

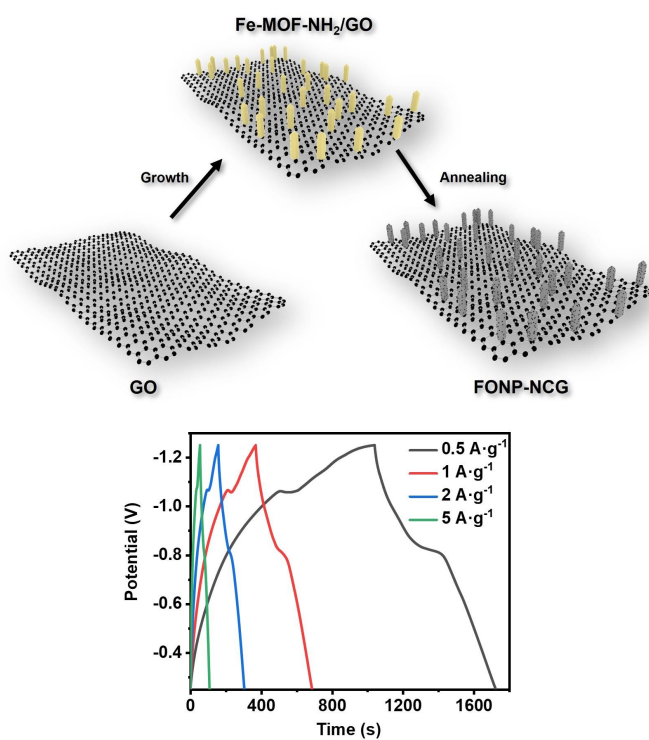
Supporting Information

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Regulating the Amount of Graphene Oxide for Enhanced Capacitive Energy Storage of MOF Derived Materials

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Experimental Procedures

1.1 Chemicals

Graphite (98.0%), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 98.0%) and were bought from Sigma-Aldrich (Shanghai) Trading Co, Ltd. Potassium hydroxide (KOH, 85%) and 2-Aminoterephthalic Acid ($\text{NH}_2\text{-BDC}$, 98.0%) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. Sulfuric acid (H_2SO_4 , 95-97%), phosphoric acid (H_3PO_4 , $\geq 85.0\%$), potassium permanganate (KMnO_4 , $\geq 98.0\%$), hydrogen peroxide (H_2O_2 , 30 wt% in H_2O), hydrochloric acid (HCl, 34%), N,N-dimethylformamide (DMF, 99.5%) and ethanol (EtOH , $\geq 99.5\%$) were obtained from Beijing Chemical Works. Conductive carbon black (Super P, $\geq 99.0\%$) was bought from Guangdong Canrd New Energy Technology Co., Ltd. All chemicals were used as received without any purification process.

1.2 Synthesis of graphene oxide (GO)

GO was prepared by a modified Hummers method. The mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (108 and 12 mL, respectively) and graphite (1 g) were placed in a 250 mL flask with mechanical agitation. When the mixture was cooled with an ice bath, KMnO_4 (3g) was added slowly and carefully. After being stirred for 3 days at room temperature (RT), H_2O_2 solution (10 mL, 30%) was added to stop the oxidation. After 1 h stirring, deionized water (100 mL) was added and the mixture was kept stirring for another 1 h. The products were collected by centrifugation, and washed with 1 M HCl aqueous solution five times to remove metallic impurities and then with deionized water repeatedly until the pH reached 5. During the washing process with deionized water, the graphite was exfoliated, which resulted in a dispersion of GO sheets. Finally, the products were dispersed in 200 mL deionized water.

1.3 Synthesis of FONP-NCG

Typically, a certain amount (1, 2.5, 5 and 7.5 mL, respectively) of GO solution was centrifuged and redispersed in 25 mL DMF and subsequently 135 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added. After 30 min stirring, 90 mg $\text{NH}_2\text{-BDC}$ was added. The mixture was then stirred for an additional 1 h before transferring into an conical flask for crystallization at 120 °C for 4h. The resultant dark brown product was collected by centrifugation and washed several times with DMF and EtOH to remove the excess reactants, then dried in an oven. To obtain FONP-NCG composite, the as-prepared Fe-MOF- NH_2/GO was placed in a tube furnace and heated under N_2 gas flow at 500 °C for 1h with a heating rate of 5 °C/min. The FONP-NC composite was synthesized under the same conditions without the addition of GO.

1.4 Characterization

The morphologies and sizes of samples were characterized by a transmission electron microscope (TEM, Hitachi HT-7700) operated at 100 kV and a scanning electron microscope (SEM, JEOL JSM-7600) with an accelerating voltage of 5 kV. The high-resolution TEM and elemental mapping were performed by a field emission electron microscope (JEM-2100F) operated at 200 kV. Powder X-ray diffraction (XRD) was tested on a Shimadzu XRD-6000 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) was accomplished on a Thermo ESCALAB

250Xi system with an Al K α X-ray source. The inductively coupled plasma (ICP) measurement was performed on an inductively coupled plasma-atomic emission spectrometer (ICP-AES, SHIMADZU ICPS-7500).

1.5 Electrochemical measurements

A CHI 660D (Chenhua, Shanghai) workstation was used to test all the electrochemical measurements, using a typical three-electrode system at RT with carbon rod as counter electrode as well as saturated calomel electrode (SCE) as reference electrode. All the inks were made by mixing 5 mg samples with 50 μ L of 5% Nafion solution and 950 μ L ethanol. After 1 h sonication, the 5 μ L ink was dried onto glass carbon electrode. The loading density of the active materials is about 1.25 g m⁻². The electrochemical results were obtained in 6 M KOH aqueous solution. Electrochemical impedance spectroscopy (EIS) was performed at non-faradic region from 100000 to 10⁻¹ Hz with a 5-mV voltage range.

Figures

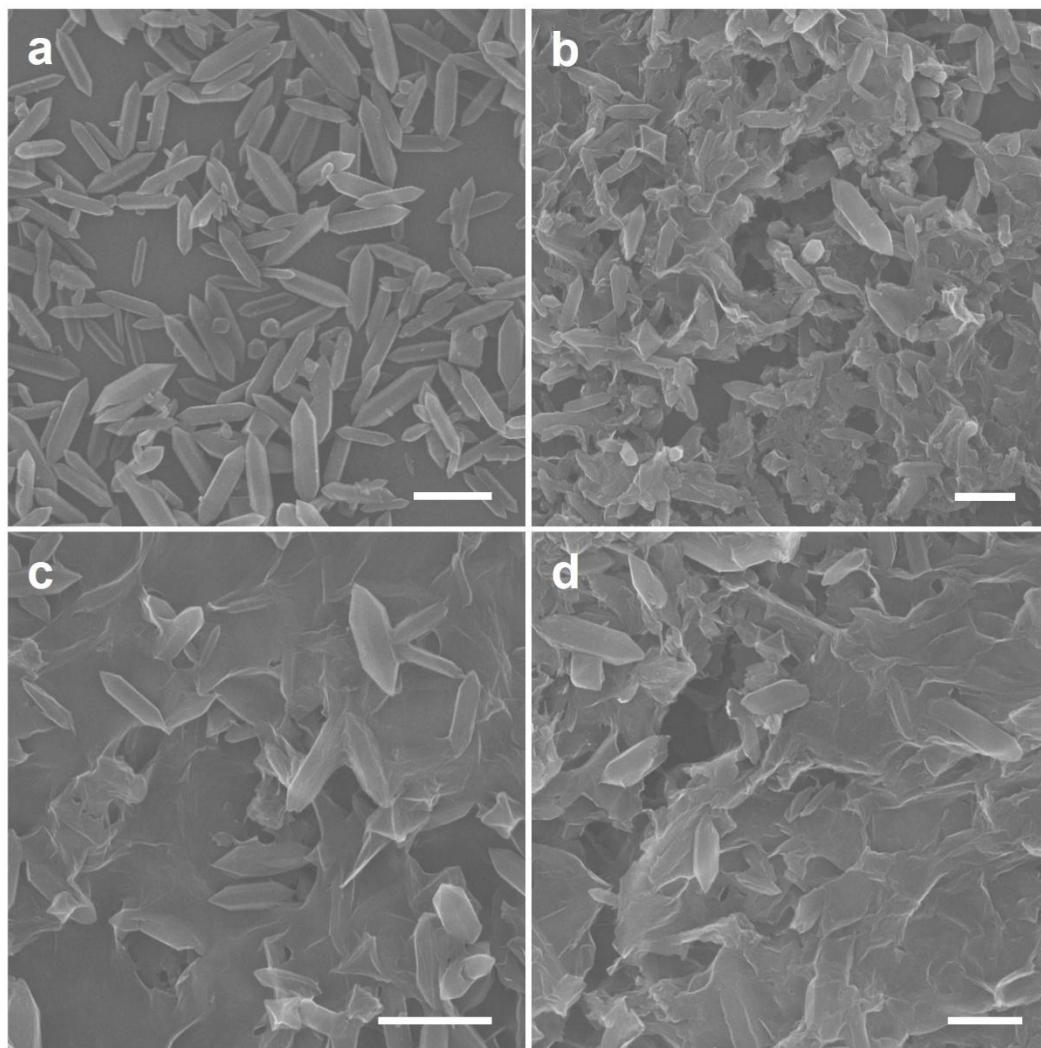


Figure S1. SEM images of as-prepared (a) Fe-MOF-NH₂, (b) Fe-MOF-NH₂/GO-2.5, (c) Fe-MOF-NH₂/GO-5 and (d) Fe-MOF-NH₂/GO-7.5. All the scale bars: 1 μm.

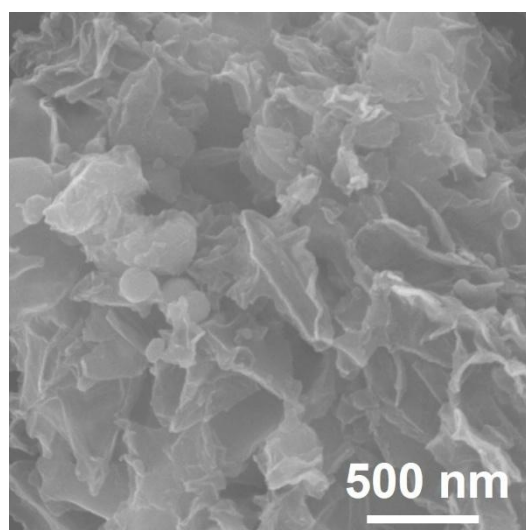


Figure S2. SEM image of FONP-NCG.

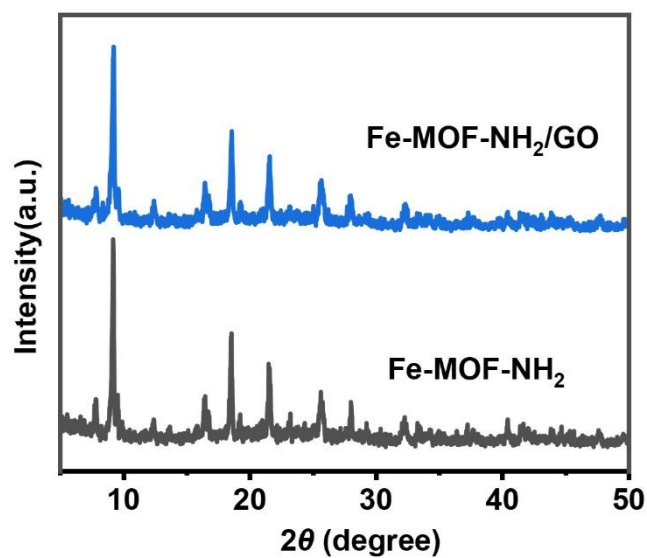


Figure S3. XRD patterns of as prepared Fe-MOF-NH₂, Fe-MOF-NH₂/GO.

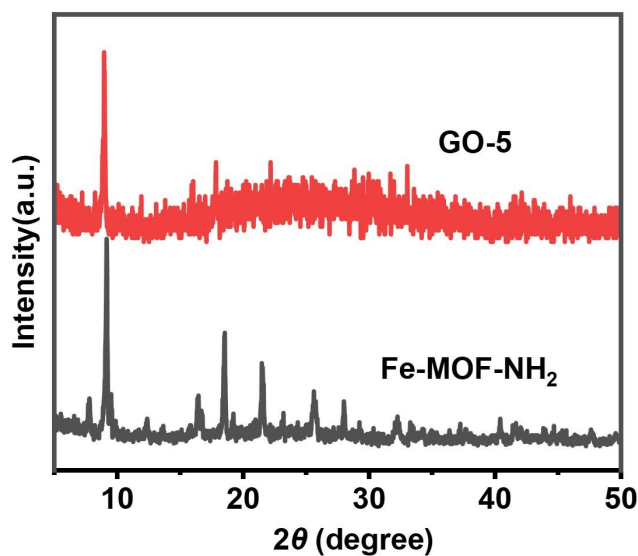


Figure S4. XRD patterns of as prepared Fe-MOF-NH₂, GO-5. For convenience, the samples are also denoted as GO-0, which is the FONP-NC without adding GO into the growth solution, and GO-1 to GO-7.5, which are a series of FONP-NCG composites prepared with adding various amounts of GO solution from 1 to 7.5 mL into the MOF precursors solution.

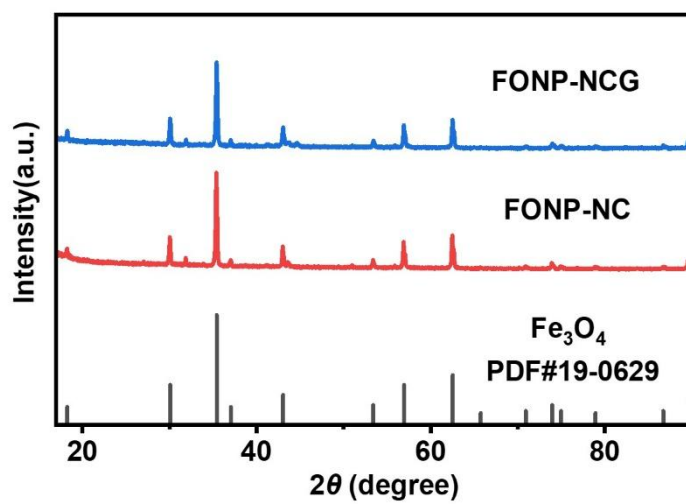


Figure S5. XRD patterns of as prepared FONP-NC and FONP-NCG.

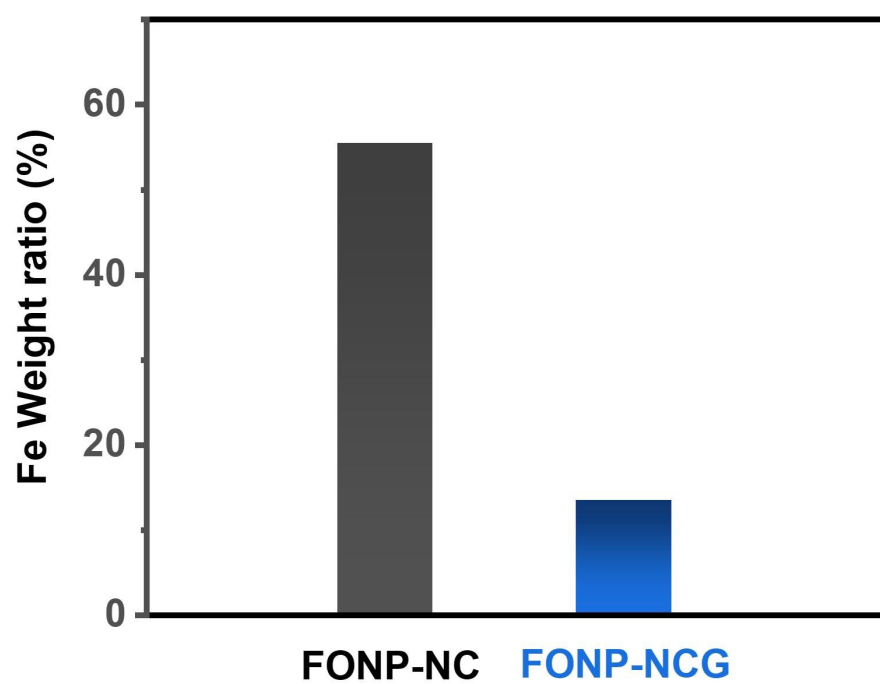


Figure S6. ICP results of Fe loading in FONP-NC and FONP-NCG.

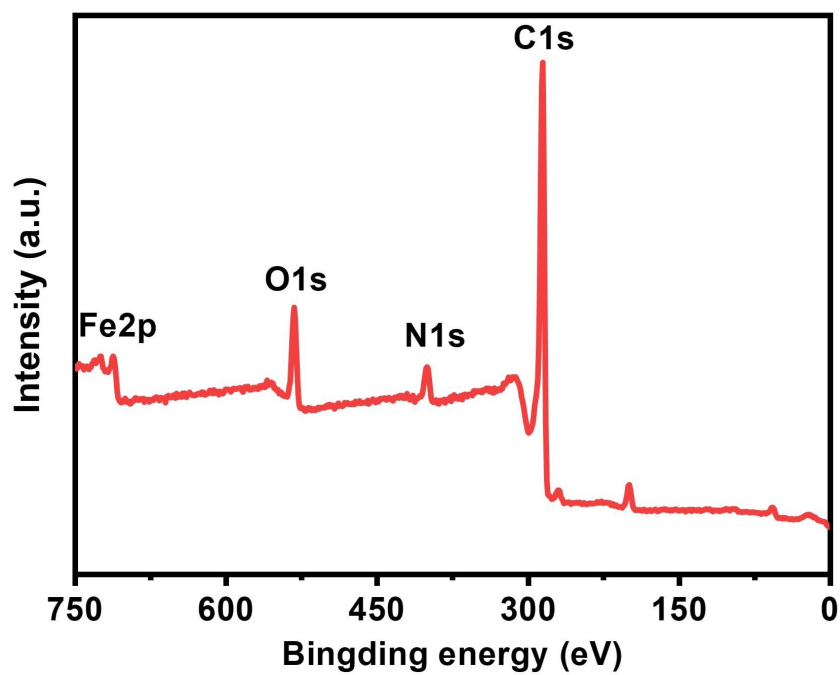


Figure S7. XPS survey spectrum of FONP-NCG.

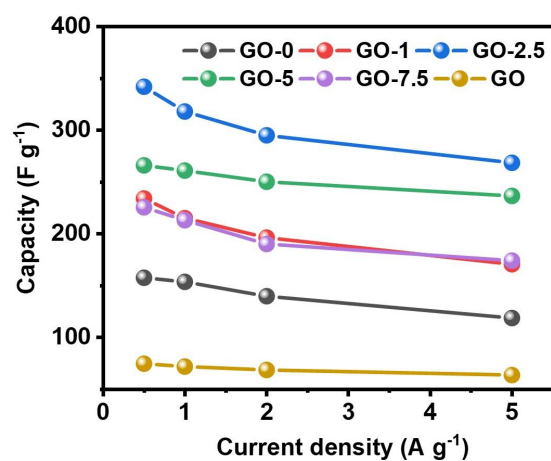


Figure S8. Rate performance of FONP-NCG with various addition of GO, and rGO at various constant current densities.

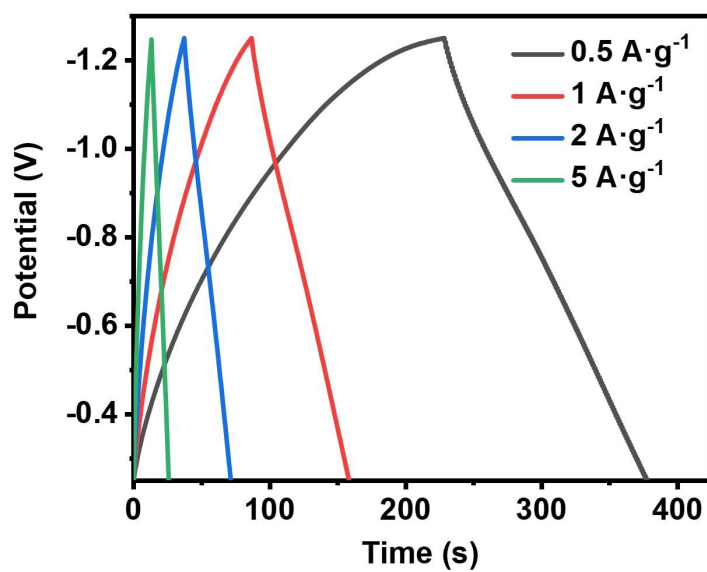


Figure S9. Charge/discharge curves of rGO at various current densities.

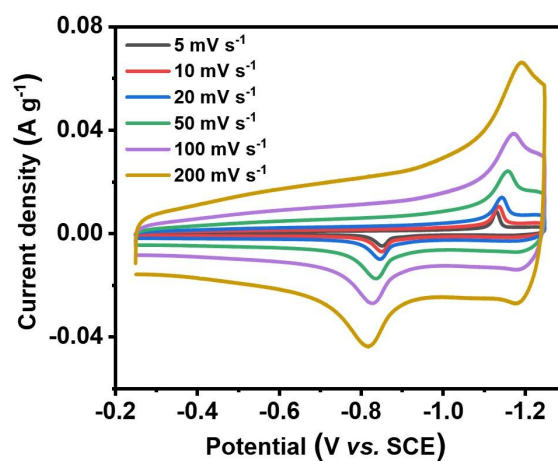


Figure S10. Representative CV curves of FONP-NCG at different scan rate.

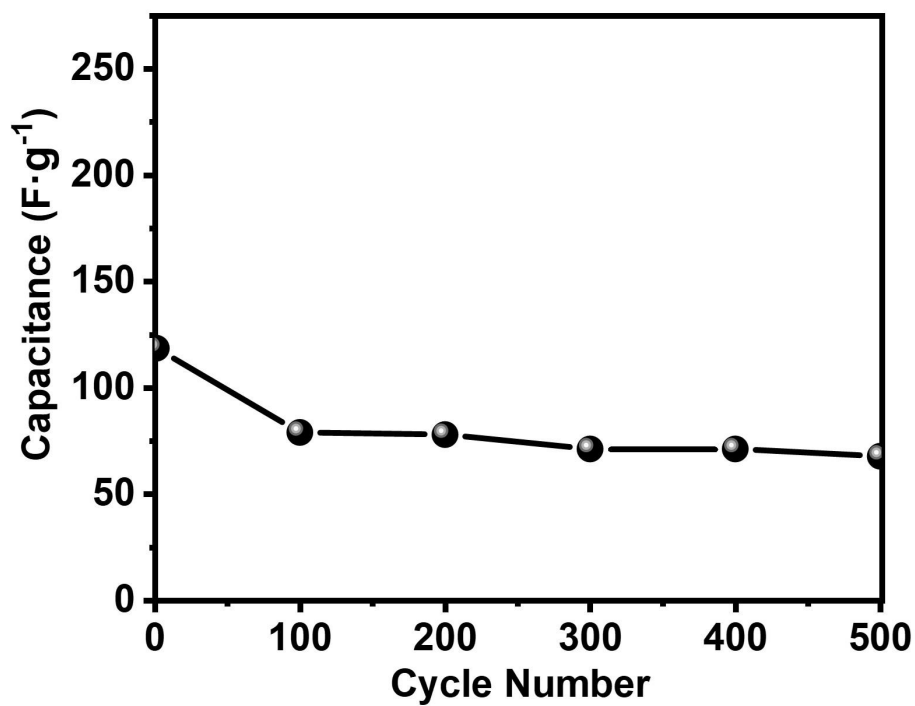


Figure S11. Cycling stability of FONP-NC composite at a current density of 5 A g⁻¹.

Author Contributions

Yongji Qin: Investigation, Visualization, Writing-original draft. Jingquan Yang: Writing-review & editing. Hao Wang: Writing-review & editing. Meiling Lian: Writing-review & editing. Peipei Jia: Resources. Jun Luo: Resources, Supervision, Validation. Xijun Liu: Formal analysis, Writing-review & editing. Junfeng Liu: Resources, Supervision, Validation.

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