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Supplementary Information

Single atom Ce catalysts for rechargeable Zn−Air batteries

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1. Materials Synthesis

Graphene oxide (GO) was synthesized according to the method described in the literature.[1] 100 mg of GO and 3.1 mg of $Ce(NO_3)_3\cdot 6H_2O$ were dispersed into 50 mL of deionized water, and a uniformly dispersed suspension was obtained by ultrasound for 30 min. After removing the water by a rotary evaporation, a black solid $Ce(NO_3)_3$-GO was obtained. The target catalyst Ce_1-NG-800 was obtained by annealing the mixture of $Ce(NO_3)_3$-GO and melamine powder in a tube furnace at 800 °C in a nitrogen atmosphere for 2 h, and the heating rate was 10 °C/min. By changing the calcination temperature and doping amount, a series of catalysts were synthesized, namely x-Ce_1-NG-T, where X = 0.8, 1.0, 1.2, and 1.5 wt.%, and T = 600, 700, 800, and 900 °C.

The synthesis of control sample Ce_1-G was as follows: $Ce(NO_3)_3$-GO was directly calcined in a tubular furnace at 800 °C for 2 h. Without the addition of $Ce(NO_3)_3$ precursor, the mixture of GO and melamine powder was calcined in a tube furnace to obtain NG. Without adding both $Ce(NO_3)_3$ and melamine powder, G was obtained under the same conditions.

2. Electrocatalytic characterization

The oxygen reduction performance was tested with a rotating ring-disc electrode (RRDE) and CHI 760E electrochemical workstation, in which the counter electrode is platinum wire, the reference electrode is calomel electrode, and the electrolyte is 0.1 M KOH. Uniform catalyst ink was obtained by dispersing 4 mg catalyst in 400 μL 0.25% nafion/ethanol solution with 30 min of ultrasound. The electrochemical test was carried out by adding 6 μL of catalyst ink to a RRDE with a diameter of 4 mm. Linear sweep voltammetry (LSV) curve was performed at a sweep speed of 5 mV s^{-1} at rotation rate of 1600 rpm. The cyclic voltammetry (CV) curve was performed during the kinetic region (0.6 V-1 V) at a sweep speed of 50 mV s^{-1}. The i-t stability test was performed at 0.6 V.

According to the LSV curves collected at different rotation rates (900, 1225, 1600, 2025, and 2500 rpm), the electron transfer number (n) was calculated from the slope of the K-L equation by their Koutecky-Levich (K-L) diagram (J^{-1} vs. $w^{-1/2}$) linear fit line:

$$\frac{1}{j}=\frac{1}{J_k}+\frac{1}{J_L}=\frac{1}{J_k}+\frac{1}{0.62nFAC_0D_0^{\frac{2}{3}}v^{-\frac{1}{6}}w^{\frac{1}{2}}}$$

The hydrogen peroxide yield (H_2O_2) and electron transfer numbers (n) were obtained from the RRDE using the following equations:

$$n=4\frac{I_D}{I_D+(I_R\,/\,N)}$$

$$H_2O_2=200\frac{I_R\,/\,N}{I_D+(I_R\,/\,N)}$$

The oxygen evolution performance was tested under the same conditions with 0.1 M KOH as electrolyte. Linear sweep voltammetry (LSV) curve was performed at a sweep speed of 5 mV s^{-1}.

3. Zinc–air battery testing

Zn-air battery performances were assessed in 6 M KOH + 0.2 M $Zn(Ac)_2$ on a battery test system (LANHE CT2001A). The anode comprised of a polished zinc plate (0.5 mm in thickness), whereas the cathode was crafted by applying the catalyst ink onto a 1 cm^2 composite carbon substrates surface, achieving a loading of 1 mg cm^{-2}. Catalyst ink was prepared by mixing 100 μL of 1 % Nafion/ethanol solution, 500 μL of ethanol and 2 mg catalyst. The polarization curve was measured at a scan rate of 10 mV s^{-1}. The galvanostatic recharge/discharge cycling measurements were collected at a current density of 5 mA cm^{-2} with each charge and discharge cycle lasting 20 minutes.

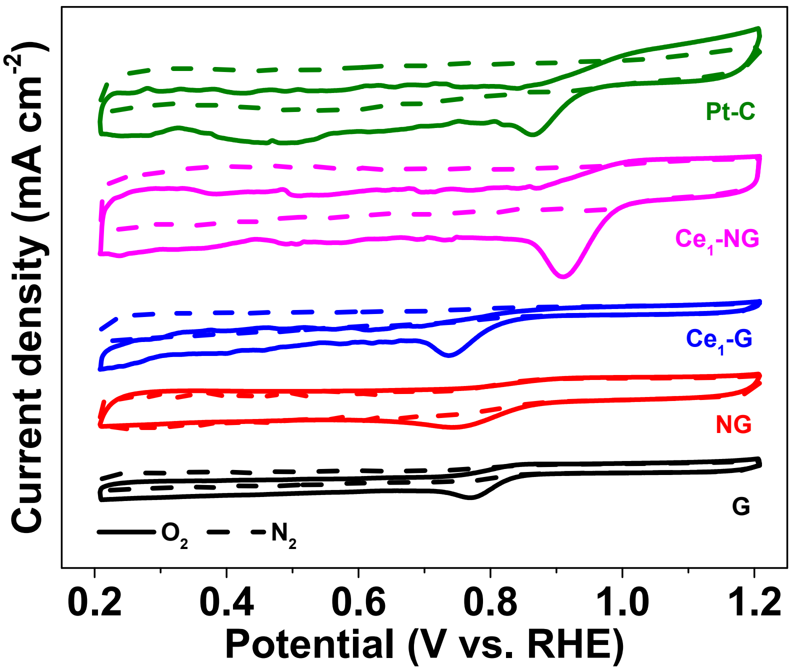

Fig. S1. CV curves of G, NG, Ce$_1$-G, Ce$_1$-NG and Pt-C in N$_2$- and O$_2$-saturated 0.1 M KOH (dashed lines: N$_2$; solid lines: O$_2$).

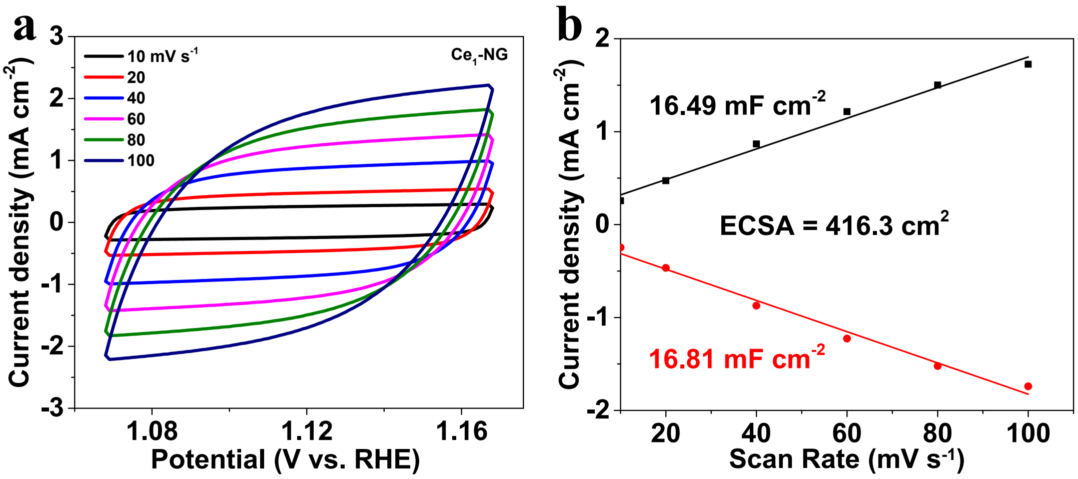

Fig. S2. (a) CVs of Ce$_1$-NG measured in a non-Faradaic regionat scan rate of 10 mV s^{-1}, 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, and 100 mV s^{-1}. (c) Capacitive *j* vs scan rate.

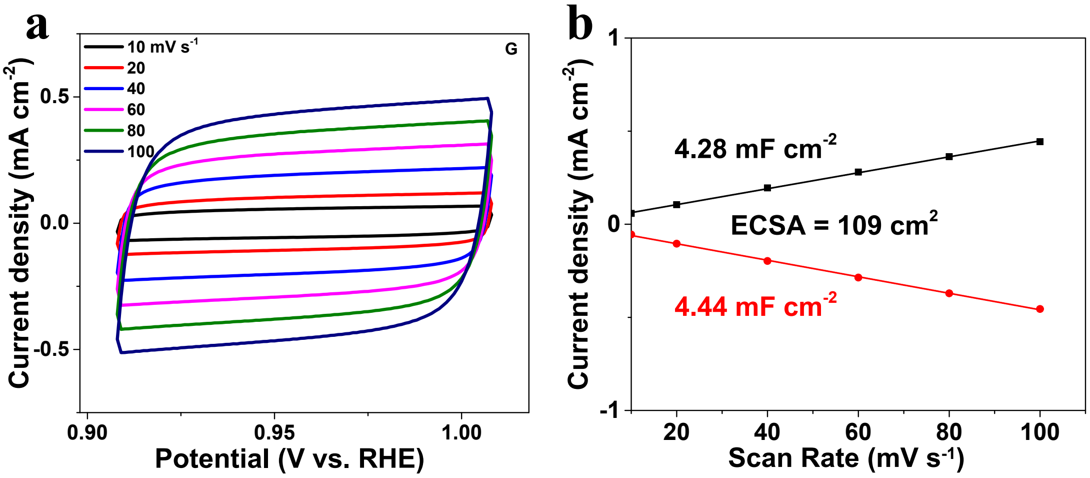

Fig. S3. (a) CVs of G measured in a non-Faradaic regionat scan rate of 10 mV s^{-1}, 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, and 100 mV s^{-1}. (c) Capacitive *j* vs scan rate.

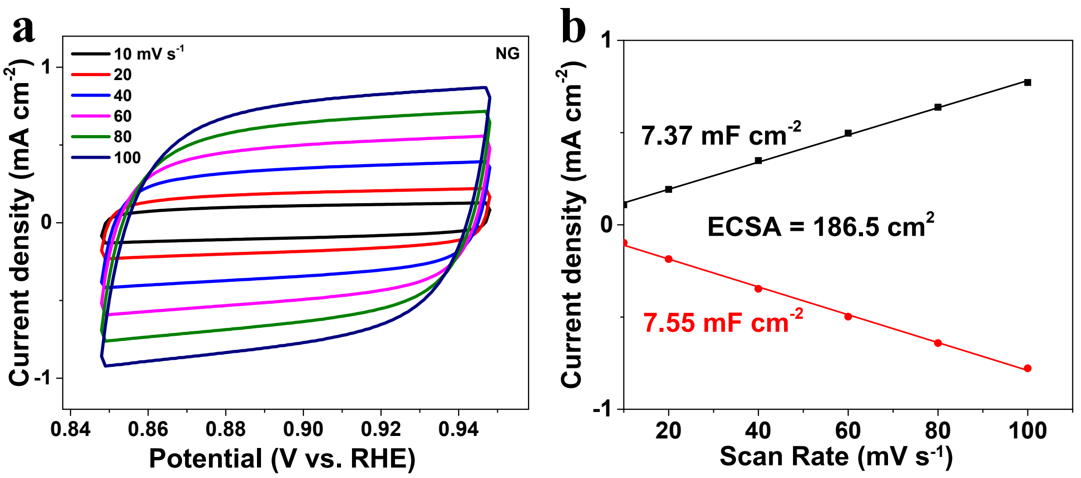

Fig. S4. (a) CVs of NG measured in a non-Faradaic regionat scan rate of 10 mV s^{-1}, 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, and 100 mV s^{-1}. (c) Capacitive *j* vs scan rate.

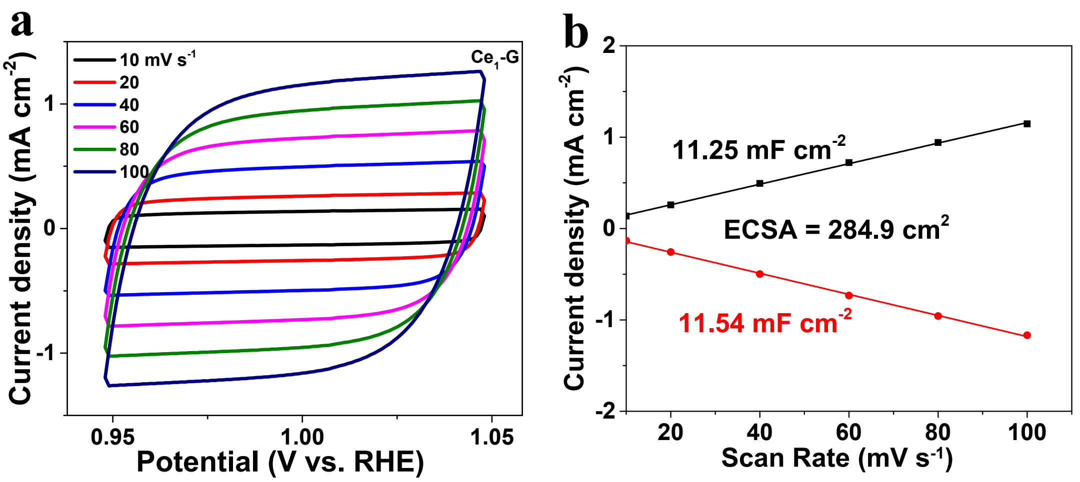

Fig. S5. (a) CVs of Ce$_1$-G measured in a non-Faradaic regionat scan rate of 10 mV s^{-1}, 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, and 100 mV s^{-1}. (c) Capacitive *j* vs scan rate.

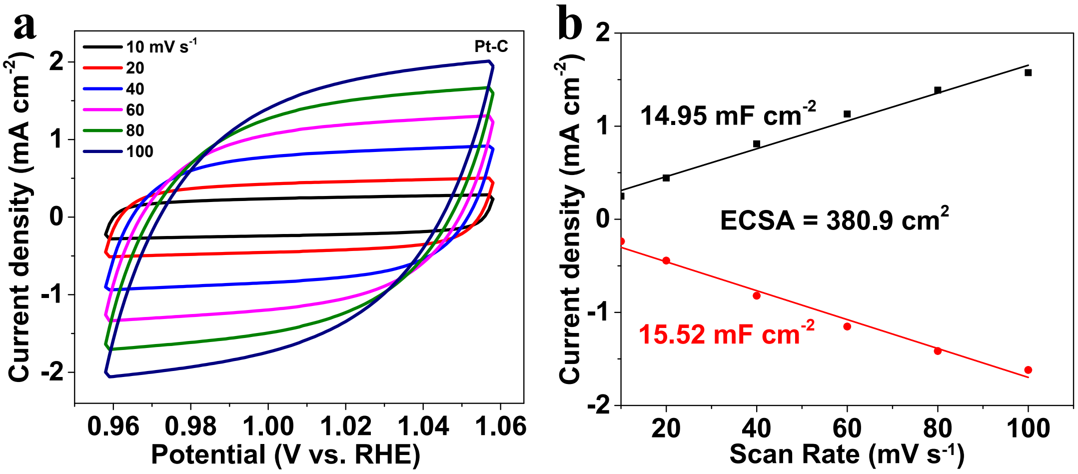

Fig. S6. (a) CVs of Pt-C measured in a non-Faradaic regionat scan rate of 10 mV s^{-1}, 20 mV s^{-1}, 40 mV s^{-1}, 60 mV s^{-1}, 80 mV s^{-1}, and 100 mV s^{-1}. (c) Capacitive *j* vs scan rate.

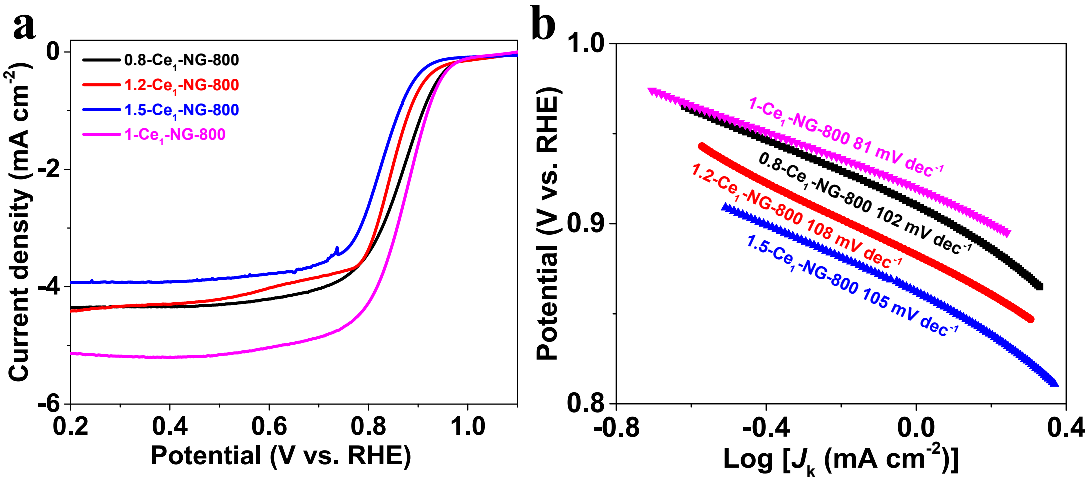

Fig. S7. (a) ORR polarization curves of x-Ce$_1$-NG-800, where x = 0.8, 1.0, 1.2, and 1.5 wt.%. (b) Tafel slopes.

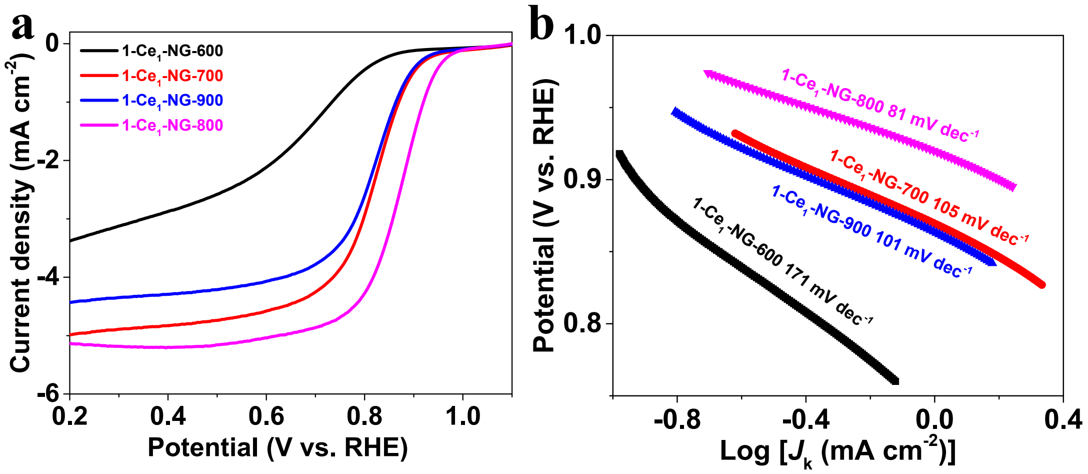

Fig. S8. (a) ORR polarization curves of 1-Ce$_1$-NG-T, where T = 600, 700, 800, and 900 °C. (b) Tafel slopes.

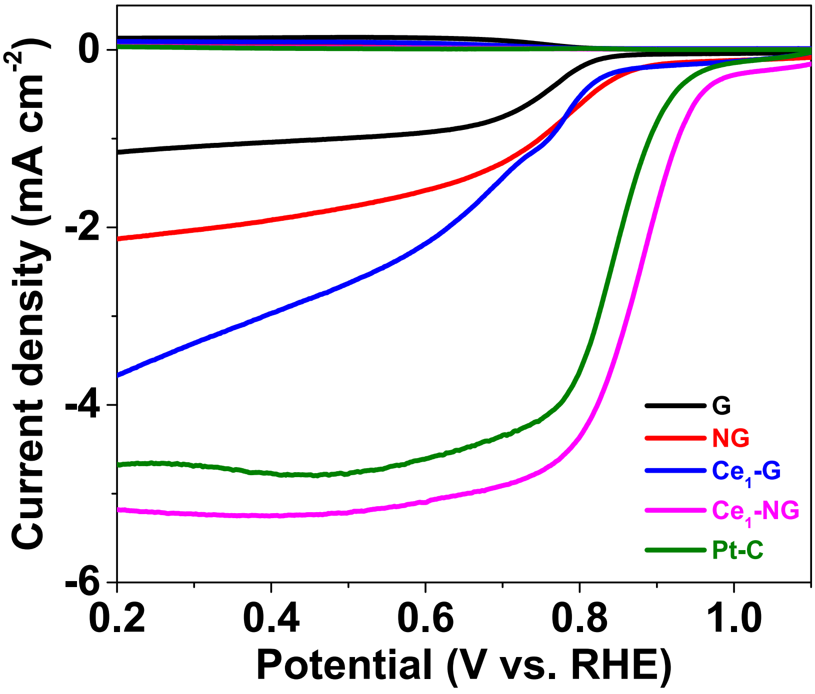

Fig. S9. Rotating ring-disk electrode voltammogram of G, NG, Ce$_1$-G, Ce$_1$-NG, and Pt/C for ORR in 0.1M KOH solution at a rotation rate of 1600 rpm.

References

1. J. Guan, Z. Duan, F. Zhang, S. D. Kelly, R. Si, M. Dupuis, Q. Huang, J. Q. Chen, C. Tang and C. Li, Water oxidation on a mononuclear manganese heterogeneous catalyst, *Nat. Catal.*, 2018, **1**, 870-877.