursor (N-precursor) was added as a means to draw comparisons between materials later on. The amount of N-precursor added is as follows outlined in Table S2. The 7 samples were loaded into a Teflon lined stainless steel autoclave, and then heated at 150°C for 6 h. This process was done for the two chosen nitrogen containing precursors: ethylenediamine and ammonia. After being cooled to room temperature, the hydrogel samples were dialyzed in deionised water for 24 hours to remove impurities.

The working electrode was fabricated from 1×2.5 cm² piece of 1mm nickel foam (NF) sheet which was cleaned by ultrasonication in acetone, ethanol and deionised water, respectively. The NF was then immersed into the graphene oxide/N-precursor mixture following sonication for 30 min to drive the successful filling of the solution into the pores of the NF. Then the mixture was hydrothermally treated at 150°C for 6 h and dialyzed for 2 days. The subsequent cobalt nanoclusters were then deposited in-situ on the N-graphene hydrogels/NF composite through electrodeposition.

Cobalt electrolyte preparation. A 1L stock solution of 0.1M KPi electrolyte (pH 7) was prepared using K₂HPO₄ (10.71 g) and KH₂PO₄ (5.24 g) and Milli-Q water (18 M Ω cm⁻¹). Cobalt solutions used for electrochemical deposition were made from hexahydrate cobalt chloride (CoCl₂.6H₂O). A 0.5 mM cobalt solution was prepared by adding cobalt chloride (0.1194 g) to the 1 L KPi stock solution.

In-situ electrodeposition. A CHI 760 electrochemical workstation was used to carry out the electrodeposition of the nanoclusters onto the hydrogels. A three electrode cell held 200 mL of Cobalt containing electrolyte. The working electrode was a sample of the N-graphene hydrogels/NF composite which was then immersed in the solution. Pt wire was used as the auxiliary electrode and a standard Ag/AgCl electrode was used as the reference. Electrolysis was carried out at 1.29 V without stirring or iR compensation for the required time.

2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Philips 1130 X-ray diffractometer (40 kV, 25 mA, Cu K α radiation, λ =1.5418 Å); Raman spectra were recorded on an iHR550 Raman microscope from HORIBA scientific with 532 nm solid laser as the excitation source. FTIR spectra were recorded on a Nicolet 6700 spectrometer. UV-vis spectra were obtained by using a SHIMADZU UV-2600 spectrophotometer. Imaging of the material morphologies was obtained using SEM (QUANTA450) and TEM (Tecnai G2 Spirit TEM).

3. Electrode Preparation and Electrochemical Testing

CV was conducted at a scan rate of 50 mV s⁻¹ while LSV and Tafel plots were conducted at a scan rate of 5mV s⁻¹. EIS was recorded under the following conditions: AC voltage amplitude 5 mV, frequency ranges 10⁵ to 0.1 Hz, and open circuit. The calculate overpotentials, the measured electrode potentials were first converted to potentials vs. RHE using: $E_{Measured}(RHE) = E(Ag/AgCl) + 0.210$ V. The thermodynamic potential for the OER was calculated by correcting the standard potential for the pH of the solution: $E_{Thermodynamic}(RHE) = E^{\circ} - 0.059 \times pH$. The overpotentials were corrected for contact resistance and calculated using: $\eta = E_{Measured}(RHE) - E_{Thermodynamic}(RHE) - iR^2$, 3.

NG hydrogel performance tests. To determine the optimal nitrogen doping content, NG samples were firstly tested on glassy carbon electrode by the following procedure. Specifically, 2.1 mg of NG hydrogel catalyst and 210 μ l of 1 wt% Nafion solution were dispersed in 840 μ l of 3:1 IPA solution to obtain a dispersion of 2 mg catalyst per ml. These samples were then sonicated for 30 min to form a homogeneous ink. 20 μ l of the ink (containing 40 μ g of catalyst) was then loaded

onto a glassy carbon electrode (GCE) of 5 mm in diameter to obtain a loading of ~0.2 mg/cm² and left to dry. Electrochemical characterisation was performed using a standard three-electrode cell with a 760 workstation (Pine Research Instruments, US). The GCE served as the working electrode of the three-electrode cell. Platinum (Pt) wire acted as a counter electrode and Ag/AgCl/KCl (3 M) acted as a reference electrode. The electrolyte used in the cell was a 1 M KOH solution and was prepared using Milli-Q water (18 M Ω cm⁻¹) and KOH pellets (99.99% weight, Sigma-Aldrich). The best performing N-graphene hydrogels would then be used to support the cobalt nanoclusters in the NF composite.

 IrO_2 performance test: Electrochemical testing of IrO_2 was conducted in the similar condition to that of NG hydrogel except that the electrolyte used was 0.1 M KPi solution (pH 7).

NGCo electrode testing. Electrochemical testing of the NGCo-NF composite was carried out in the same manner as testing of the NG hydrogel. However, the working electrode of this cell was a sample of the composite NGCo-NF and a graphite rod was used as the counter electrode. The electrolyte used in the cell was 0.1 M KPi solution (pH 7) and was prepared in the same manner as the KPi solution used for the cobalt electrolyte

II. Supplementary Results



Figure S1. SEM (A) and TEM (B) images of individual graphene.



Figure S2. XPS spectrum of N-doped graphene hydrogel.



Figure S3. EDS spectrum of NGCo.



Figure S4. TEM elemental mapping displaying the distribution of N (white), C (magenta), Co (blue) and O (green) within NGCo.



Figure S5. (A) The amount of cobalt deposited in-situ onto the NG hydrogels vs. deposition time.(B) LSV plot of NGCo; inset shows corresponding data re-plotted as a function of overpotential, η.

The amount of cobalt deposited was calculated using Faraday's law. The charge, Q, passed was calculated from the i-T curves (Figure 4A).

$$Q = \int_{0}^{t} I(t).dt$$
$$n = \frac{Q}{F}$$

where:

I(t) = the i-T curve functiont = deposition time (s)n = amount of cobalt deposited (mol)

F = Faraday's constant = 9.6485 × 10⁴ C/mol



Figure S6. LSV plot of IrO₂ at 5 mV s⁻¹ in Kpi electrolyte



Figure S7. LSV plot of NGCo before and after 12 h amperometric test.



Figure S8. Optical image of the three electrode cell with (A) GCE as the working electrode for NG hydrogel testing and (B) NGCo-NF as the working electrode for NGCo testing.



Figure S9. Catalytic current density at 1 V vs. Ag/AgCl of NG hydrogels prepared with different type and amount of nitrogen precursor used in the hydrothermal treatment.



Figure S10. CV plots of the 1st (black line) and 20th (red line) cycles for NG hydrogels (**A**) prepared using 75 wt% ammonia in the hydrothermal mixture (75-NH3) and (**B**) prepared using 45 wt% ethylenediamine in the hydrothermal mixture (45-EDA).

Table S1. D and G peak intensity ratios for Raman spectra of GCo, NG, NGCo and NGCo (Dry) samples.

Material	D Shift (cm ⁻¹)	G Shift (cm ⁻¹)	I _D	I _G	I _D /I _G
GCo-NF	1350	1599	1538.7	1070.5	1.44
NG-NF	1354.7	1599.2	325.2	282.9	1.15
NGCo-NF	1351.5	1591.5	1467.3	1297.9	1.13
NGCo-NF (Dry)	1348	1596	1847.3	1406.9	1.31

Table S2. Volumes of ethylenediamine or ammonia precursor added to each sample.

			N-Precursor 1	N-Precursor 2
Sample No	Mass GO prese nt (mg)	N- Precu rsor (wt%)	Volume Ethylenediamine Added (µL)	Volume NH₄OH (30wt%) Added (µL)
1	4	0	0	0
2	4	15	1	2.5
3	4	30	2	5
4	4	45	3.5	10
5	4	60	6.5	20
6	4	75	13.5	40
7	4	90	40	120

Reference

- S1. W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc, 1958, 80, 1339-1339.
- S2. M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei and H. J. Dai, *J. Am. Chem. Soc*, 2013, **135**, 8452-8455.
- S3. C. C. L. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, J. Am. Chem. Soc, 2013, 135, 16977-16987.