Electronic Supplementary Information

New strategy to prepare N-doped holey graphene for high-volumetric supercapacitors

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Material preparation：

All chemicals used were analytical grade and without any further purification. N-HG were synthesized by carbonization and activation process of glucose using zinc nitrate hexahydrate (ZNH) as chemical reagent and template. A mixture of 2 g ZNH and 0.5 g glucose are dissolved in 5ml of deionized water to form transparent solutions. The transparent solutions were put into the stove at 220 °C under air environment directly. After several minutes， the brownness foamy product was generated. Next, the brownness foamy product was placed in a porcelain boat, and heated in a horizontal tube furnace up to the setting temperature at a rate of 10 °C min^{-1} and maintained at this temperature for 1 h under N_2 flow. The resultant black powder was immersed in dilute HCl aqueous solution to remove ZnO template, and subsequently washed with adequate deionized water. For comparison, we also prepared the N-HG by adjusting the carbonization temperature, named as N-HG-600, N-HG-800. For instance, the N-HG-800 is corresponding to carbonization temperature of 800 °C.

Structure Characterization:

The morphologies of the samples were observed by JEM-2100 microscope (Japan, JEOL) with an accelerating voltage of 200 kV and a field emission scanning electron microscope (FE-SEM, Carl Zeiss Ultra Plus, Germany) at 20 kV. X-ray diffraction (XRD) analysis was carried out using a D8 Advance, Bruker AXS Corporation, Germany. X-ray photoelectron spectra (XPS) were acquired with a Japan Kratos Axis Ultra DLD spectrometer using a monochromatic Al Kα source (1486.6 eV).The specific surface area and pore structure of the N-HG samples were determined by N2 adsorption–desorption isotherms at 77 K (ASAP 2460, Micromeritics, USA) after being vacuum-dried at 200 °C overnight. The specific surface area value was determined by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated with the Barret-Joyner-Halenda (BJH) method. Raman spectroscopy was performed using a Bruker Senterra dispersive Raman microscopy with a laser at a wavelength of 532 nm.

Electrochemical measurements：

All electrochemical measurements were carried out by a CHI 760C electrochemical workstation at ambient temperature. To prepare the electrode, N-HG were mixed with carbon black and poly (tetrafluoroethylene) at a mass ratio of 80:10:10, pressed onto nickel foam current collector (1 cm×1 cm), and followed by drying at 100°C for 12 h in a vacuum oven. The electrochemical tests were firstly performed with a standard three-electrode setup, in which Hg/HgO was used as reference electrode, Pt foil as counter electrode and the synthesized sample as working electrode respectively. A 6M KOH aqueous solution served as electrolyte at room temperature. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 0.01 Hz to 100 kHz at the open circuit voltage with an alternate current amplitude of 5 mV.

The gravimetric capacitances (C_g) and volumetric capacitances (C_v) were calculated from the charge/discharge curves according to the following equation:

$$C_g = \frac{I \cdot \Delta t}{m \cdot \Delta V}$$

$$\rho = \frac{m}{v}$$

$$C_v = C_g \cdot \rho$$

Where I is the constant charge/discharge current density, Δt is the discharge time, ΔV is the discharge voltage, m is the mass of the active materials, ρ is the density of electrode materials, C_v is the volumetric capacitance. The thickness of the N-HG-600 film (cross sectional part) was estimated by SEM to be 59.64 μm，0.5×0.5 cm of the HG-600 derived carbon film was cut to calculate the V of N-HG-600.

The energy density (E) and power density (P) were calculated from the charge/discharge curves according to the following equation:

$$E = 0.5\, CV^2$$

$$P = \frac{E}{t}$$

where C is the capacitance of the symmetric supercapacitor, V is the voltage range and t (s) is the discharge time.

Figures S1-S9：

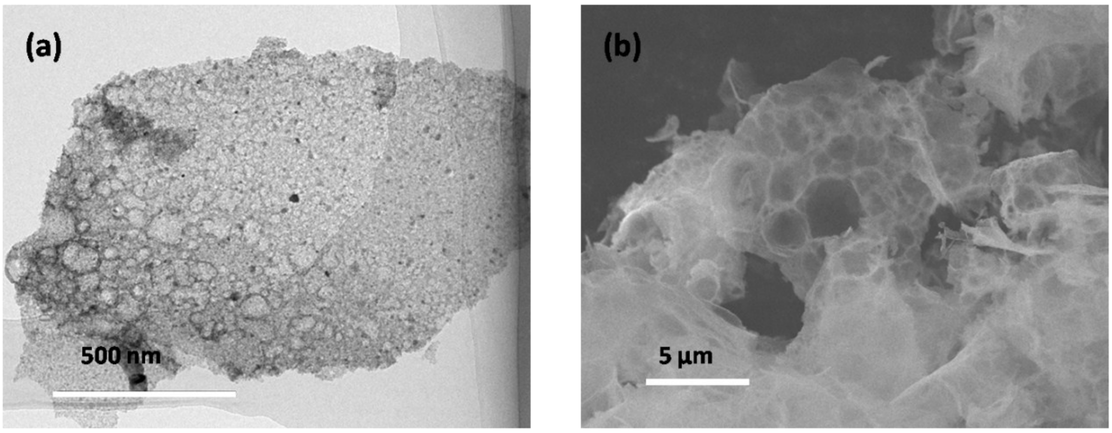

Fig.S1 TEM (a) and SEM (b) image of as-prepared ZnO/C/ZnO.

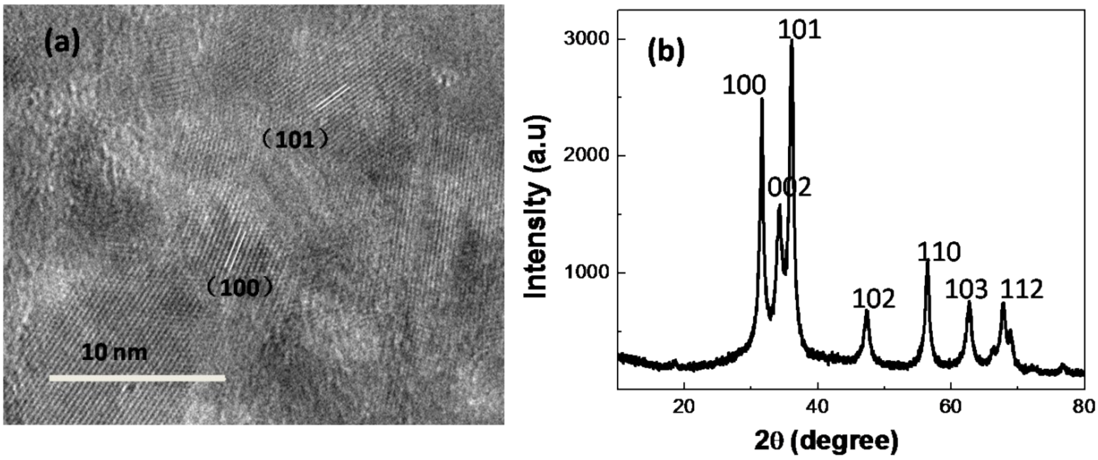

Fig.S2 High-magnification TEM image (a) and XRD pattern (b) of as-prepared ZnO/C/ZnO.

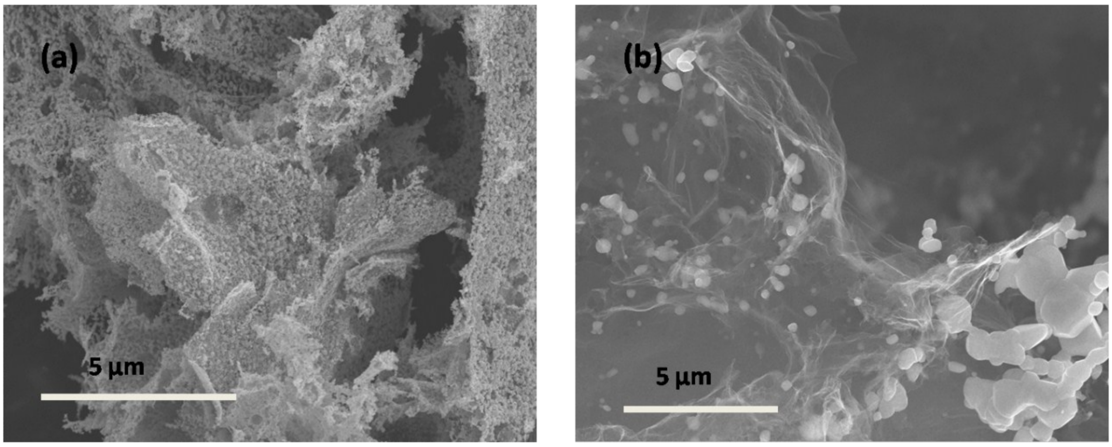

Fig.S3 (a) ZnO/C/ZnO annealed at 600 ^{o}C; (b) ZnO/C/ZnO annealed at 800 ^{o}C.

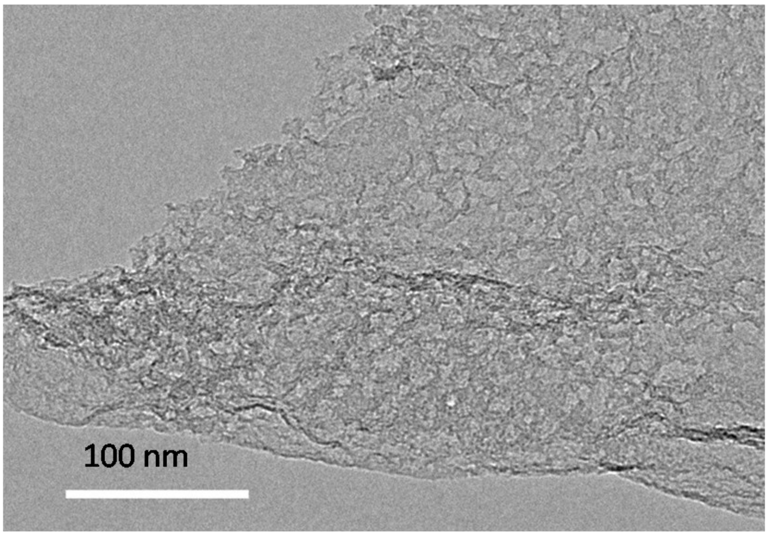

Fig.S4 TEM image of N-HG-800.

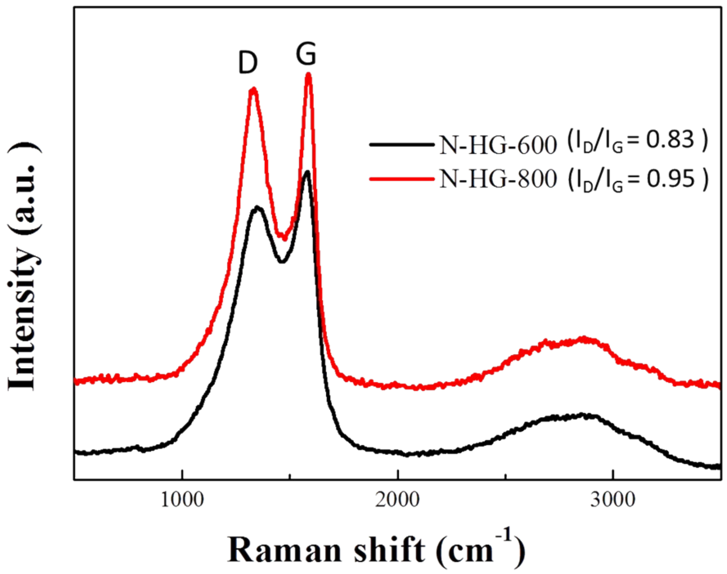

Fig.S5 The Raman spectra of N-HG-600 and N-HG-800.

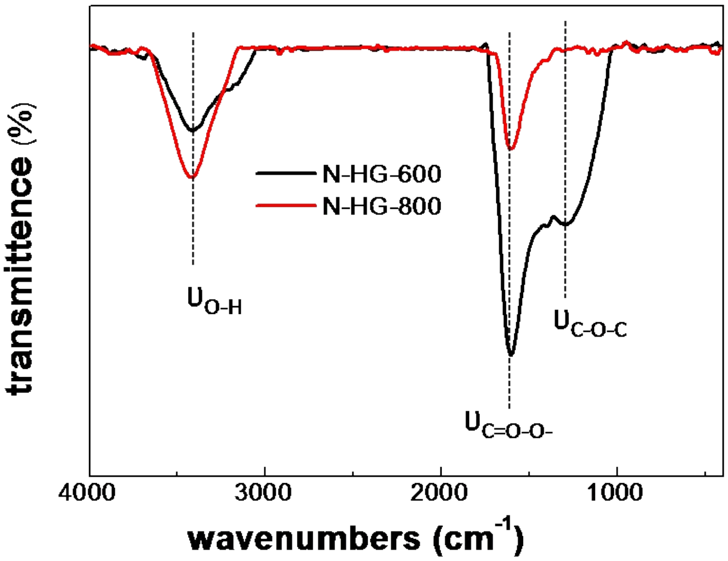

Fig.S6 Typical FTIR spectra of N-HG-600 and N-HG-800.

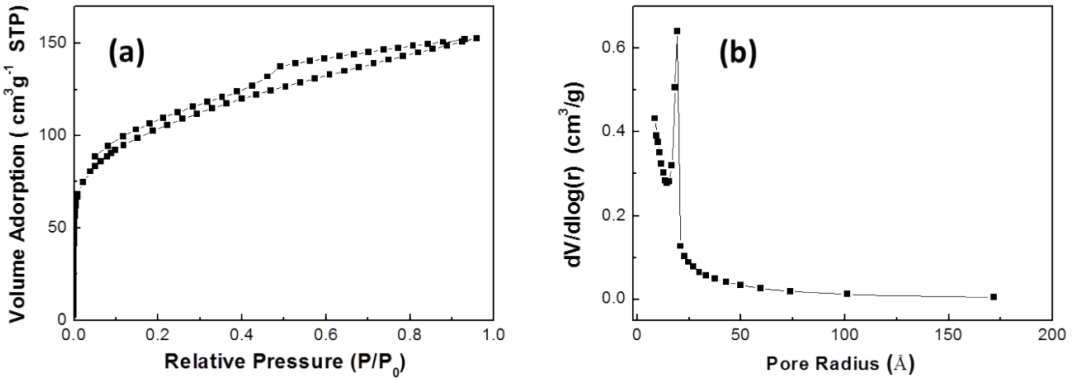

Fig.S7 (a) The Nitrogen adsorption isotherms of N-HG-600 at 77 K; (b) the pore size distributions of N-HG-600.

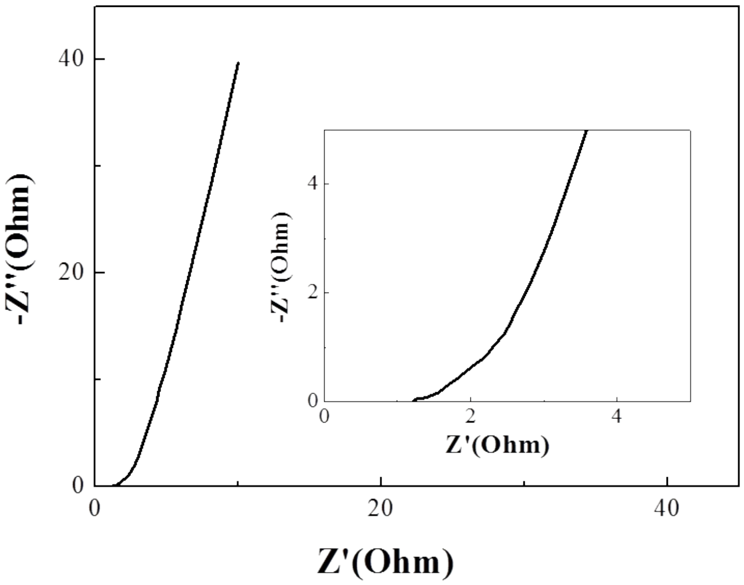

Fig.S8 EIS of N-HG-600 electrodes.

The projected length of the Warburg-type line (the slope of the 45° portion of the curve) on the real axis characterizes the ion diffusion process from solution into the intersheet region of N-N-HG-600. The short 45° Warburg region for N-HG-600 electrodes, suggesting the rapid ion diffusion within the N-HG-600 electrode due to its amount of in-plane holes.

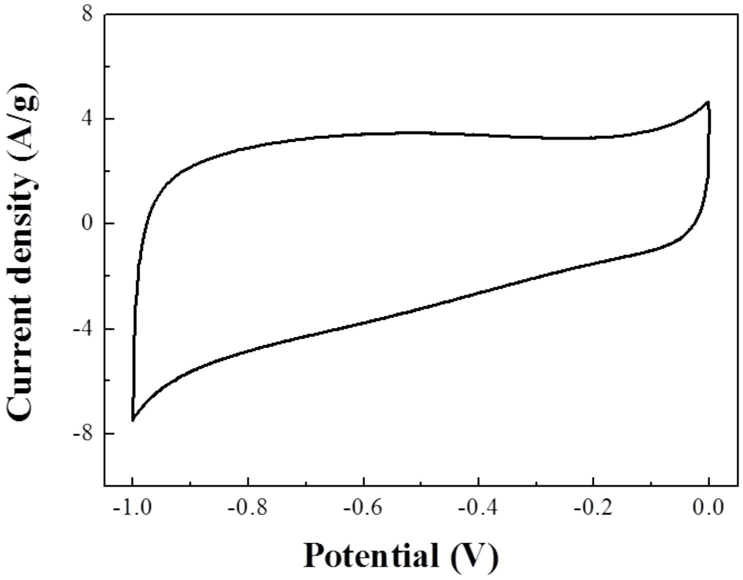

Fig.S9 CV of N-HG-800 electrode at 20 mV/s.

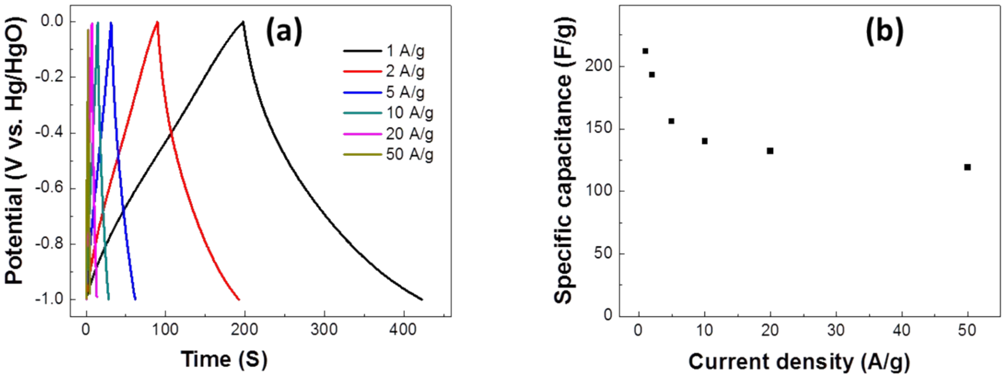

Fig.S10 (a) Galvanostatic charge/discharge curves of the N-HG-800 electrode at various current densities; (b) Gravimetric capacitances of the N-HG-800 electrode at different current densities.

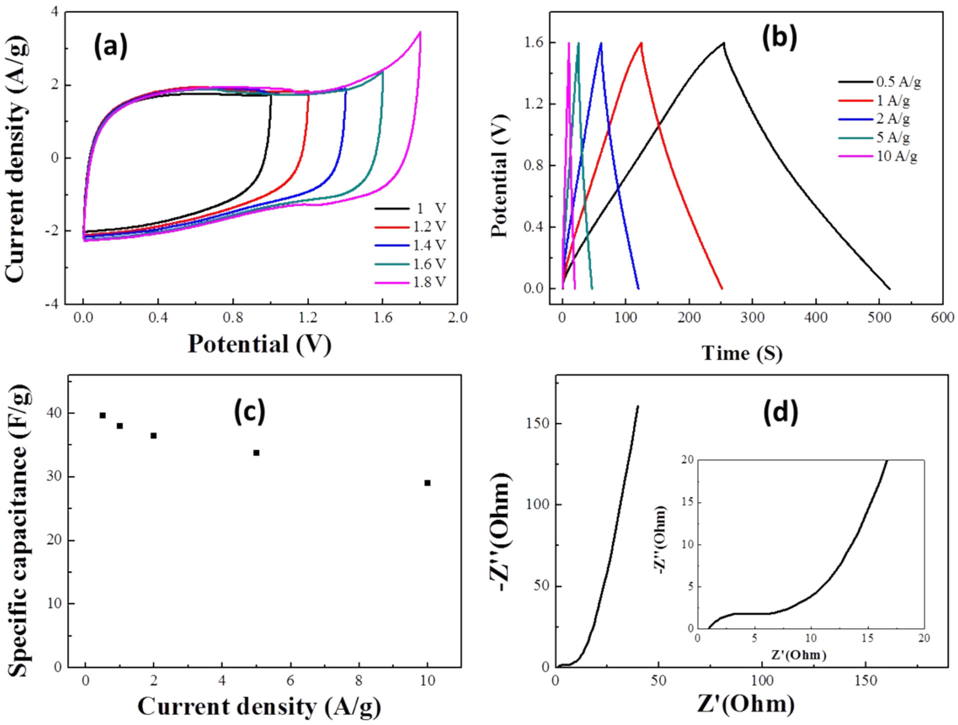

Fig.S11 (a) CV curves of the symmetric supercapacitor operated in different potential windows at 20 mV s^{-1}; (b) Galvanostatic charge/discharge curves of the symmetric supercapacitor at various current densities; (c) Gravimetric capacitances of the symmetric supercapacitor at different current densities; (d) EIS of the symmetric supercapacitor.

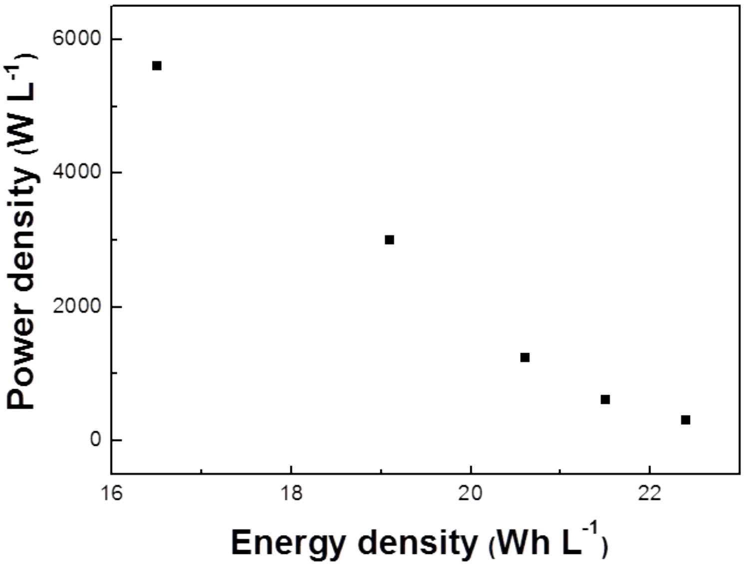

Fig.S12 Volumetric power density vs volumetric energy density based on the weight of active materials of the symmetric supercapacitor.

Table S1. The quantitative determination of N-N-HG by XPS.

Name	C1s	N1s	O1s
N-HG-600 (at. %)	81.24	9.92	8.84
N-HG-800 (at. %)	90.50	6.43	3.06

Table S2. Comparison for the N-HG-600 with previously reported graphene based high-density materials in aqueous electrolytes.

materials	**Packing density ($g\ cm^{-3}$)**	**SSA ($m^2\ g^{-1}$)**	**C_g ($F\ g^{-1}$)**	**C_v ($F\ cm^{-3}$)**	**Ref.**
N-HG	**1.12**	1330	284	234	[1]
N-HG	**0.71**	830	310	220	[2]
Graphene film	**1.33**		196.5	255.5	[3]
Graphene monolith	**1.58**	370	238	376	[4]
Functionalized graphene	**1.03**	285	456	470	[5]
graphene fibres		396	120	305	[6]
N-HG	**1.59**	**1602**	**250**	**397**	**This work**

References

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