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# sp-hybridized nitrogen doped graphdiyne for high-performance Zn-air batteries

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## Synthesis

**Synthesis of bulk graphdiyne (BGDY).** BGDY was synthesized on the surface of copper by cross-coupling reaction according to previous work.[1]

**Synthesis of few-layer graphdiyne oxide (FLGDYO).** FLGDYO was exfoliated from BGDY.[2]

**Synthesis of NFLGDY-650.** 20 mg of lyophilized FLGDYO was located in the center of tubular furnace, and 1.0 g of melamine was situated at the upstream of tubular furnace. After annealing in Ar at 650 °C for 3 h with a heating rate of 10 °C/min, the resulting NFLGDY-650 was obtained.

**Synthesis of sp-NFLGDY-900.** 20 mg of lyophilized FLGDYO was located in the center of tubular furnace, and 1.0 g of melamine was situated at the upstream of tubular furnace. After replacing the air by Ar, the valve of tube furnace is closed and then conducted the annealing process, thus affording continuously high concentration of doping sources (reactant). Then the reaction moves towards the positive direction, increasing the doping concentration. After annealing at 900 °C for 3 h with a heating rate of 10 °C/min, open the Ar gas line and cool down, the resulting sp-NFLGDY-900a was obtained. To control the sp-N content, sp-NFLGDY-900b and sp-NFLGDY-900c are fabricated by annealing FLGDYO (20 mg) with 600 mg and 200 mg of melamine, respectively.

**Synthesis of NFLGDY-900$NH_3$.** 20 mg of lyophilized FLGDYO was located in the center of tubular furnace, annealing in $NH_3$ for 3h at 900 °C. The final sample was denoted as NFLGDY-900$NH_3$.

## Structural characterization

TEM images were obtained with an FEI Tecnai F20 instrument operated at 200 kV. SEM images were acquired on a JSM-6700 microscope operated at 5.0 kV. XPS data were achieved using an ESCALab220i-XL electron spectrometer (VG Scientific) and 300-W Al Ka radiation. The binding energies in the XPS analysis were standardized with respect to C1s (284.8 eV). Powder XRD patterns were obtained using a PANalytical X'Pert PRO MPD apparatus [Cu Ka radiation ($\lambda$= 1.5405 Å)] operated at 40 kV and 30 mA. Raman spectra were executed on a JY-T64000 instrument with an argon ion laser at 532 nm as the excitation source. N K-edge XAS measurement were performed at the beamline BL10B in Hefei Synchrotron Radiation Facility, National Synchrotron Radiation Laboratory (NSRL).

**Electrochemical characterization**

**ORR tests.** The electrochemical ORR measurements were conducted with a three-electrode cell (Pine Research Instrumentation, USA). Ag/AgCl (saturated KCl) was used as the reference electrode, graphite rod was acted as counter electrode, and a rotating disk electrode (RDE, 5 mm in diameter) was served as the working electrode. Firstly, the glassy carbon electrode was polished and rinsed. Then the homogeneous ink was loaded onto the glassy carbon electrode with 5 mg catalyst dispersing in water (0.48 mL), isopropanol (0.15 mL), and Nafion (5 wt%, 70 μL). The loading amount is about 0.36 mg $cm^{-2}$. As comparison, the mass loading of Pt/C is about 0.1 mg $cm^{-2}$. All potentials in this work were calibrated to the reversible hydrogen electrode (RHE), $E_{RHE} = E_{Ag/AgCl} + 1.058$ V. All measurements were performed at a scan rate of 10 mV $s^{-1}$.

**Zn-air tests.** A home-made aqueous zinc-air battery was assembled for battery performance, in which a polished zinc foil was used as the anode. The carbon fiber paper with a gas diffusion layer serves as the air cathode. A homogeneous ink was obtained with 4 mg of catalyst, 0.8 mL of isopropanol, and 5 wt% of Nafion, and the ink was sprayed on carbon paper with a mass loading of 1 mg $cm^{-2}$. The effective contact area on air cathode is 1 $cm^2$. The electrolyte was 6.0 M KOH. Electrochemical tests were performed on electrochemical workstation (CHI 760E, CH Instrument).

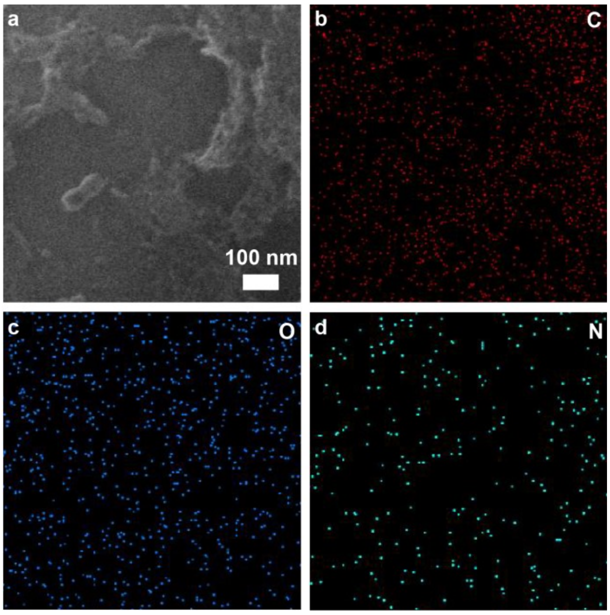


**Figure S1.** Element distribution of the sp-NFLGDY-900b, including C element, O element, and N element.

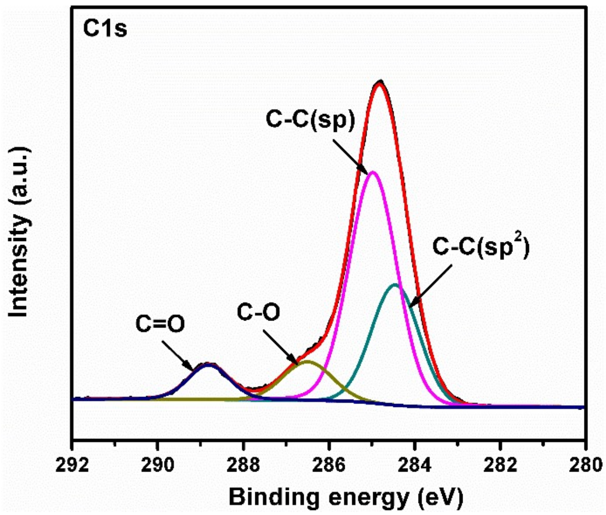


**Figure S2.** High-resolution C1s XPS spectra of pristine GDY.

The fitted characteristic peaks of C-C ($sp^2$), C-C (sp), C-O, and C=O are located at 284.5 eV, 285.0 eV, 286.5 eV, and 288.8 eV, respectively.

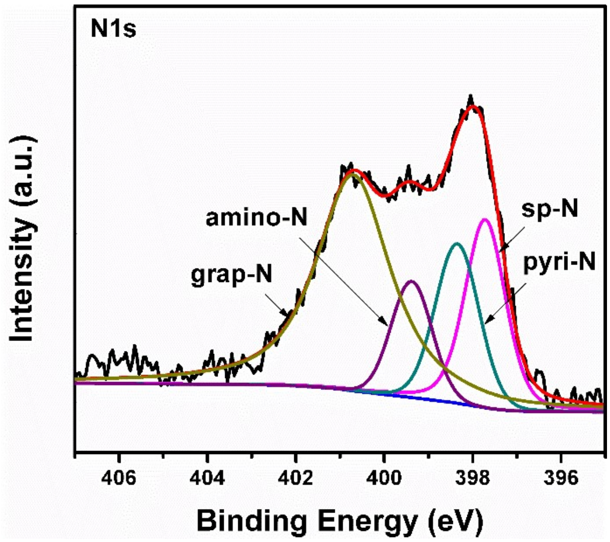


**Figure S3.** High-resolution N1s XPS spectra of sp-NFLGDY-900b.

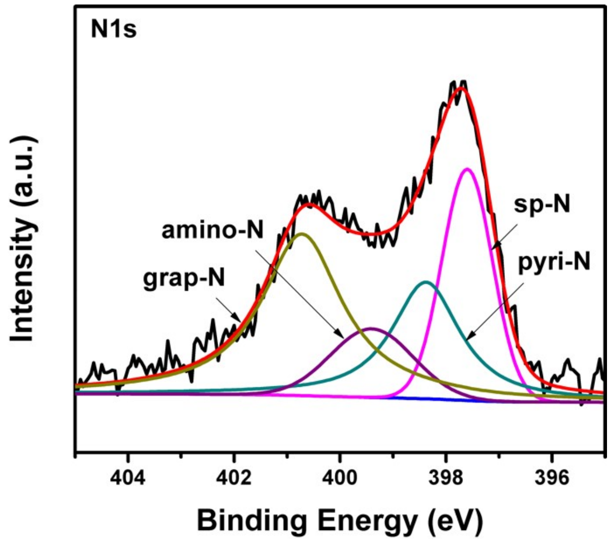


**Figure S4.** High-resolution N1s XPS spectra of sp-NFLGDY-900c.

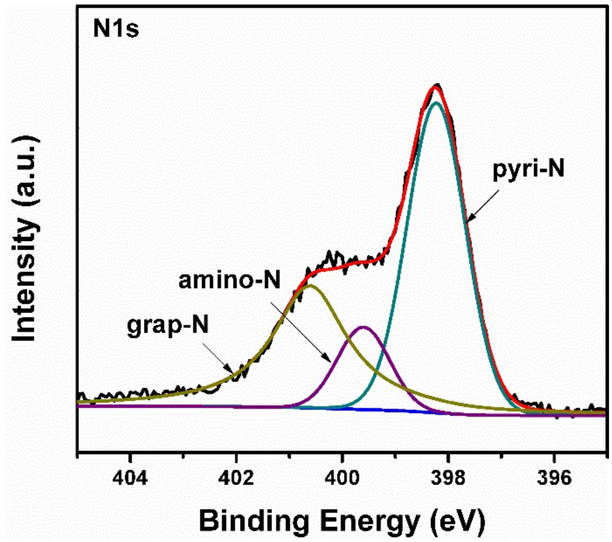


**Figure S5.** High-resolution N1s XPS spectra of NFLGDY-650.

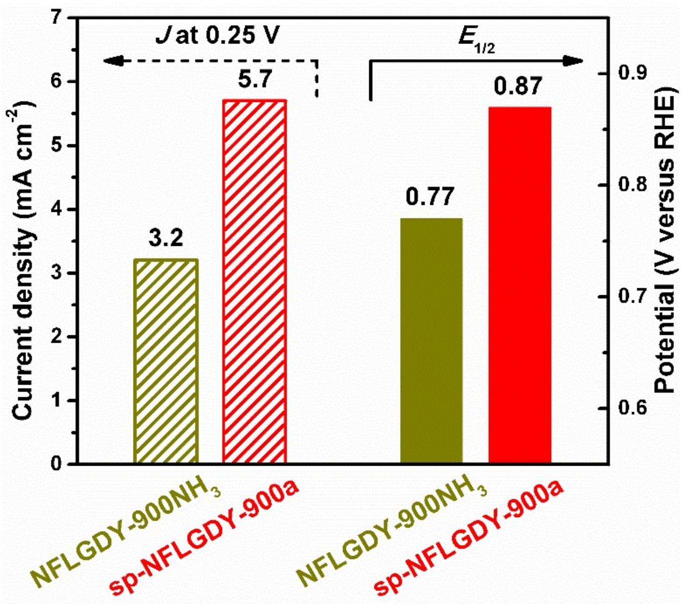


**Figure S6.** Values of $J$ at 0.25 V and $E_{1/2}$ of NFLGDY-900$NH_3$ and sp-NFLGDY-900a.

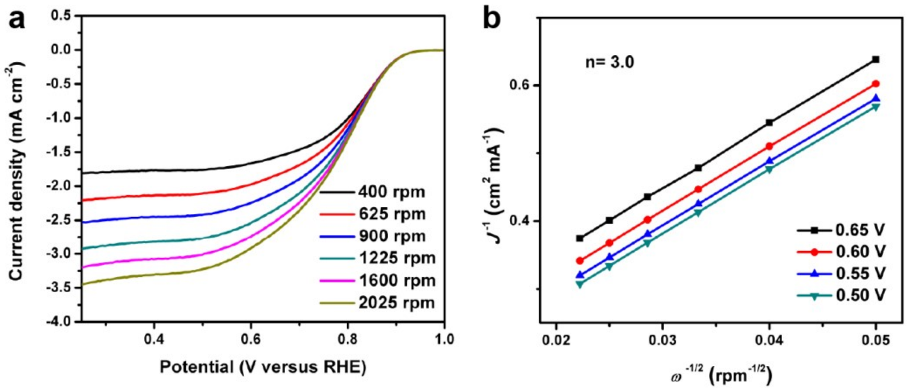


**Figure S7.** (a) Rotating disk voltammograms of NFLGDY-900NH$_3$ in $O_2$-saturated 0.1 M KOH at various rotation rates. (b) is Koutecky-Levich plots, and n denotes the electron transfer number.

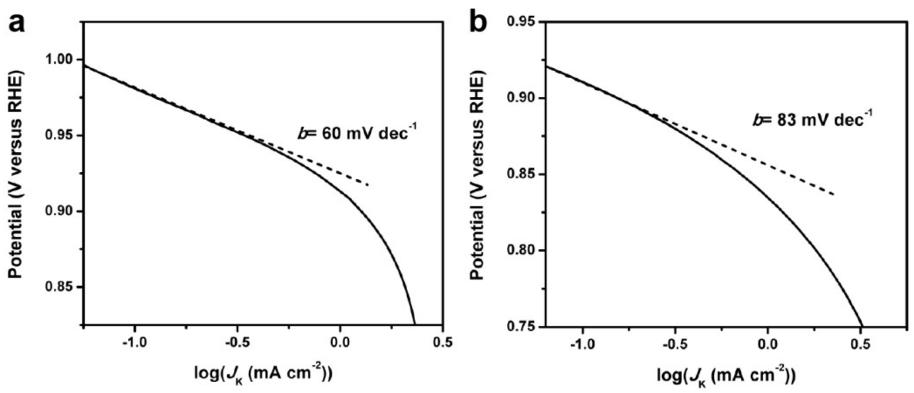


**Figure S8.** (a) Tafel plot of sp-NFLGDY-900a, where b denotes the value of Tafel slope. (b) Tafel plot of NFLGDY-900NH$_3$.

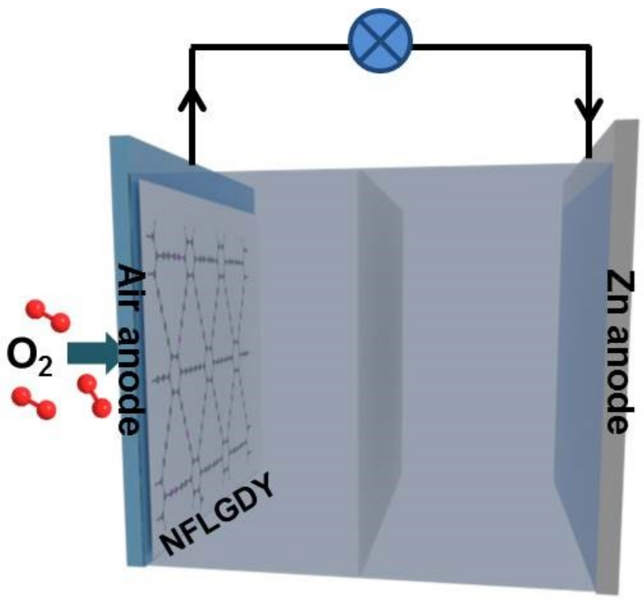


**Figure S9.** Illustration of the basic configuration of primary Zn-air battery.

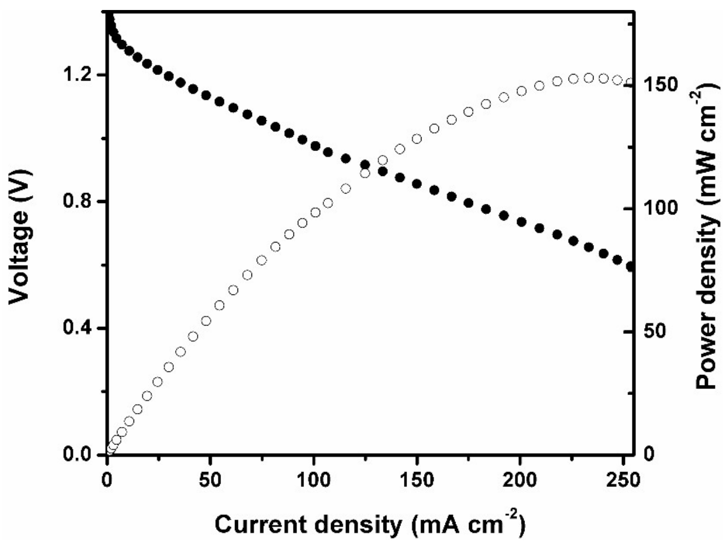


**Figure S10.** Polarization curve and power density curve of NFLGDY-900$NH_3$.

**Table S1.** The content of different N configuration in various samples obtained from XPS.

| Sample | N (at%) | sp-N (at%) | pyri-N (at%) | amino-N (at%) | grap-N (at%) |
|---|---|---|---|---|---|
| NFLGDY-650 | 8.41 | - | 4.20 | 1.00 | 3.21 |
| NFLGDY-900$NH_3$ | 4.88 | - | 1.71 | 1.07 | 2.10 |
| sp-NFLGDY-900a | 9.07 | 2.09 | 1.81 | 1.63 | 3.54 |
| sp-NFLGDY-900b | 8.47 | 1.69 | 1.44 | 0.93 | 4.41 |
| sp-NFLGDY-900c | 4.04 | 0.97 | 0.97 | 0.44 | 1.66 |

**Table S2.** ORR performance of the electrocatalysts.

| Sample | Onset potential (V) | $E_{1/2}$ (V) | $J$ at 0.25 V (mA $cm^{-2}$) |
|---|---|---|---|
| NFLGDY-650 | 0.89 | 0.77 | 3.52 |
| NFLGDY-900$NH_3$ | 0.90 | 0.77 | 3.20 |
| sp-NFLGDY-900a | 0.98 | 0.87 | 5.70 |
| sp-NFLGDY-900b | 1.01 | 0.86 | 4.85 |
| sp-NFLGDY-900c | 0.96 | 0.77 | 3.87 |
| Pt/C | 1.01 | 0.86 | 5.42 |

**Table S3.** Performance comparison of the Zn-air batteries with different catalysts.

| Catalysts | Open Circuit Voltage (V) | Peak Power Density (mW $cm^{-2}$) | Ref. |
|---|---|---|---|
| **sp-NFLGDY-900a** | **1.503** | **195.7** | **This work** |
| Pd/N doped hydrogen-substituted graphyne | 1.519 | 143 | J. Mater. Chem. A, 2021, 9, 14507. |
| N doped graphdiyne | 1.54 | 84 | Nano Energy 2021, 85, 106024. |
| pyridinc N-graphdiyne | 1.51 | 130 | Appl. Catal. B: Environ., 2020, 261, 118234. |
| nitrogen-doped carbon nanotubes/graphene | 1.48 | 253 | Adv. Funct. Mater. 2020, 30, 1906081. |
| graphene hydrogel/B-doped graphene quantum dots | 1.40 | 112 | Adv. Energy Mater. 2019, 9, 1900945. |
| pyridinic-N-doped defective graphene | 1.45 | 115.2 | ACS Energy Lett. 2018, 3, 1183. |
| carbon fiber@porous carbon | - | 91.4 | Energy Storage Mater. 2018, 15, 124. |
| carbon nanotube assembly | 1.41 | 157.3 | Nano Energy 2017, 39, 626. |

**Reference**

1. Li, G.; Li, Y.; Liu, H.; Guo, Y.; Li, Y.; Zhu, D. Architecture of graphdiyne nanoscale films. *Chem. Commun.* **2010**, 46, 3256-3258.

2. Zhao, Y.; Wan, J.; Yao, H.; Zhang, L.; Lin, K.; Wang, L.; Yang, L.; Liu, L.; Song, L.; Zhu, J.; Gu, L.; Liu, L.; Zhao, H.; Li, Y.; Wang, D. Few-layer graphdiyne doped with sp-hybridized nitrogen atoms at acetylenic sites for oxygen reduction electrocatalysis. *Nat. Chem.* **2018**, 10, 924-931.