

Supporting Information

Metal-Organic-Framework derived Co@CN modified horizontally aligned graphene oxide array as free-standing anode for lithium-ion batteries

Yong Wang,^{a, b} Jiawei Li,^c Xinyang Li,^b Hong Jin,^c Wajid Ali,^b Zhongxiao Song,^a
Shujiang Ding^{b, *}

^a State Key Laboratory for Mechanical Behaviour of Materials, Xi'an Jiaotong University, Xi'an 710049, China

^b Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, Department of Applied Chemistry, School of Chemistry, Xi'an Jiaotong University & Shaanxi Quantong Joint Research Institute of New Energy Vehicles Power, Xi'an Jiaotong University, Xi'an 710049, China

^c Xi'an Jiaotong University Suzhou Academy, Suzhou 215123, China

*E-mail: dingsj@mail.xjtu.edu.cn

Experimental Section

Preparation of ZIF-67. Typically, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.18 g, Aldrich) and 2-methylimidazole (2.62 g, Aldrich) were dissolved in deionized water (40 mL) and stirring for 5 min. The solution was placed at room temperature for 24 h. After that, purple powders were collected by centrifugation, washed several times with deionized water, and dried at 60 °C.

Preparation of GO/Co@CN. First, 100 mg of PVA powders (Aldrich) and 200 mg of GO powers (XFNANO) were added in 20 mL deionized water and magnetic stirring for 4 h. Then, 400 mg of as-prepared purple ZIF-67 powders were added in suspension and magnetic stirring for 1 h. Next, the GO/ZIF-67 composites were collected by centrifugation. Finally, the GO/ZIF-67 composites were annealed at 600 °C to prepare the GO/Co@CN.

Preparation of HAGO. First, 100 mg of PVA powders (Aldrich) and 200 mg GO powers (XFNANO) were added in 20 mL deionized water magnetic stirring for 4 h to form a uniform slurry. Next, the slurry was pour into a freeze device for 5 min, then transferred to freezer dryer for 48 h to remove the ice, and obtained a gray blocky composite (**Figure S12a**). Finally, the blocky composite was cut into slices with different thicknesses and annealed at 600 °C to prepare the HAGO array.

Preparation of HAGO/Co@CN. First, 100 mg of PVA powders (Aldrich) and 200 mg GO powers (XFNANO) were added in 20 mL deionized water magnetic stirring for 4 h. Next, 400 mg of as-prepared purple ZIF-67 powders were added in suspension and magnetic stirring for 1 h to form a uniform slurry. After, the slurry was pour into a

freeze device for 5 min, then transferred to freezer dryer for 48 h to remove the ice, and obtained a purple blocky composite (**Figure S12b**). Finally, the blocky composite is cut into slices of different thicknesses and annealed at 600 °C to prepare the HAGO/Co@CN array.

Electrochemical measurements. The as-obtained HAGO and HAGO/Co@CN array were used as the free-standing electrodes without current collector. The control electrodes of GO/Co@CN were prepared by mixing GO/Co@CN powder, super P and CMC binders with a mass ratio of 8:1:1 to form a slurry. The slurry was cast on a copper foil using a doctor blade, dried at 80 °C for 12 h under vacuum. The Half-cell test was performed in a CR 2032 type coin cell assembled with Li metal (500 μm) as the counter electrode. The electrolyte was 1 M LiPF₆ in EC/DEC (v/v 1:1) with 10 wt% fluoroethylene carbonate (FEC) additive. Galvanostatic cycling test was carried out between 0.01 V and 3 V on a Neware battery testing system. For the full cell, to compensate for the irreversible loss of active Li, the HAGO/Co@CN anodes were pre-cycled for 3 cycles and displayed a reversible areal capacity of 2.8 mAh cm⁻² (mass loading is 5.4 mg cm⁻²). The pre-cycled HAGO/Co@CN anodes were paired with a commercial NCM₆₂₂ cathodes (Canrd New Energy Technology Co., Ltd, mass loading is 18 mg cm⁻² and reversible areal capacity is 2.7 mAh cm⁻²) with an N/P ratio of ~1.04. The full cell was cycled between 1 and 3 V at a current density of 1 C (1C=180 mAh g⁻¹). Cyclic voltammetry (CV) was carried out on an ZAHNER of Germany electrochemical workstation between 0.01–3 V. Electrochemical impedance spectroscopy (EIS) was implemented on an IM-6 of ZAHNER of Germany

electrochemical workstation between 0.01–100 kHz.

Characterizations. The morphology and microstructure were characterized by transmission electron microscope (TEM, Zeiss) and scanning electron microscope (SEM, Zeiss). The crystal structure of the composite was investigated by X-ray diffraction (XRD, CuK α , D8 Advance, Bruker, Germany) at 40 kV and 40 mA. The bonds were tested by an X-ray photoelectron spectroscopy (XPS, AMICUS, Shimadzu, Japan). TGA (METTLER TOLEDO) was conducted to detect the content of Co nanoparticles in the composite. Raman spectroscopy (LabRam HR Evolution) was performed to analyze the reduction of the samples.

Compaction density test. First, the electrode sheet was cut into a size of 30mm \times 20mm. Then, the electrode sheet is rolled in a rolling mill, the linear speed of the two rolls of the rolling mill is 2.0 m/min, and the rolling pressure is 1 MPa. Next, weigh the weight and thickness of the electrode sheet and current collector. Finally, compaction density was calculated by the equation of areal density / (thickness after pole piece rolling – thickness of current collector).

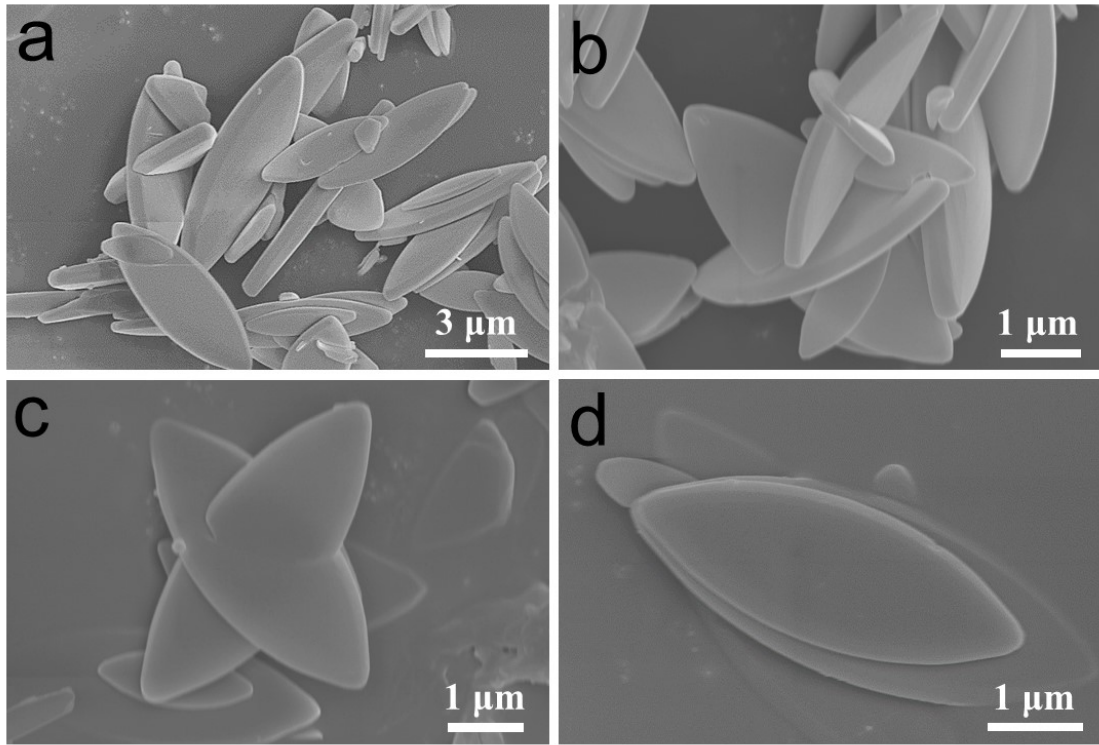


Fig. S1 (a-d) The SEM images of ZIF-67 nanosheets with different magnifications.

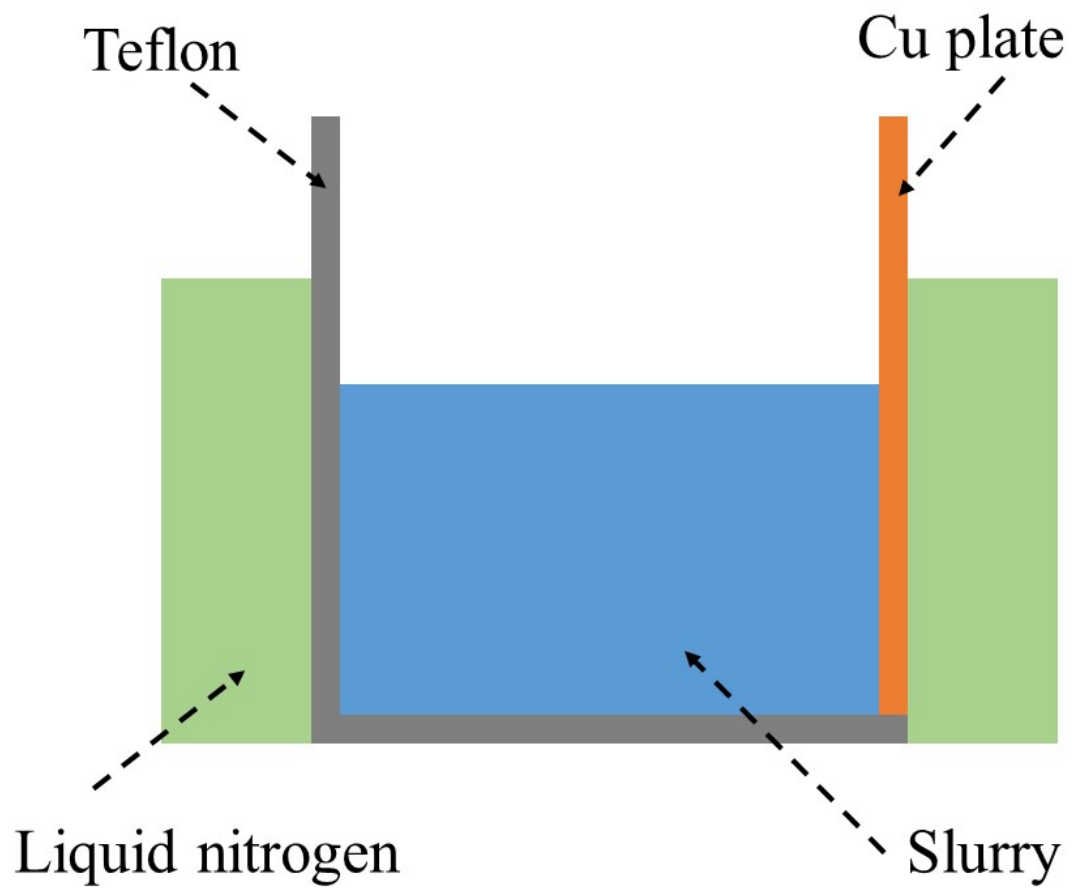


Fig. S2 Schematic of designed freeze device.

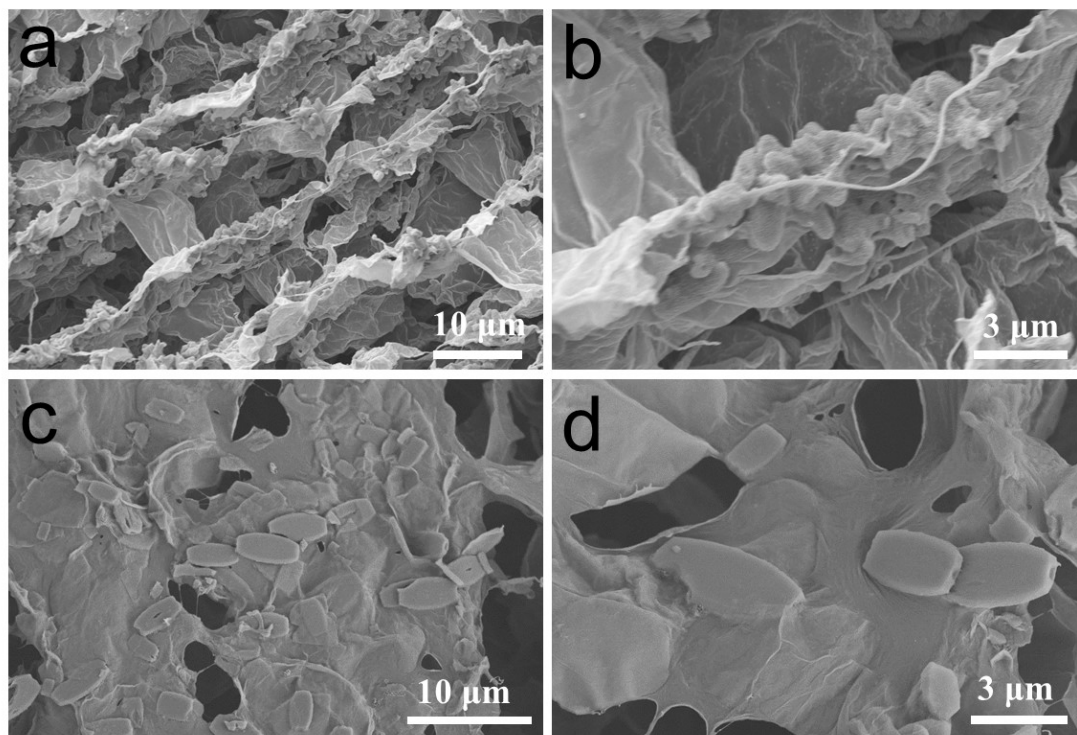


Fig. S3 (a-b) Cross-section SEM images of the HAGO/ZIF-67 composite with different magnifications. (c-d) Top-view SEM images of the HAGO/ZIF-67 composite with different magnifications.

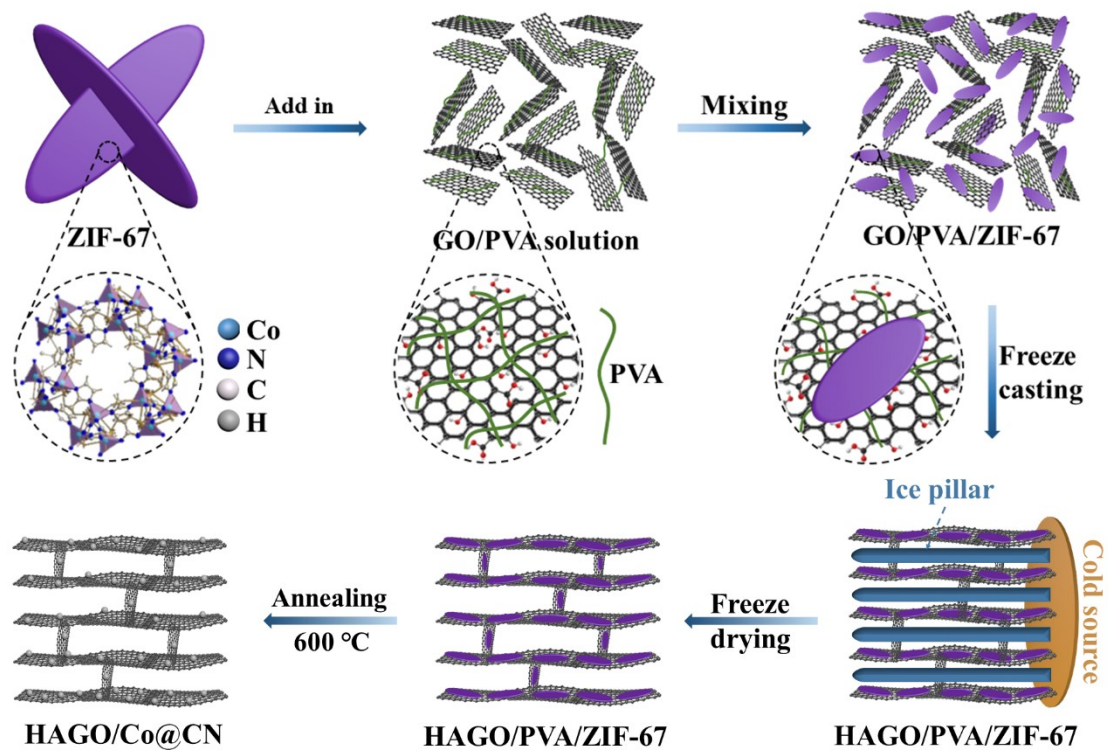


Fig. S4 Schematic diagram of freeze-casting process of the HAGO/Co@CN electrodes.

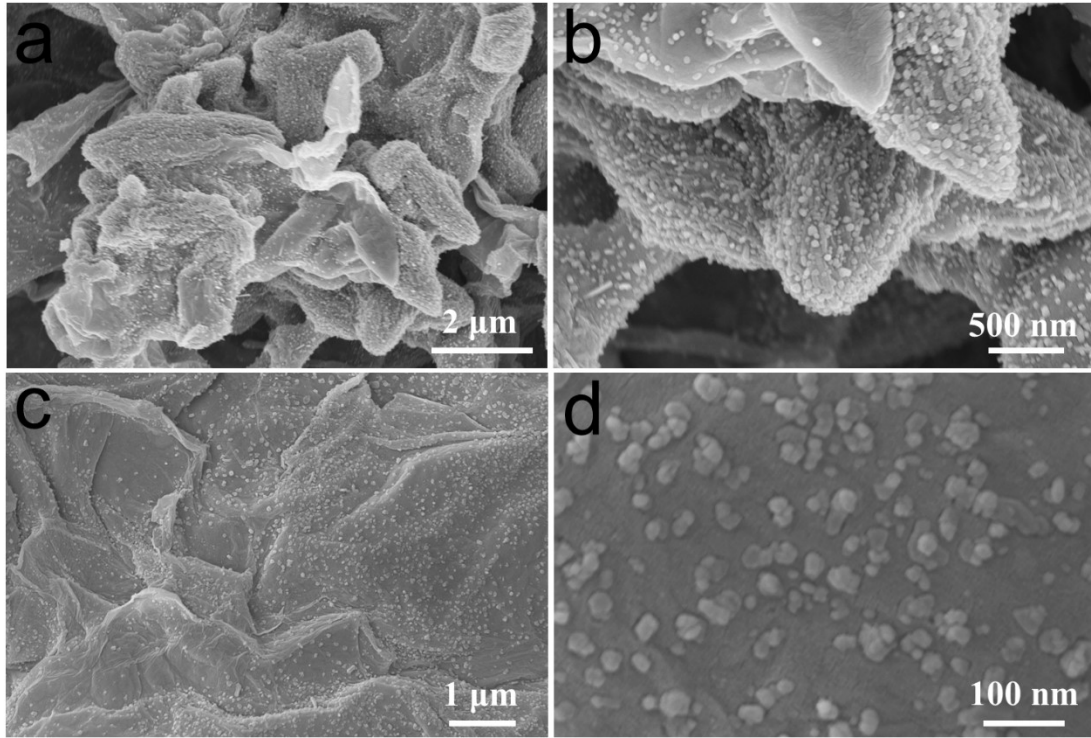


Fig. S5 (a-d) Surface SEM images of the HAGO/Co@CN after pyrolysis with different magnifications.

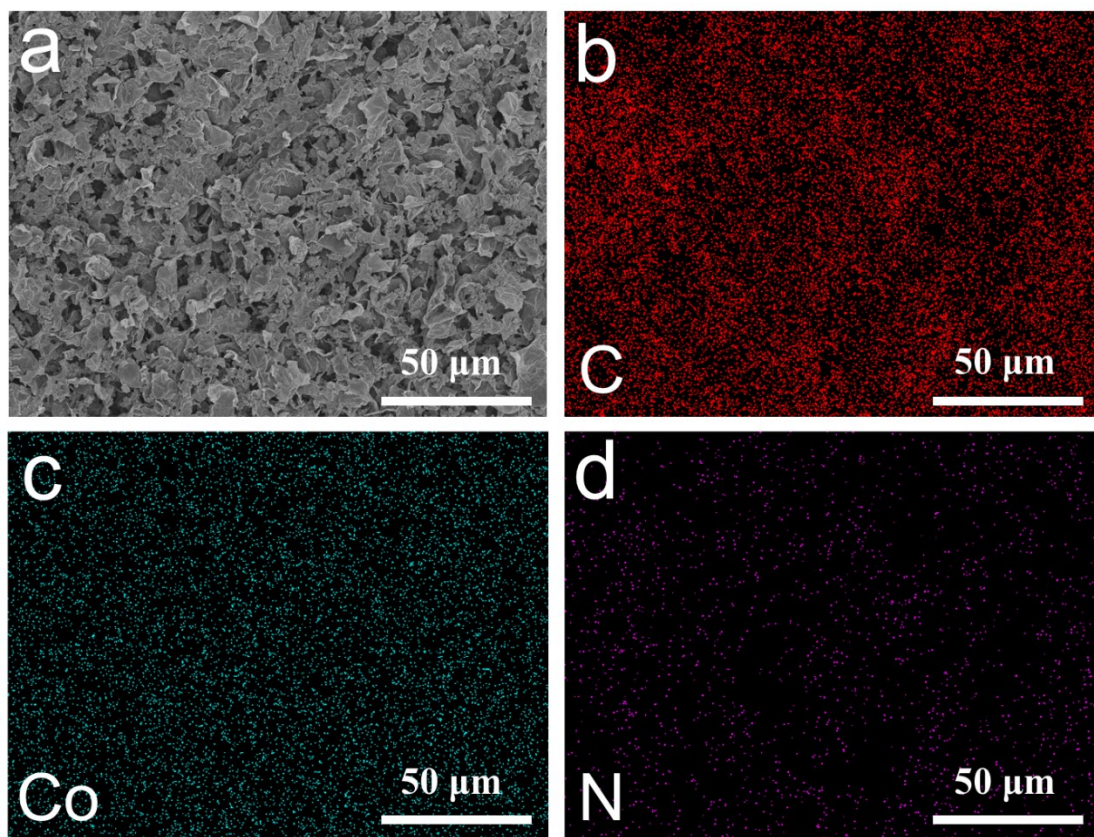


Fig. S6 Top-view SEM image and corresponding element distribution of HAGO/Co@CN electrode.

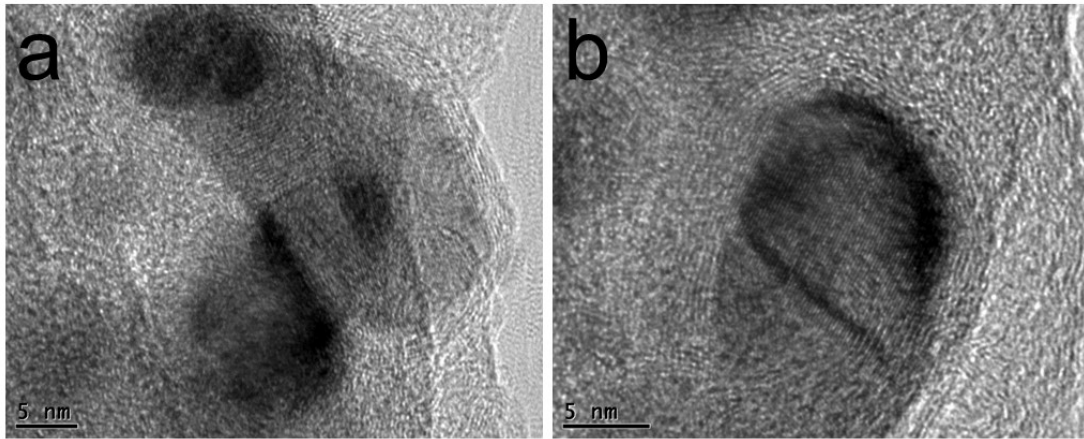


Fig. S7 The high resolution TEM images of HAGO/Co@CN surface.

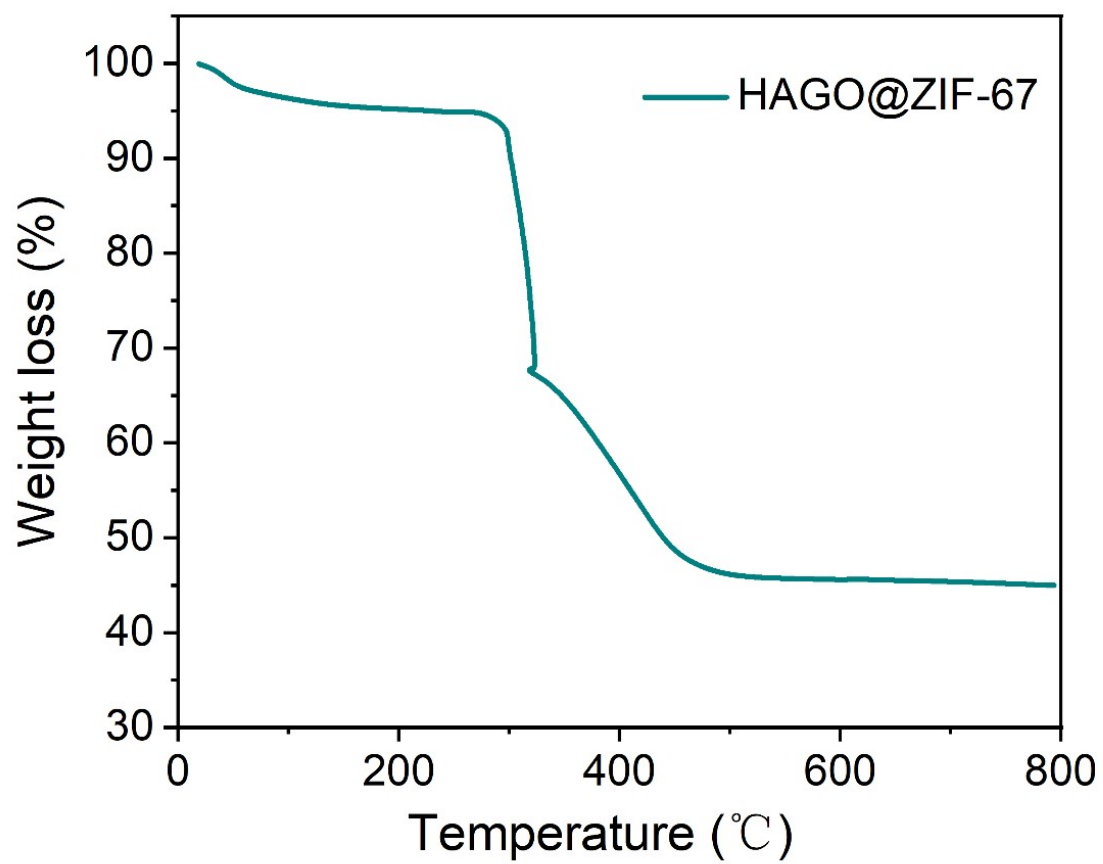


Fig. S8 TGA curve of HAGO/Co@CN was tested in air from room temperature to 800 °C.

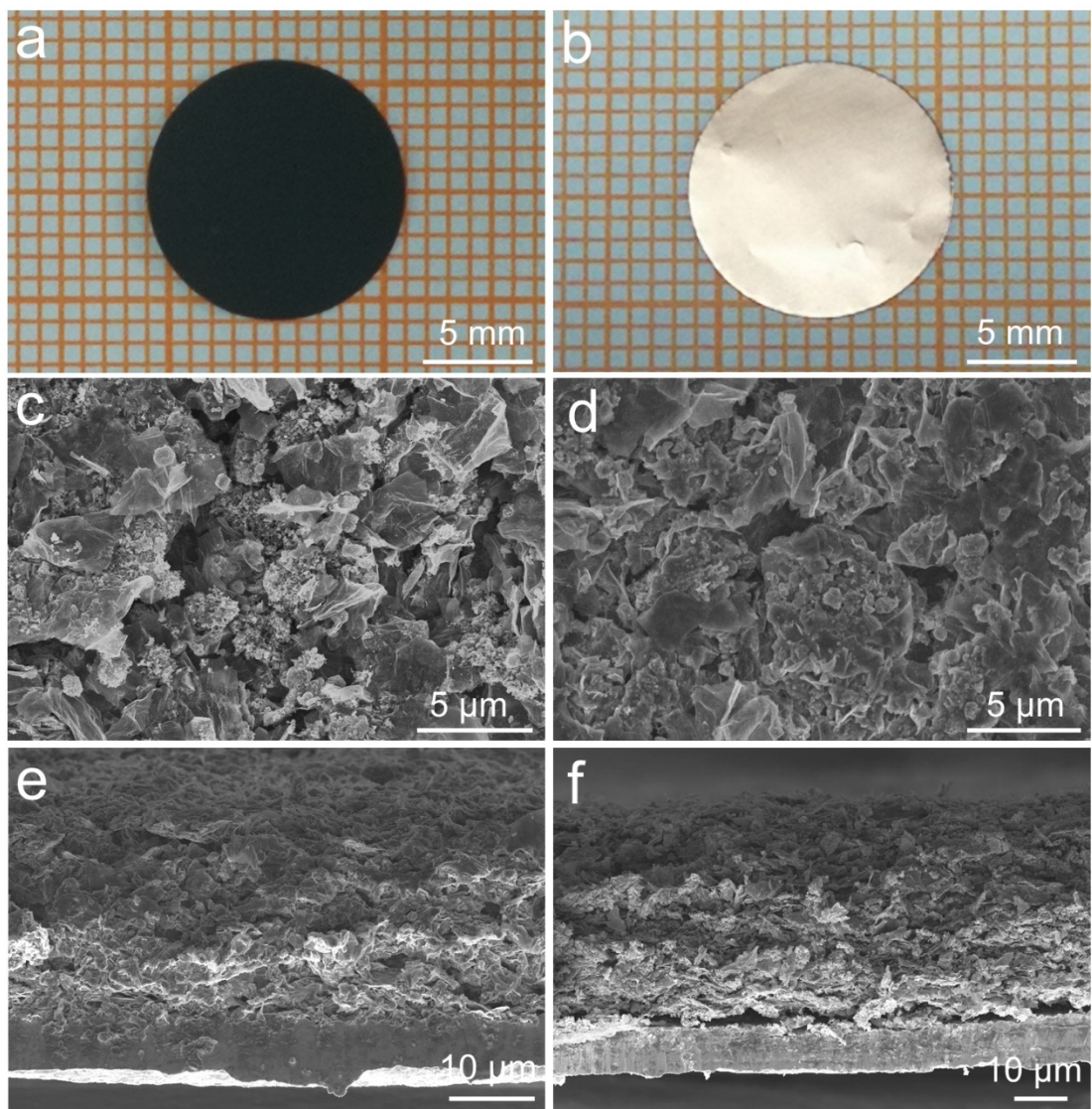


Fig. S9 (a-b) The digital photos of GO/Co@CN control electrode. (c-d) Top-view SEM images of the GO/Co@CN control electrode. (e-f) Cross-sectional SEM images of the GO/Co@CN control electrode.

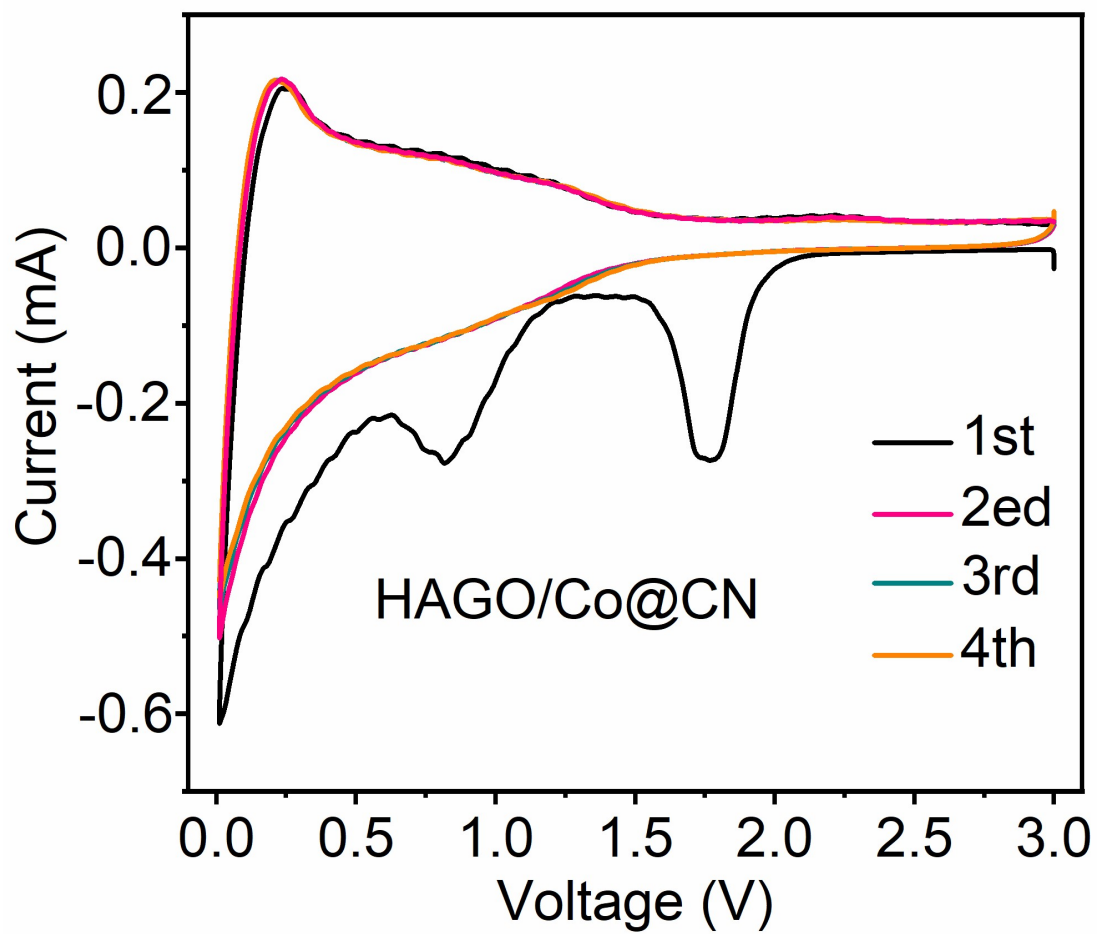


Fig. S10 CV curves of the HAGO/Co@CN electrodes.

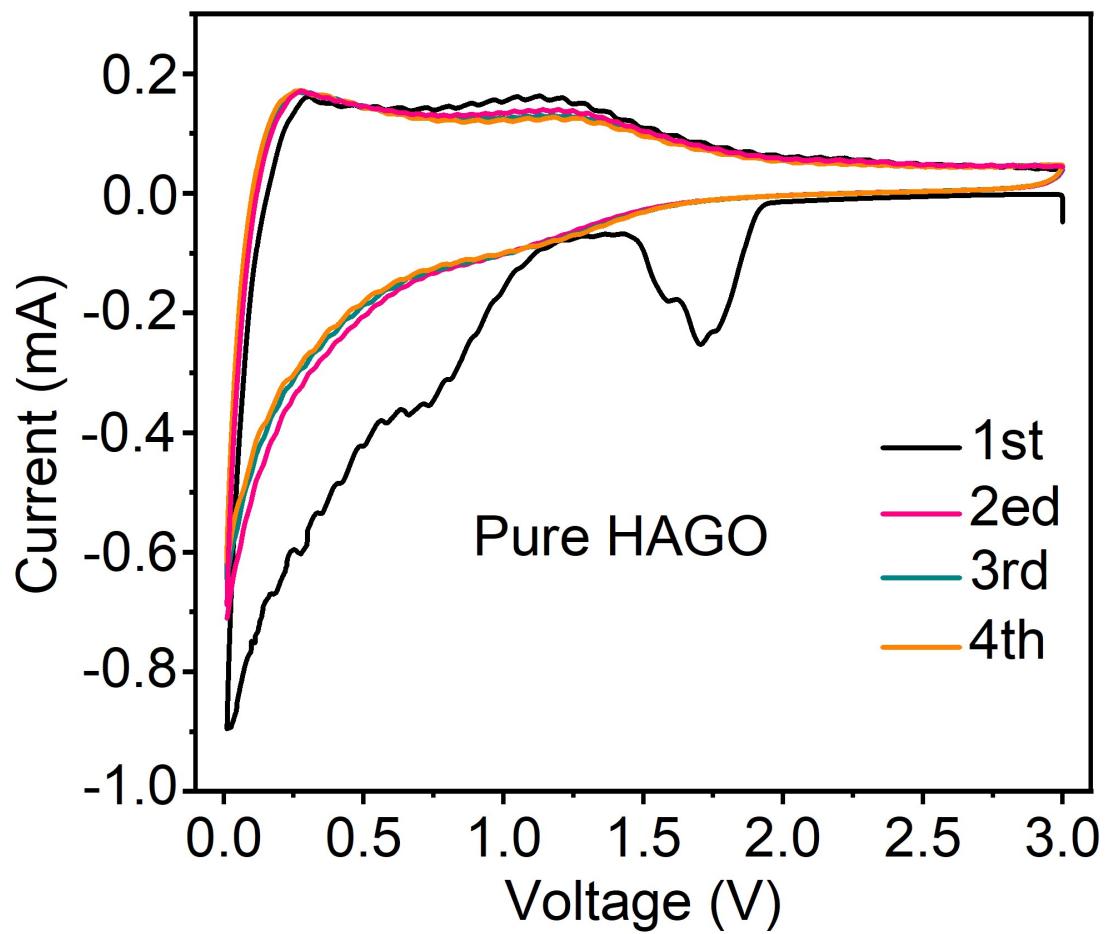


Fig. S11 CV curves of the HAGO electrodes.

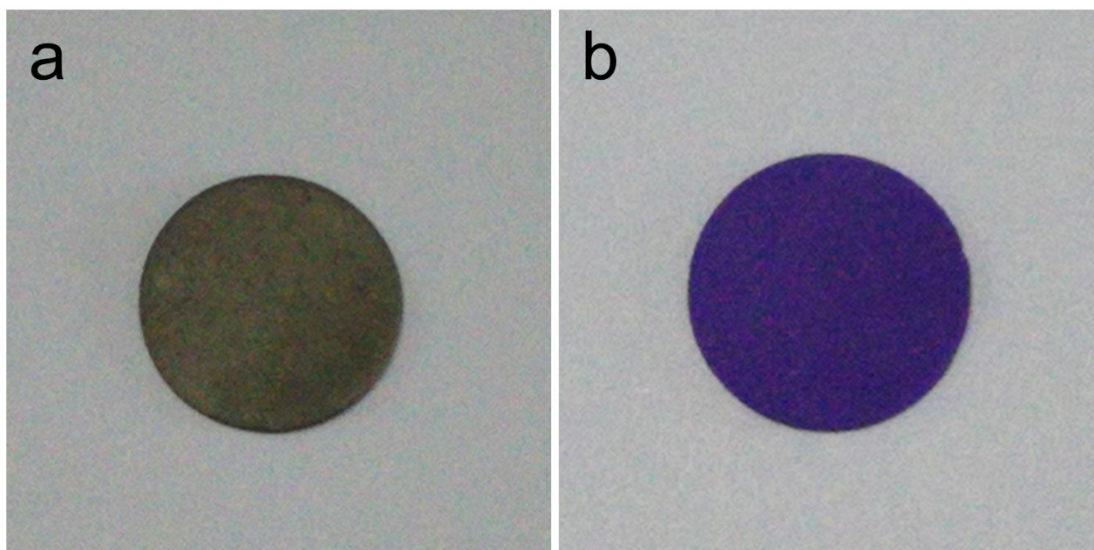


Fig. S12 (a) The gray blocky composite of HAGO. (b) The purple blocky composite of HAGO/ZIF-67.