

Supporting Information

Hierarchically porous graphene-based hybrid electrodes with excellent electrochemical performance

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I. Experimental Section

1. Preparation of hierarchically porous graphene-Ni(OH)₂ hybrids

Low defect density graphene was produced by exfoliation of bulk graphite in N-methyl-2-pyrrolidone (NMP) at a starting concentration of 0.1 mg/mL according to the previous report.^[1] Specifically, natural flake graphite (50 mg) was dispersed in NMP (500 mL) with sonication in a low power sonic bath for 30 min. The resultant dispersion was then centrifuged for 90 min at 500 rpm. Afterwards, decantation was carried out by pipetting off the top half of the dispersion. A homogeneous dark dispersion was obtained and used as the starting material.

In order to prepare holey graphene sheets, the graphene dispersion (100 mL) was vigorously stirred, while KMnO₄ solution (80 mg of KMnO₄ dissolved in 5 mL of de-ionized water) was introduced rapidly. The mixture was kept in a covered beaker under ambient conditions for 1 h. The as-generated product was then collected and treated with hot hydrochloric acid (60 °C) for 30 min, and finally washed with DI-water and ethanol, respectively.

To synthesize hierarchically porous holey graphene-Ni(OH)₂ structure (hGN), the as-prepared holey graphene was dispersed in NMP (100 mL) by sonication for 30 min. Then Ni(NO₃)₂ aqueous solution (200 mg of Ni(NO₃)₂·6H₂O dissolved in 5 mL de-ionized water) was added. The mixture was loaded into a Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. After being cooled to room temperature, the product was collected, washed, and finally dried at 60 °C. The percentage of Ni(OH)₂ was 93.8 wt% in the hybrid. For the purpose of comparison, hGN-L, the counterpart of hGN with lower mass ratio of Ni(OH)₂ (85.7 wt% in the hybrid), was prepared; pure Ni(OH)₂ was prepared

in the absence of holey graphene using a similar procedure; the graphene-Ni(OH)₂ (GN) counterpart was prepared using graphene instead of holey graphene; the physically mixed (PGN) counterpart of hGN was prepared by physically mixing holey graphene and Ni(OH)₂ for 30 min; the reduced graphene-Ni(OH)₂ (rGN) counterpart was prepared by using 0.1 mg/mL of graphene oxide (obtained by Hummer's method^[2]) to replace low defect density graphene, followed by its coupling with Ni(OH)₂ in a similar way as in the case of hGN.

2. Characterization

Powder X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda \approx 1.54 \text{ \AA}$). Raman spectra were recorded on a Renishaw Raman microscope. The excitation line at 514.5 nm provided by an argon ion laser was used. Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851e thermogravimetric analyzer from 50 to 600 °C at a heating rate of 10 °C·min⁻¹ in N₂ flow. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI5300 X-ray photoelectron spectrometer, using Al K α ($h\nu = 1486.7 \text{ eV}$) X-ray as the excitation source. Morphologies of the as-obtained products were observed on a transmission electron microscope (TEM, JEOL JEM-2100) and field emission scanning electron microscope (FESEM, QUANTA-450). Moreover, the Brunauer-Emmett-Teller (BET) surface area and pore volumes were evaluated by using nitrogen adsorption-desorption isotherms measured at 77 K on a TriStar II 3020 Micrometrics apparatus. The BET specific surface area was calculated using adsorption data at a relative pressure range of $P/P_0 = 0.05\text{-}0.20$. Pore size distribution was derived from the adsorption branch using Barrett-Joyner-Halenda (BJH) method modified by Kruk et al.^[3] The total pore volume was estimated from the amounts adsorbed at a relative pressure (P/P_0) of 0.99.

3. Electrode preparation and electrochemical testing

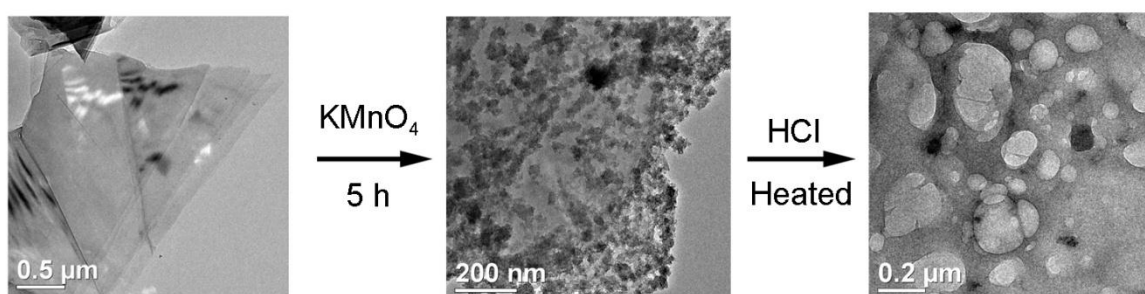
The electrochemical properties of the as-obtained materials were investigated using a three-electrode cell configuration at room temperature. The working electrodes were fabricated by mixing the prepared powders with 15 wt% acetylene black and 5 wt% polytetrafluorene-ethylene (PTFE) binder. A small amount of DI-water was added to the mixture to produce a homogeneous paste. The mixture was pressed onto nickel foam current-collectors (1.0 cm \times 1.0 cm) to make electrodes. The mass of the active material was in a range of 3.5~6.3 mg. Before each electrochemical test, the prepared electrode was soaked overnight in a 6 M KOH solution. Electrochemical characterization was carried out using a three-electrode cell with 6 M KOH aqueous solution as the electrolyte. Platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All electrochemical measurements were conducted on a CHI 660B electrochemical workstation (Shanghai CH Instrument Company, China).

The average specific capacitance (C_s) was evaluated from the CV data according to the following formula: $C_s = \frac{1}{mv(V_f - V_i)} \int_{V_i}^{V_f} I(V)dV$, where m is the mass of the active electrode material, v is the scan rate, V_f and V_i are the integration potential limits of the voltammetric curve, and $I(V)$ is the voltammetric current.

The C_s obtained from galvanostatic charge-discharge data was calculated according to $C_s = I/[m(dV/dt)]$ using the discharge curves, where I is the constant discharge current, m is the mass of these samples, and dV/dt can be obtained from the slope of the discharge curve given by the instrument.

II. Supplementary Results

a



b

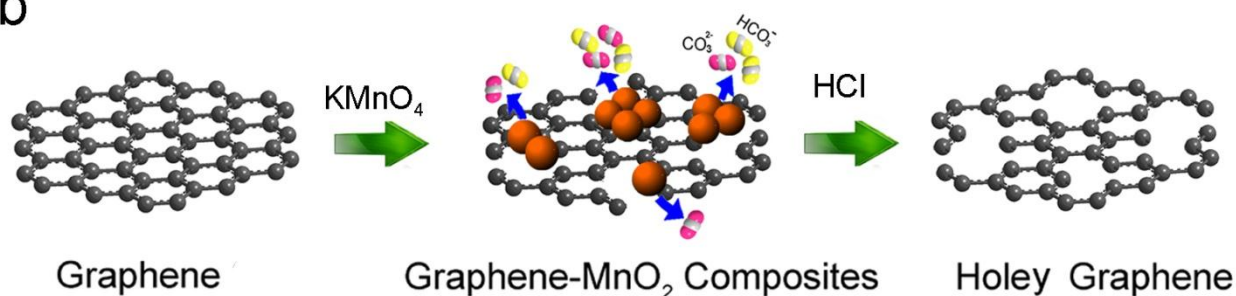


Figure S1. TEM images (panel a) and schematic illustration (panel b) of the formation of hG.

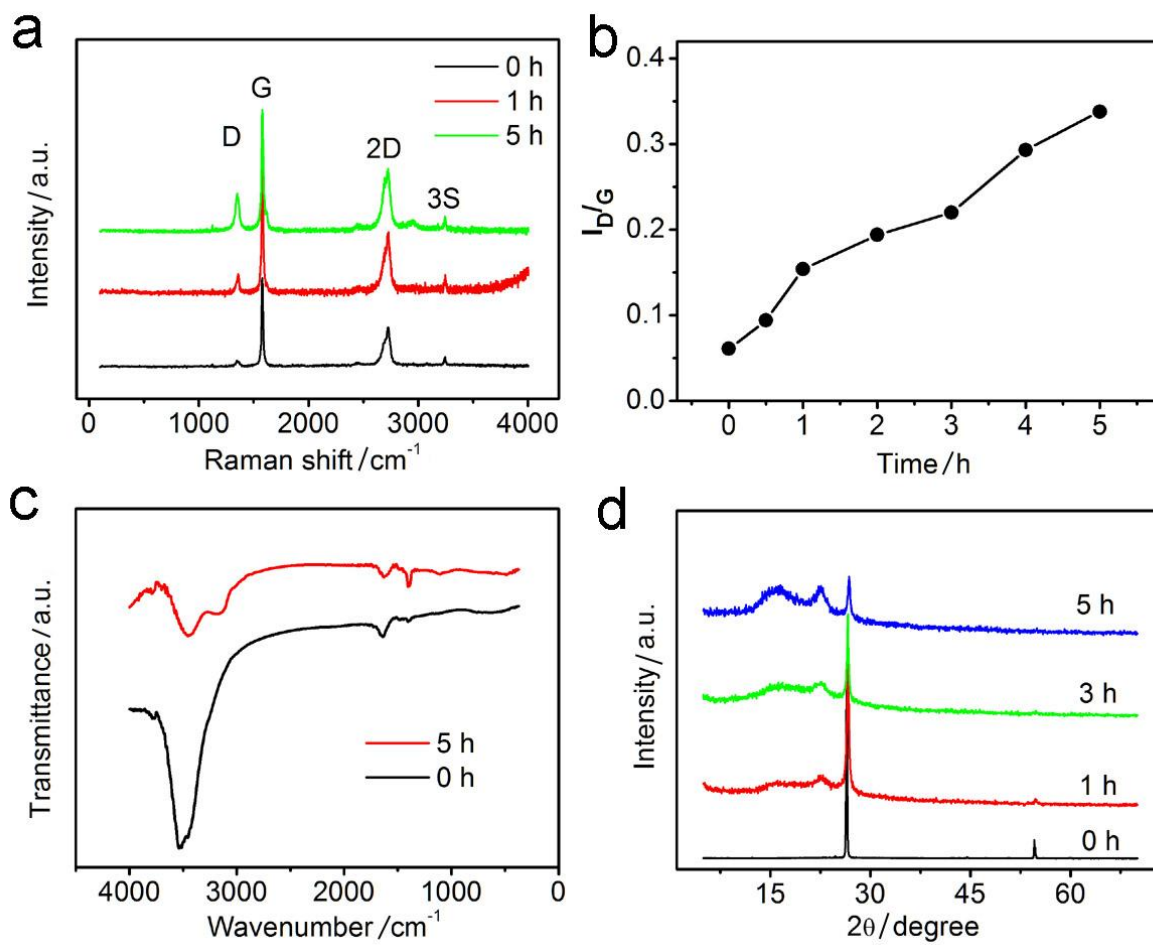


Figure S2. (a) Raman spectra (b) Raman I_D/I_G intensity ratio (c) FTIR spectra and (d) XRD patterns of the hG prepared with different duration of KMnO_4 treatment.

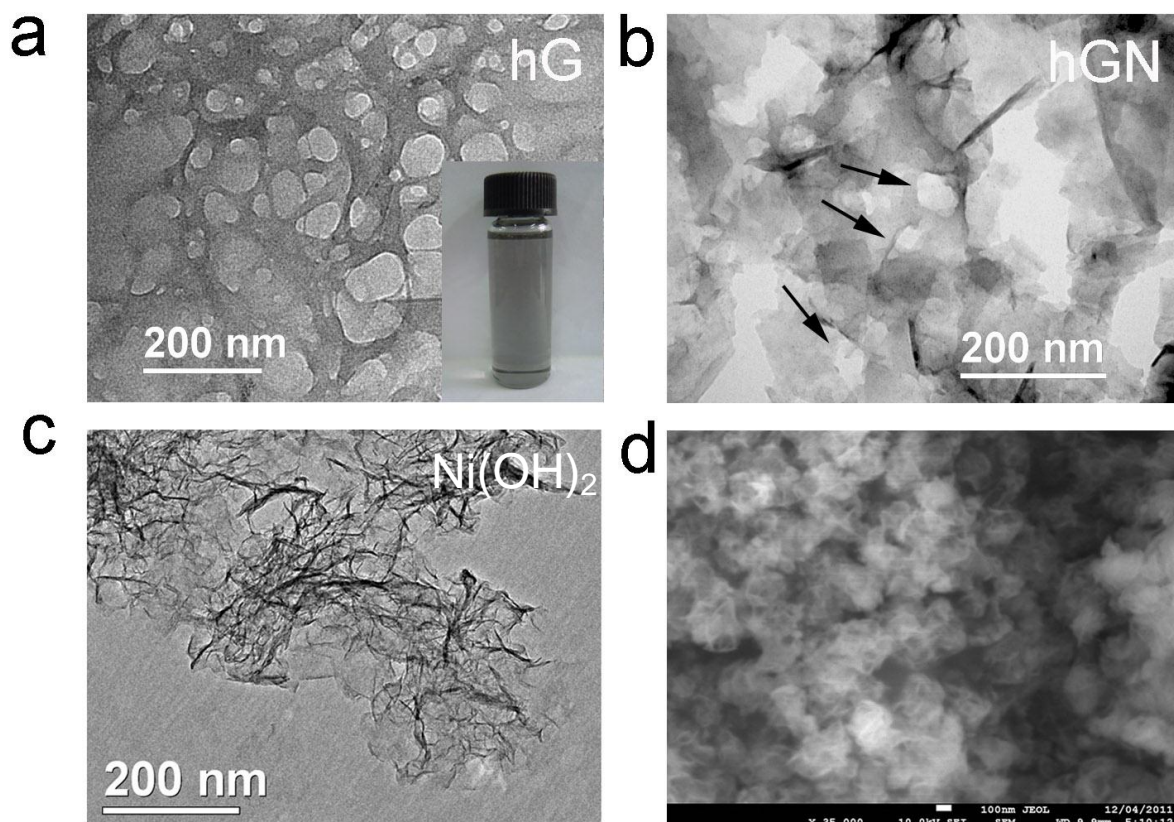


Figure S3. (a-b) TEM images of hGN in comparison to holey graphene (hG); the arrows in (b) indicate the holes in hG present in the hybrid; (c-d) TEM and SEM images of Ni(OH)₂ nanosheets. The inset in (a) is an optical image of hG dispersion in NMP solvent (0.1 mg mL⁻¹).

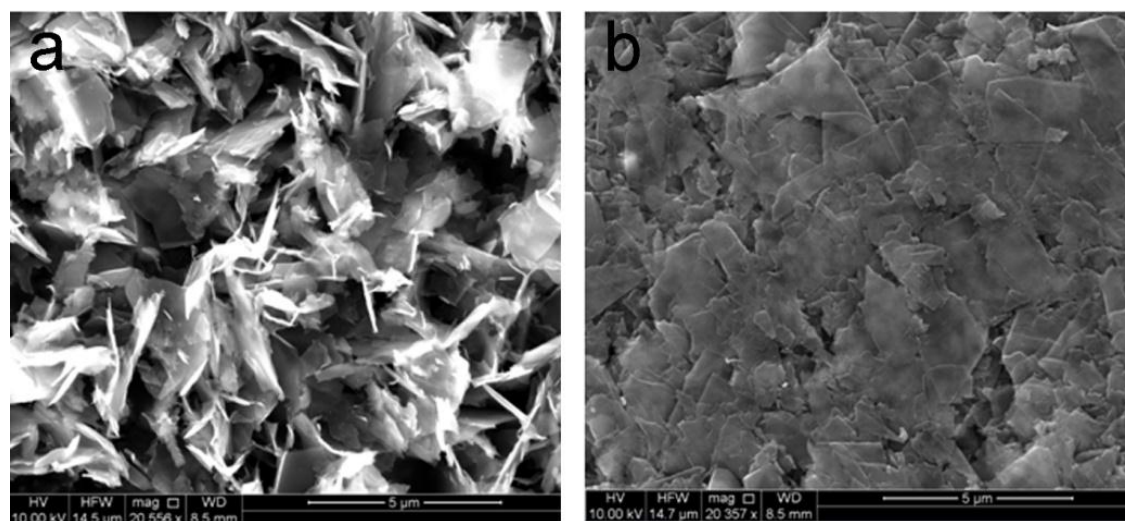


Figure S4 SEM images of (a) hGN, and (b) hG

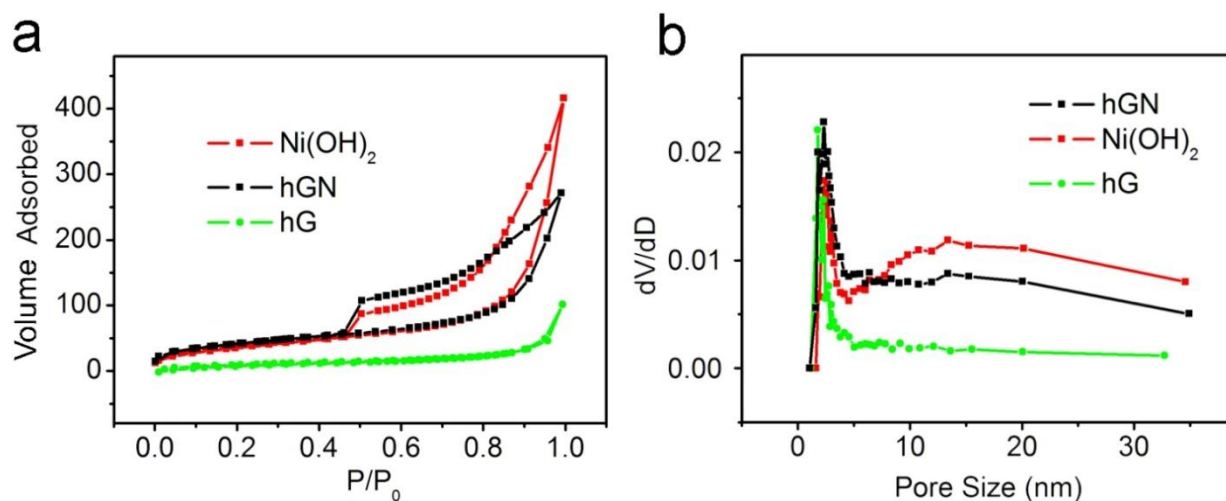


Figure S5. Nitrogen adsorption-desorption isotherms (expressed in cm³ STP/g) and the corresponding pore size distributions (expressed in cm³g⁻¹nm⁻¹) for hGN, hG and Ni(OH)₂.

Table S1. Adsorption-based analysis of hierarchically porous graphene-Ni(OH)₂ samples.

Samples	Ni(OH) ₂ (wt %)	S _{BET} (m ² /g)	C _{BET}	V _t (cm ³ /g)	V _{mi} (cm ³ /g)	D _{mi} (nm)	V _{me} (cm ³ /g)	D _{me} (nm)	V _{mc} (cm ³ /g)
Ni(OH) ₂	100	139	57	0.64	0.02	2.5	0.49	13	0.13
hGN	93.8	152	71	0.42	0.04	2.3	0.37	14	0.01
hGN-L	85.7	192	66	0.56	0.04	2.3	0.48	15	0.04
hG	0	36	30	0.15	0.02	1.8	0.10	-	0.03

S_{BET}- BET surface area calculated in the range of relative pressures from 0.05-0.20

C_{BET} – constant C in the BET equation of multilayer adsorption

V_t – single-point pore volume calculated from the volume adsorbed at the relative pressure = 0.99

V_{mi} – volume of pores below 4 nm (micropores and small mesopores) obtained by integration of the pore size distribution obtained by the Kruk-Jaroniec-Sayari (KJS) method^[3]

V_{me} – volume of mesopores from 4 to 50 nm obtained by integration of the KJS PSD curve

V_{mc} – volume of small macropores obtained by subtracting the volume of micropores and mesopores from the single-point pore volume (refers to all pores accessible to nitrogen molecules). Note that the volume of larger macropores cannot be measured by nitrogen adsorption at -196°C; however, mercury porosimetry (commonly used for macropore size analysis) is rather not applicable for the materials studied because their structure would be severely distorted by mercury infiltration

D_{mi} – the width of small pores at the maximum of the KJS PSD curve

D_{me} – the width of mesopores at the maximum of the KJS PSD curve

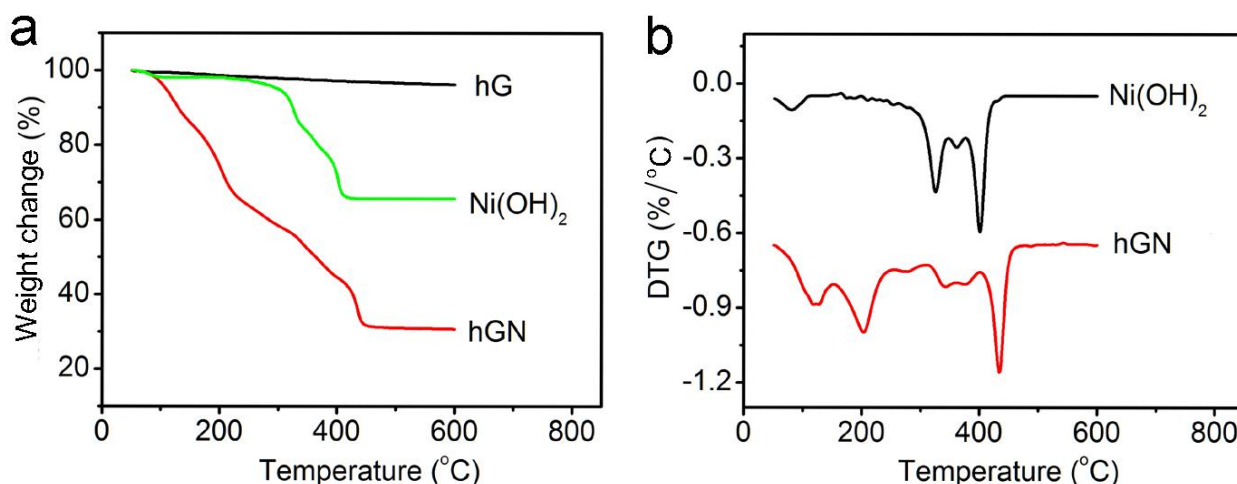


Figure S6 TG (panel a) and DTG (panel b) profiles for hGN, hG and Ni(OH)₂.

Thermogravimetric analysis (TGA) and DTG provide additional information about hGN. The rates of weight loss observed for hG and Ni(OH)₂ were 3.3% and 34.5% in N₂ atmosphere from 50 to 600 °C; while unexpectedly, hGN displayed the weight lost as much as 68.9% at the same test conditions. The weight loss from 250 to 400 °C detected in both Ni(OH)₂ and hGN can be attributed to the transition of Ni(OH)₂ to NiO. The additional weight loss of hGN at 100~200 °C might be due to removal of adsorbed water and solvent (NMP) molecules from the pores of hGN structure, suggesting the presence of pores in hGN.

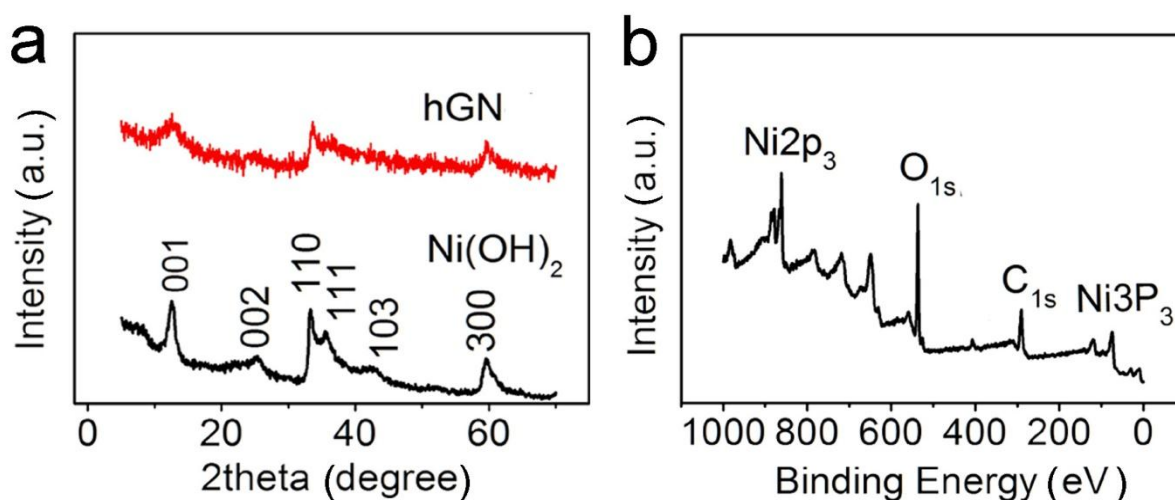


Figure S7 (a) XRD profiles of Ni(OH)₂ and hGN; (b) XPS sweep scan of hGN.

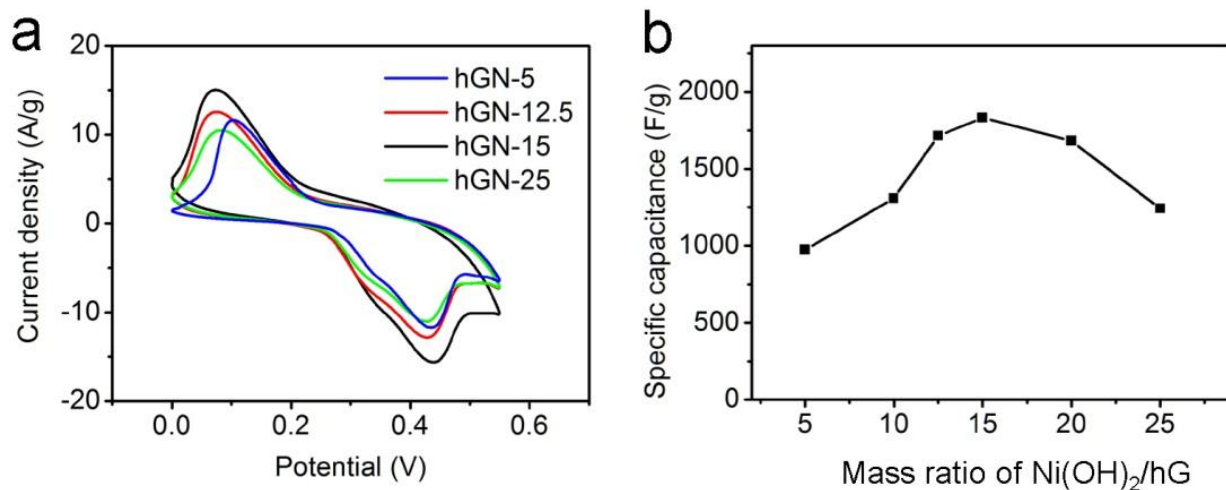


Figure S8. (a-b) CV profiles and the calculated specific capacitance for the hGN samples with different mass ratios.

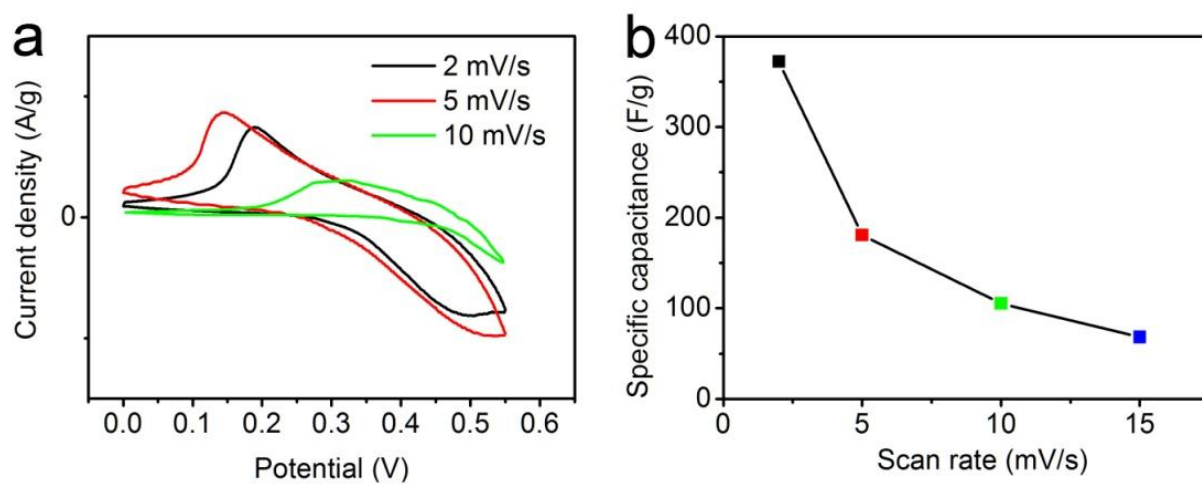


Figure S9. (a-b) CVs and the calculated specific capacitance for Ni(OH)₂ at different scan rate.

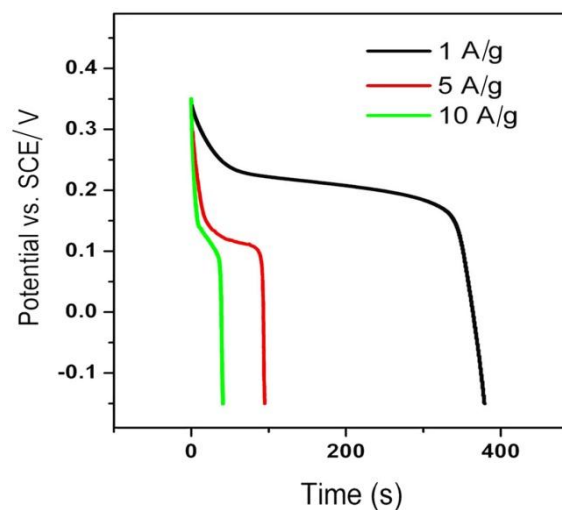


Figure S10. Discharge plots for GN at different current densities.

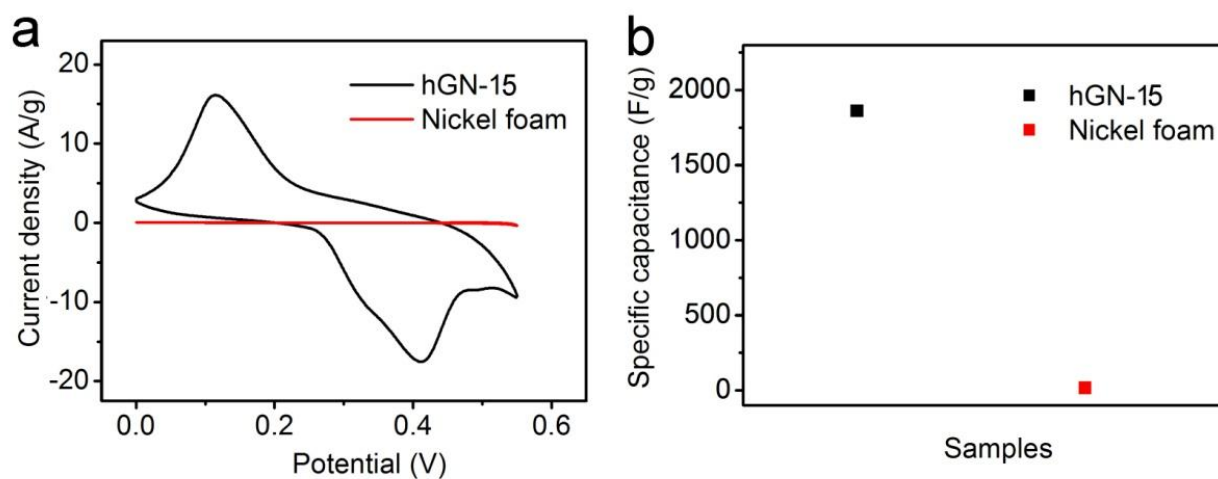


Figure S11. CV plots and the specific capacitance for hGN and nickel foam.

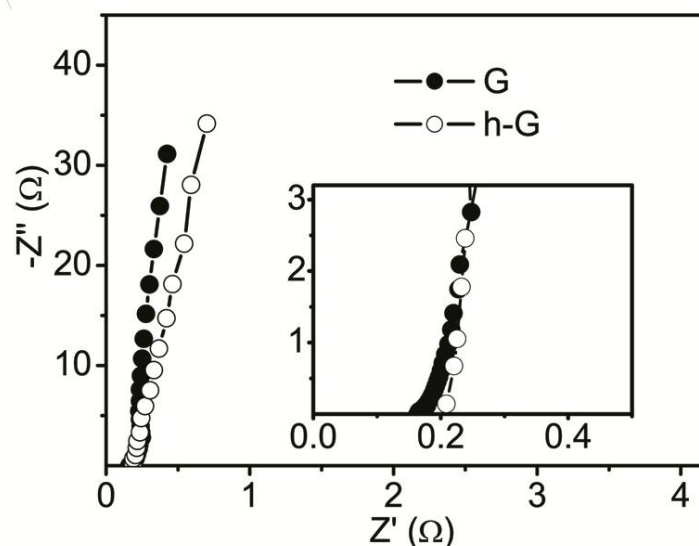


Figure S12. EIS analyses of graphene (G) and holey graphene (hG).

References

- [1] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, J. N. Coleman, *Nat. Nanotechnol.* **2008**, *3*, 563-568.
- [2] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339-1339.
- [3] E. P. Barrett, L. G. Joyner, P. P. Halenda, *J. Am. Chem. Soc.* **1951**, *73*, 373-380.