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Supporting Information

Defects induced tunable oxygen functional groups evolution for sodium storage in porous graphene

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Experimental Section

Preparation of samples: (1) The preparation of graphene hydrogels: Graphite oxide powder (Carmery, Shanxi Institute of Coal Chemistry, Chinese Academy of Sciences) was ultrasonically dispersed into deionized water for 2 h, forming a 3 mg/mL graphene oxide (GO) dispersion. The obtained 70 mL GO suspension was sealed into a stainless steel autoclave, and kept at 180 °C for 12 h. Afterwards, when cooling down to ambient temperature, the graphene hydrogels were treated by freeze drying for 36 h and obtained the dry hydrogels.

(2) The preparation of porous graphene: The synthesized wet hydrogels were soaked separately into cobalt acetate, nickel acetate and ferric nitrate solutions (0.06 M) for 12 h. Then the hydrogels were dried and calcined at 800 °C for 1 h with a heating rate of 5 °C /min. Next, the samples were treated with diluted HCl solution to remove metals atoms, and washed to neutral with deionized water before dried at 60 °C in a vacuum oven. The resulted samples treated by cobalt acetate, nickel acetate and ferric nitrate solutions were denoted as Co-PG, Ni-PG, and Fe-PG, respectively. For comparison, the prepared graphene hydrogels was calcined at 800 °C for 1 h excepting for soaking into metal salts solutions.

Materials characterization: The scanning electronic microscopy (SEM, TESCAN MAIA 3 LMH) and transmission electron microscopy (TEM, JEM-2010) were applied to observe the morphology of samples. The specific surface area was estimated using Brunauer-Emmett-Teller (BET) and the pore width distribution was analyzed according to Barrett-Joyner-Halenda (BJH) model. X-ray diffraction (XRD, Rigaku MiniFlex600) patterns and Raman spectra (Thermo Fischer DXR spectrometer) were performed to examine the structural features. X-ray absorption near-edge structure (XANES) spectroscopy measurements were conducted at the 4B9B beamline of the photoelectron spectroscopy station at the Beijing Synchrotron Radiation Facility. X-ray photoelectron spectroscopy (XPS, ESCA Lab 220 i-XL electron spectrometer, VG, UK) was performed to determine the oxygen functional groups. Thermogravimetric-mass spectrometry analysis (TG-MS) was implemented to conduct accurate analysis for surface functional groups using thermogravimetric analyzer (Setaram Setsys Evolution 16/18). Samples (20–50 mg) were heated in Ar (50 mL/min) at a rate of 5 °C/min to 1100 °C, and the evolved gases during pyrolysis treatment were monitored by a PFEIFFER OMNI star mass spectrometer.

Electrochemical measurements: The electrochemical performances of fabricated materials were measured with CR 2025 coin cells. Typically, for the working electrode, active materials, super P and PVDF were mixed with weight ratio of 8:1:1 into N-methyl-2-pyrrolidone (NMP) solvent under constant stirring and form homogenous slurry. The slurry was spread over Cu foil and dried at 100 °C in a vacuum oven, and the mass loading of the electrode is about 1 mg cm^{-2}. The electrolyte was 1 M $NaCF_3SO_3$ dissolved in the diglyme solution, metallic sodium was used as a counter electrode and separated from the work electrode by glass fiber membrane. Cyclic voltammetry (CV) profiles were recorded by CHI1000C electrochemical work station at the voltage range of 0.01~3 V. The galvanostatic charge/discharge cycling performance was carried out on Land 2001A testing system.

The electrochemical impedance spectra (EIS) data was acquired by CHI660E electrochemical work station, tested in the frequency range of 0.1~100 k Hz. Galvanostatic intermittent titration technique (GITT) measurements were conducted through battery test system under a 0.05 A g^{-1} current pulse with 10 min duration and 1 hours rest.

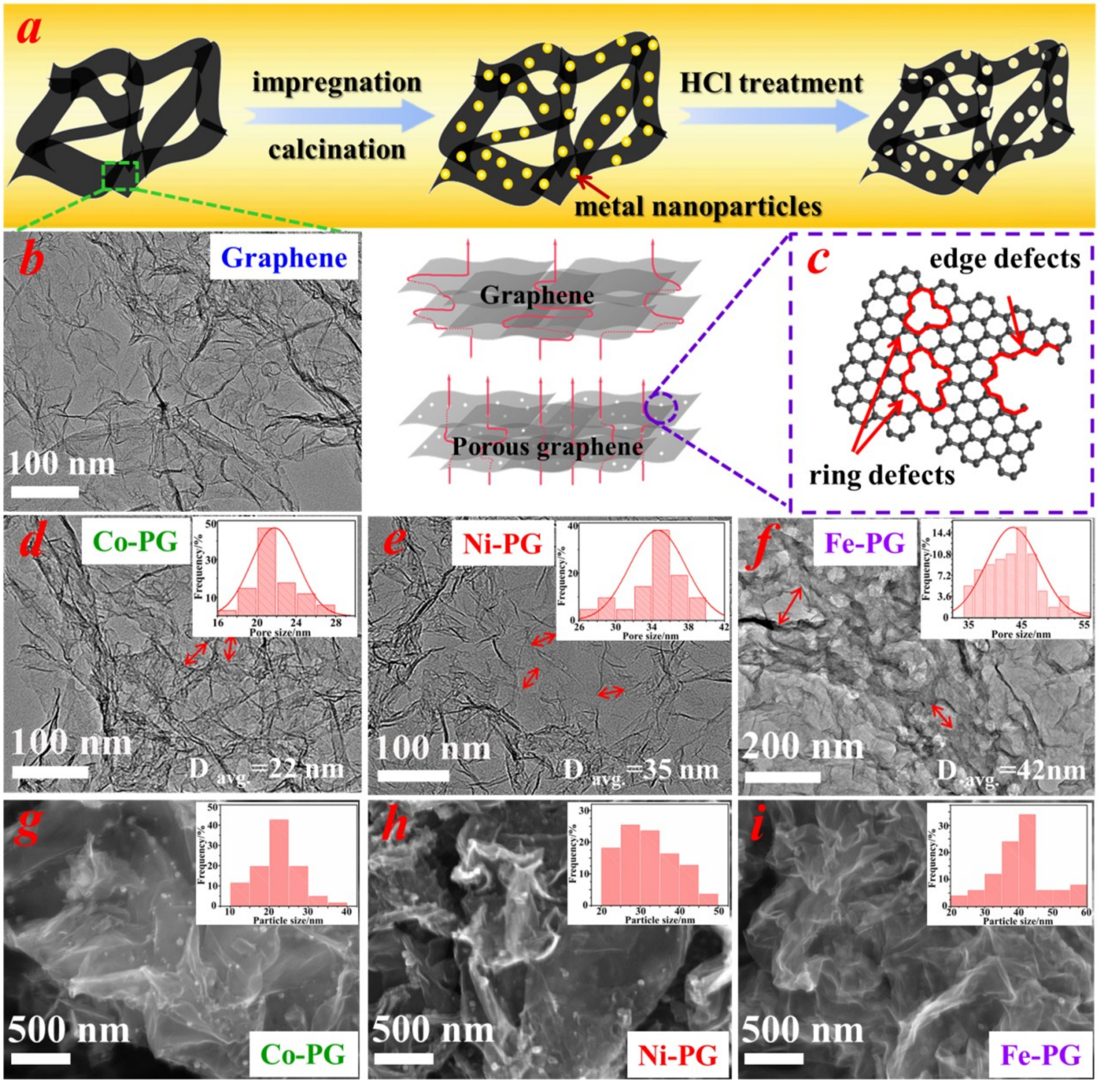

Fig. S1 (a) Schematic diagram of the synthesis of porous graphene via metal etching method, (c) the structural characters of defective graphene, TEM images of (b) graphene and (d) Co-PG, (e) Ni-PG, and (f) Fe-PG samples; SEM images of (g) Co-PG, (h) Ni-PG and (i) Fe-PG

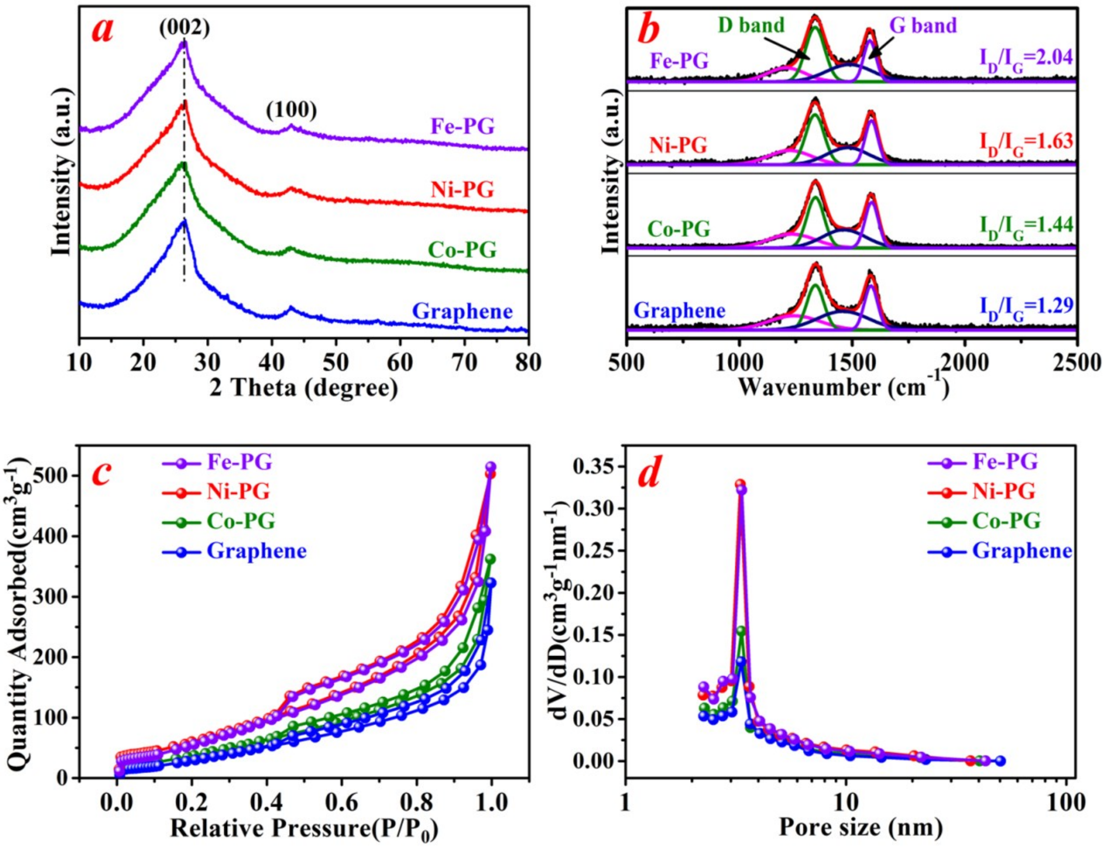

Fig. S2 (a) XRD patterns and (b) the fitted Raman spectra; the (c) nitrogen adsorption/desorption isotherms and (d) the pore-size distribution curves of samples

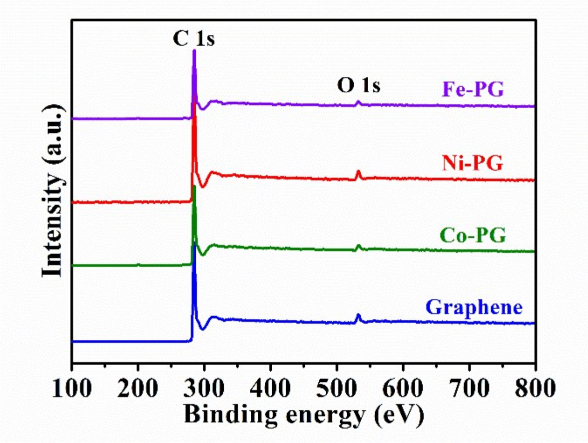

Fig. S3 XPS survey spectra of all the samples

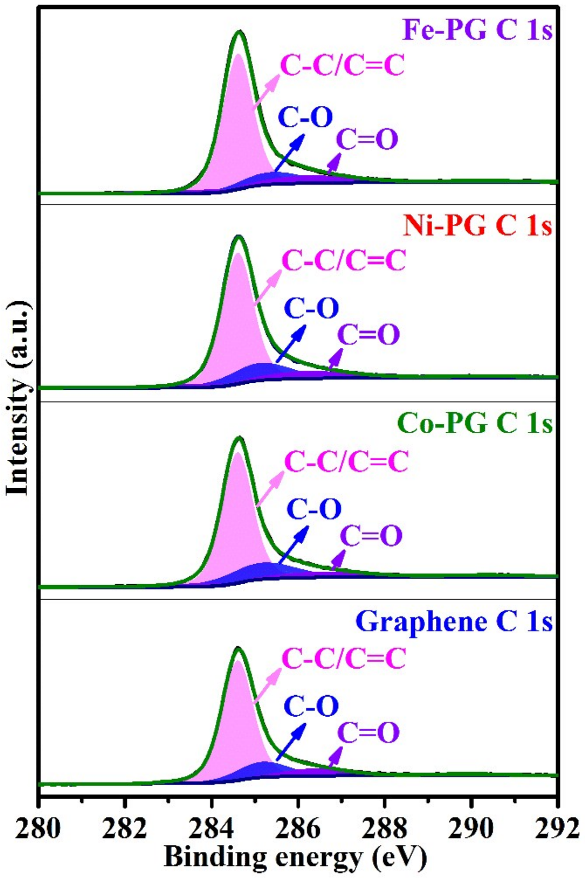

Fig. S4 XPS C 1s spectra of all the samples

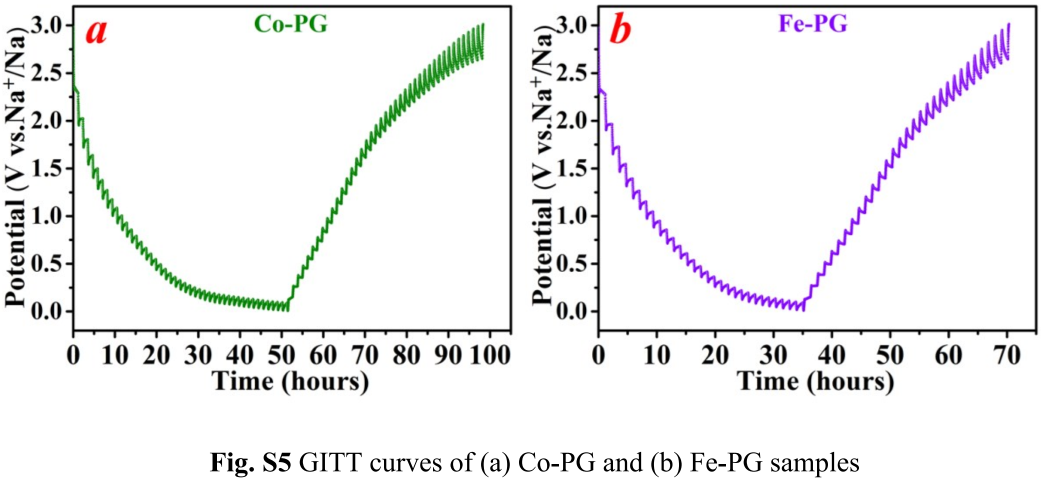

Fig. S5 GITT curves of (a) Co-PG and (b) Fe-PG samples