

Electronic Supplementary Information

Iridium Incorporated in Deoxygenated Hierarchical Graphene as a High-Performance Cathode for Rechargeable Li-O₂ Battery

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Experimental Section

Synthesis of DHG Synthesis of DHG was described in our previous work. Firstly, graphene oxide was prepared by one modified hummers method. And then the as-prepared graphite oxide (1g) was put into an autoclave (100 ml) that was connected to a high vacuum pump by a steel tube. After the barometer on the steel tube line pointing to -1 bar, the autoclave was introduced into a muffle furnace under 900 °C for 2 minute. During the exfoliation process, the high vacuum pump was still operating. The obtained graphene was heated to 900 °C at 5 °C min⁻¹ from room temperature, and held for 4 h in argon atmosphere to prepare deoxygenated hierarchical graphene (DHG).

Synthesis of Ir@DHG Iridium was introduced via a facile ethylene glycol reducing method that 85 mg chloroiridic acid (Ir content 35 wt%, Sino-Platinum metals Co.,LTD) and 35 mg DHG was mixed in 50 ml ethylene glycol, and then 5 mL 1M NaOH was added under stirring. The mixed solution was stirred for 15 min at room temperature, subsequently heated under reflux to 130 °C for 3h. After cooling to room temperature, 5 ml 1M HCl was added and the solution was stirred for 12 h. Then another 5 mL 1M HCl was added and stirred for another 12 h. All the experiments were conducted under N₂ atmosphere. The resulting solution was filtered, washed and dried to obtain Ir@DHG. At last, Ir@DHG was heat treated under H₂/Ar atmosphere at 300 °C for 3 h to enhance the combination between iridium

nanoparticles and graphene. The iridium content in Ir@DHG was measured by thermogravimetric analysis in air flow and the value is 36.5 wt%.

Physical Characterization Scanning electron microscopy (SEM) was conducted on QUANTA 200F (FEI) at an acceleration voltage of 20 kV. X-ray photoelectron spectroscopy was carried out on a surface analysis system (ESCALAB250) equipped with monochromatic Al-K alpha radiation. All of the XPS spectra were peak fit and analyzed using XPS Peak4.1 and the spectra were calibrated according to the C1s peak (284.6 eV). N₂ adsorption/desorption was tested at 77 K using an ASAP 2020 system. Brunauer-Emmett-Teller (BET) method was applied to determine the surface area. Pore volumes and the pore size distribution (PSD) curves were calculated from the desorption branches using the Barrett-Joyner-Halenda (BJH) model. X-ray diffraction was recorded on DX-2700 x-ray diffractometer. Transmission electron microscopy was detected by Tecnai G2 Spirit (FEI) at an acceleration voltage of 120 kV. Thermogravimetric analysis was carried out on Thermogravimetric/Differential Thermal Analyzer (Pyris Diamond TG/DTA) with a heating rate of 5 °C min⁻¹ from 50 °C to 800 °C in air flow.

Electrochemical Measurements The cathode was prepared by mixing 10 mg DHG (or 15.7 mg Ir@DHG) with PTFE solution (5 wt. %, 50 mg) in propylene glycol (5 ml) by means of ultrasonic dispersion. The resulting slurry was coated on the carbon paper (16 mm in diameter) with a loading of 0.05 mg_{graphene} per electrode. The coated electrode was dried for 24h at 80 °C under vacuum to remove residual solvent. The electrochemical cells used to investigate discharge/charge performance were based on a modified swagelok design. The single cell was assembled with the cathode, a lithium anode (16 mm in diameter, 40 um in thickness) and a glass filter (Whatman) in a glove box (H₂O<1 ppm, O₂<1 ppm). The electrolyte used here was 0.1 M LiClO₄ in tetraethylene glycol dimethyl ether/dimethylsulfoxide (volume ratio 1:2). A stainless spring was used to ensure good contact of every cell parts. Except for the oxygen inlet and outlet, the cell was completely sealed. The discharge/charge performance was recorded by LAND 2100 system (Wuhan, China). The electrochemical impedance spectroscopy (EIS) was measured by Solarton 1287 test system in a frequency range of 10⁵ Hz to 10⁻¹ Hz.

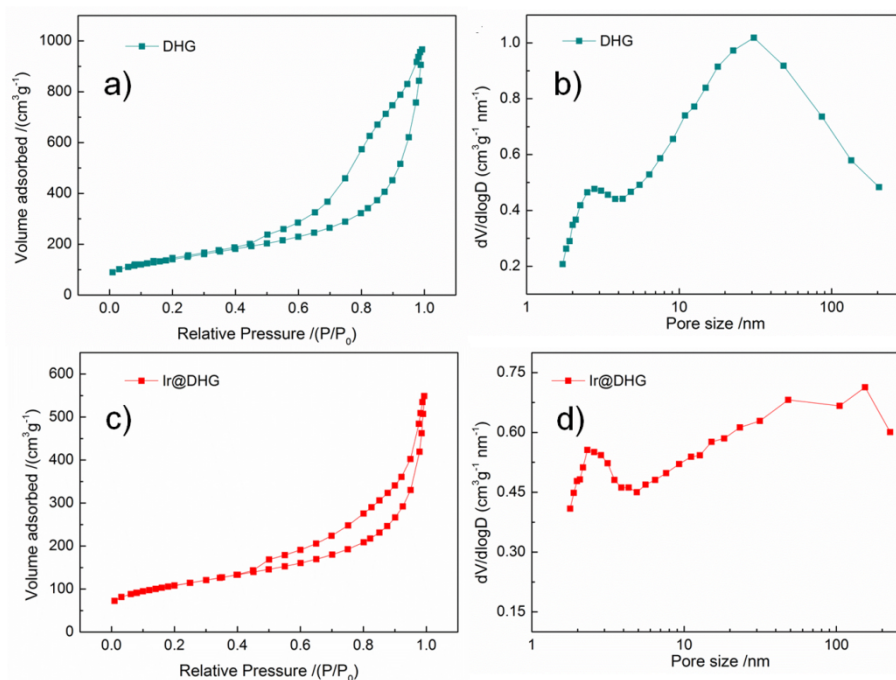


Figure S1 Nitrogen adsorption-desorption isotherms of DHG (a) and Ir@DHG (c), and the corresponding pore size distribution curves of DHG (b) and Ir@DHG (d).

Table S1 The surface area and pore volume parameters for DHG and Ir@DHG, respectively.

	Surface area($\text{m}^2 \text{g}^{-1}$)	Pore Volume($\text{cm}^3 \text{g}^{-1}$)
DHG	498.9	1.51
Ir@DHG	372.5	0.83
Ir@DHG (excluding Ir)	583.9	1.31

Ir@DHG has a surface area of $372.5 \text{ m}^2 \text{g}^{-1}$ and a pore volume of $0.83 \text{ cm}^3 \text{g}^{-1}$. For DHG, the surface area is $498.9 \text{ m}^2 \text{g}^{-1}$ and the pore volume is $1.51 \text{ cm}^3 \text{g}^{-1}$. However, when excluding Ir, the pore volume for Ir@DHG is $1.31 \text{ cm}^3 \text{g}^{-1}$, which is 86.8% of DHG suggesting well preserved pore structure during the iridium functionalizing process. And after excluding Ir, the surface area for Ir@DHG is $583.9 \text{ m}^2 \text{g}^{-1}$, which is $85 \text{ m}^2 \text{g}^{-1}$ higher than DHG. We speculate the extra surface area comes from the nanosized iridium particles.

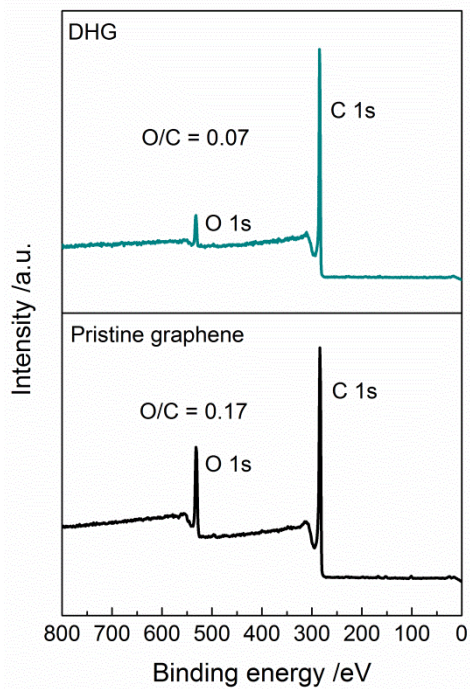


Figure S2 XPS survey of DHG and pristine graphene.

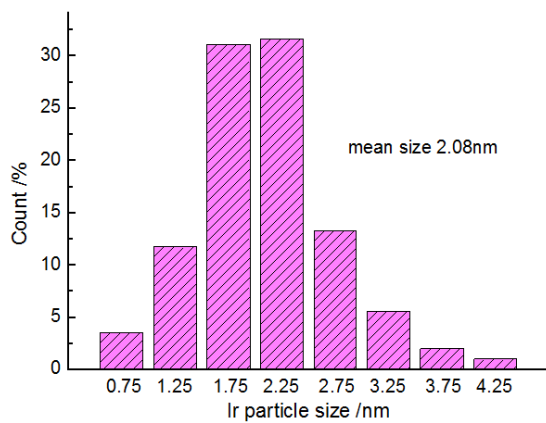


Figure S3 The particle size distribution of iridium in Ir@DHG

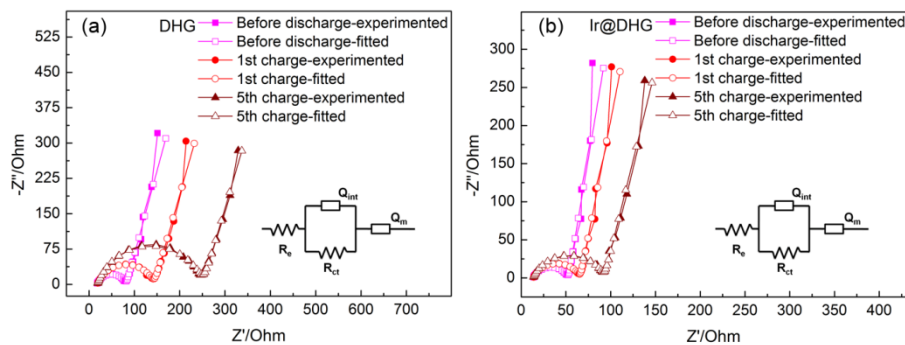


Figure S4 The fitted EIS data for Li-O₂ cells equipped with DHG cathode (a) and Ir@DHG cathode (b), respectively.

Table S2. Equivalent circuit parameters of Li-O₂ cells equipped with DHG cathode and Ir@DHG cathode, respectively.

Sample	R _e /Ω	R _{ct} /Ω
DHG(Before discharge)	17.1	65.1
DHG(1st Charge)	18.3	126.0
DHG(5th Charge)	18.3	233.5
Ir@DHG(Before Discharge)	13.5	39.2
Ir@DHG(1st Charge)	13.6	52.5
Ir@DHG(5th Charge)	13.5	79.4

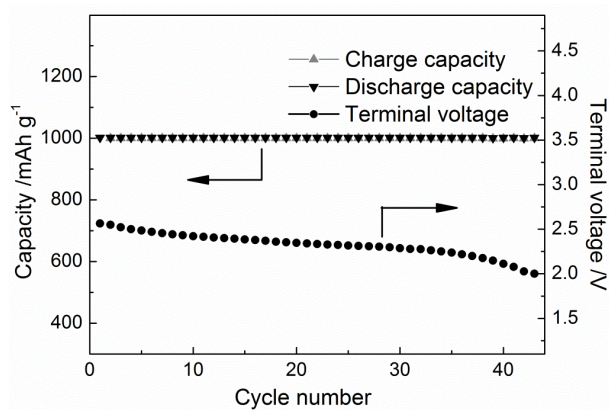


Figure S5 The variation of voltage on the terminal of discharge of Super P cathode under limited capacity of 1000 mAh g⁻¹_{carbon} at a current density of 2000 mA g⁻¹_{carbon}.

Table S3 Summary of electrochemical performance of Li-O₂ batteries based on noble metal catalyst.

Sample	Rate capability/mA g ⁻¹	Cycle performance/ Controlling capacity
3Dom carbon with Pd/FeOx[S1]	100 mA g _{carbon} ⁻¹	68/500 mAh g _{carbon} ⁻¹
TOH Au@SP[S2]	500 mA g _{carbon} ⁻¹	30/1000 mAh g _{carbon} ⁻¹
Au/Super P[S3]	100 mA g ⁻¹ /100 mA g _{carbon} ⁻¹	100/500 mAh g ⁻¹ , 1000 mAh g _{carbon} ⁻¹
Ru@PGE[S4]	200 mA g _{carbon} ⁻¹	100/1000 mAh g _{carbon} ⁻¹
Ru@MWCNTP[S5]	500 mA g ⁻¹ /549 mA g _{carbon} ⁻¹	20/5000 mAh g ⁻¹ , 5494 mAh g _{carbon} ⁻¹
Pt3Co/CNT[S6]	200 mA g _{carbon} ⁻¹	70/1000 mAh g _{carbon} ⁻¹
PdCu/KB[S7]	200 mA g _{carbon} ⁻¹	50/1000 mAh g _{carbon} ⁻¹
Ru-CB[S8]	1000 mA g _{carbon} ⁻¹	100/1000 mAh g _{carbon} ⁻¹
Pt/CNT[S9]	2000 mA g _{carbon} ⁻¹	130/1000 mAh g _{carbon} ⁻¹

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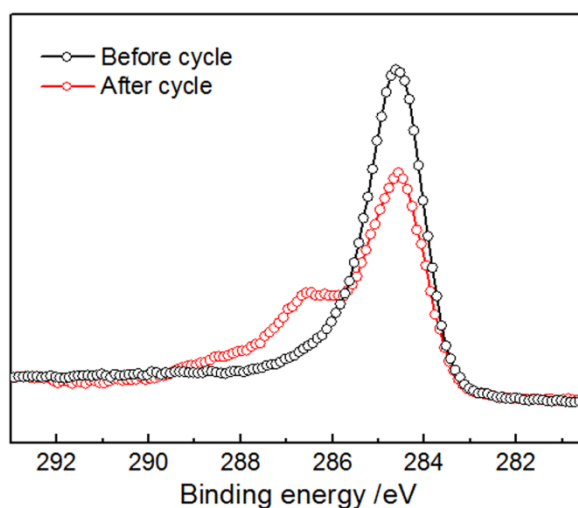


Figure S6 The XPS C 1s spectrum for Ir@DHG before and after cycling test. All the cells were tested at 2000 mA g^{-1} with a limited capacity of 1000 mAh g^{-1} .

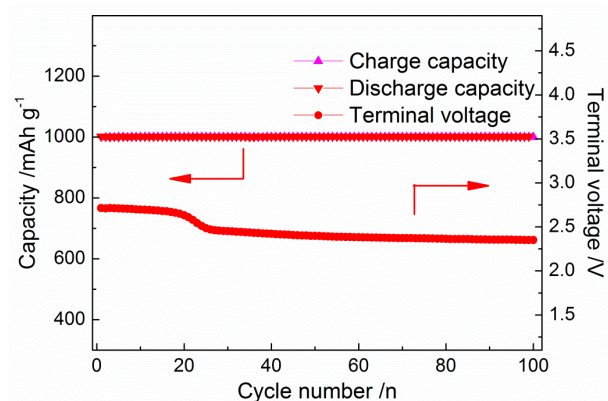


Figure S7 The variation of voltage on the terminal of discharge of Ir@DHG cathode under limited capacity of 1000 mAh g^{-1} carbon at a current density of 5000 mA g^{-1} carbon.

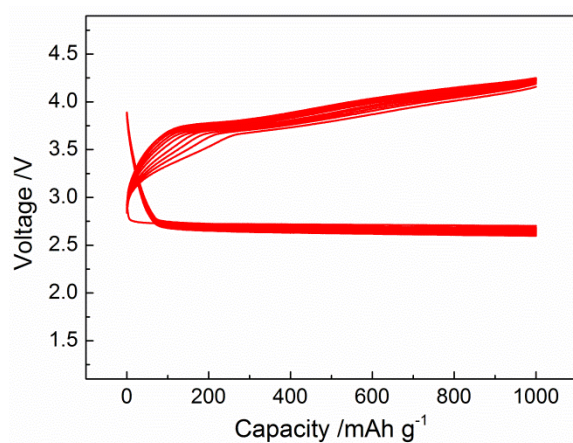


Figure S8. Discharge-charge curves of Li-O₂ cell equipped with Ir@DHG cathode with a loading weight of $0.5 \text{ mg}_{\text{graphene}}$ per electrode at a current density of 200 mA g^{-1} .

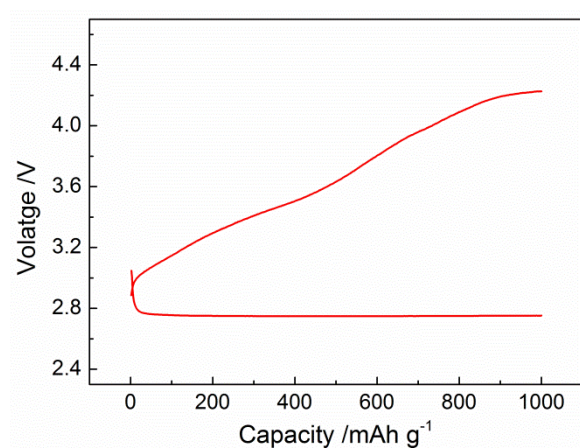


Figure S9. Discharge-charge curve of Li-O₂ cell equipped with Ir@DHG at 1000 mA g^{-1} with a limited capacity of 1000 mA g^{-1} .