Electronic Supplementary Information

MOF-Derived Hollow SiO_x Nanoparticles Wrapped in 3D Porous Nitrogen-doped Graphene Aerogel and their Superior Performance as the Anode for Lithium-ion Batteries

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Experimental Section

Materials synthesis

MOF template synthesis of hollow SiO_x nanoparticles:

Hollow SiO_2 nanoparticles were fabricated with MOF (zeolitic imidazolate framework-8 (ZIF-8)) as both the precursor and the self-sacrificing template.[1] Briefly, solution of cetyltrimethylammonium bromide (CTAB), $Zn(NO_3)_2 \cdot 6H_2O$ and 2-methylimidazole (Hmim) were mixed together in fixed proportions at room temperature, and then reacted using methanol as solvent without stirring for 24 h. The ZIF-8 nanoparticles were obtained after centrifugation, washing and drying under vacuum. The core-shell ZIF-8@SiO_2 microstructure were prepared through a versatile Stöber sol-gel method.[2, 3] Then the hollow SiO_2 nanoparticles were obtained with the hydrothermal treatment of 24 h with hydrochloric acid, and the obtained hollow SiO_2 nanoparticles powders were annealed at 1000 °C for 2 h in reductive atmosphere of hydrogen (5%) and balanced by argon (5% H_2 and 95% Argon) to produce hollow SiO_x nanoparticles.[4] The aminopropyl trimethoxysilane (APS)-modified hollow SiO_x nanoparticles were prepared with a surface modification method.[5]

Fabrication of hollow SiO_X nanoparticles @N-doped graphene aerogel ($HSiO_x$@N-GA):

Graphite oxide (GO) was synthesized with the modified Hummers method as previously reported.[6] $HSiO_x$@N-GA was synthesized with a modified process.[7] Typically, solution of GO (1 mg ml^{-1}) and solution of APS-modified hollow SiO_x nanoparticles (5 mg ml^{-1}) were homogeneously mixed under sonication (20 min), the hollow SiO_x nanoparticles@GO was obtained after centrifugation and rinsing with deionized water for several times. In the controllable experiment, the weight percent of hollow SiO_x nanoparticles was typically kept at 84%. Subsequently, hollow SiO_x nanoparticles@GO was homogeneously dispersed in urea (100 mg ml^{-1}) aqueous solution, then transferred into a Teflon-lined stainless steel autoclave, and reacted at 150 °C for 6 h. After the autoclave was naturally cooled to room temperature, the resulting N-doped graphene hydrogel embedded with hollow SiO_x nanoparticles (hollow SiO_x nanoparticles@N-doped graphene hydrogel) were rinsed with deionized water for several times, and then freeze-dried. Finally, for completing the reduction process of hollow SiO_x nanoparticles and bits of residual GO, the product was annealed at 500 °C for 2 h in reductive atmosphere (5% H_2 and 95% Argon) to generate 3D $HSiO_x$@N-GA. For comparison, hollow SiO_x nanoparticles@GA ($HSiO_x$@GA) were fabricated by the same method with the preparation process of $HSiO_x$@N-GA without adding urea. N-GA and GA were fabricated by assembly of GO by using the same hydrothermal method in the presence and without adding urea, respectively.

Materials characterization

The collected products were characterized by using powder X-ray diffraction (XRD) on a Rigaku diffractometer with Cu *Kα* radiation. X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA) was performed to analyze the chemical compositions of the synthesized samples. N_2 adsorption and desorption isotherms at 77K were measured by using a Tristar II 3020 instrument, and the specific surface area was measured by utilizing the Brunauer-Emmett-Teller (BET) method. The pore diameter and pore size distribution were calculated by the Barrett-Joyner-Halenda (BJH) model. Raman measurements were performed at room temperature by using Thermo-Fischer Almega dispersive Raman instrument with the excitation wavelength of 633 nm. Fourier transform infrared (FTIR) spectra were recorded with a Nicolet 5700 FTIR spectrometer. Thermal gravimetric analysis (TGA, Mettler Toledo TGA/DSC1 STARe System) was measured with a 10 °C min^{-1} heating rate in air flow from room

temperature up to 800 °C. A four-probe conductivity test metre was used to measure the electronic conductivity of samples at room temperature (SB120; San Feng). The morphology and microstructure of the samples were obtained from field-emission scanning electron microscope (FESEM, Hitachi S-4800), transmission electron microscope (TEM, JEOL1010) and high-resolution (HRTEM, FEI Tecnai20). The TEM and HRTEM samples were disposed by dispersion in ethanol with sonication of scraped nanoparticles, and dropping onto Cu grids with carbon-coating. A high precision electronic balance (XP105DR, Mettler Toledo) was utilized to tip the scale at all the materials.

Electrochemical Measurement

Fabrication of Electrodes and Coin Cells:

Electrodes were fabricated by mixing the as-obtained $HSiO_x$@N-GA as the active material, polyvinylidene fluoride (PVDF) as binder, N-methy1-2-pyrrolidone (NMP) as solvent, and carbon black as conductor with a mass ratio of 80:10:10 to form a mixture (slurry). The resulting slurries were pasted onto Cu foil (as a current collector), after drying at 75 °C for 12 h in vacuum oven and compressing at a given pressure, the Cu foil was cut into disks with diameter of 1.5 cm with average loading masses of *ca.* 1 mg/cm^2. The CR2032-type half-cells that were assembled in an argon-filled glove box with controlling the contents of oxygen and moisture under 1 ppm, and 1 M of $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) solvent (1:1:1 vol/vol/vol) was utilized as an electrolyte, with Celgard 2500 (polypropylene) as separator, active material as anode and metal lithium disks as cathode.

***Electrochemical Characterization*:**

The galvanostatically discharged and charged measurements of the cells were tested on a Land (CT2001A) system over a voltage range of 0.01-1.5 V (*vs.* Li/Li^+) at room temperature. Noting that "n C" means that the discharge/charge current is set up to attain the nominal capacity in "1/n" hours. For $HSiO_x$@N-GA electrode, the weight of $HSiO_x$@N-GA in the working electrode was applied to judge the specific discharge capacity of the cell, which was showed in mAhg^{-1} of $HSiO_x$@N-GA. On the basis of the equation described below, we could calculate a theoretical capacity (Q) of the hypothetical mixture of $HSiO_x$@N-GA, as follows:

$$Q_{theoretical}=Q_{hollow\ SiOx\ nanoparticles}\times \text{mass percentage of hollow } SiO_x \text{ nanoparticles} + Q_{N\text{-}GA}\times \text{mass percentage of N-GA}$$
$$=2400\times 83.74\% + 372\times 16.26\% = 2070.72\ \text{mAhg}^{-1}$$

(The theoretical capacity (Q) of SiO_x was calculated on the basis of theoretical capacity of SiO previously reported,[8] owing to the average valence state of Si in $HSiO_x$@N-GA is calculated to be ca. 2.11, the value that is on the verge of the theoretical valence state of Si (2.0) in SiO.)

Cyclic voltammetry (CV) curves were collected by a CHI660C electrochemistry workstation at 0.1 mV·s^{-1} between 0.01-3.0 V (vs. Li/Li^+). Electrochemical impedance spectroscopy (EIS) of the as-prepared anodes were measured on a PARSTAT 2273 electrochemical station over a frequency range of 10 000-0.1 Hz with an amplitude of 5 mV. Recurrence of the electrochemical data was verified by repeating the experiments until obtaining at least another anode of the same specimen.

S1. Photograph illustration of the preparation procedure of $HSiO_x$@N-GA.

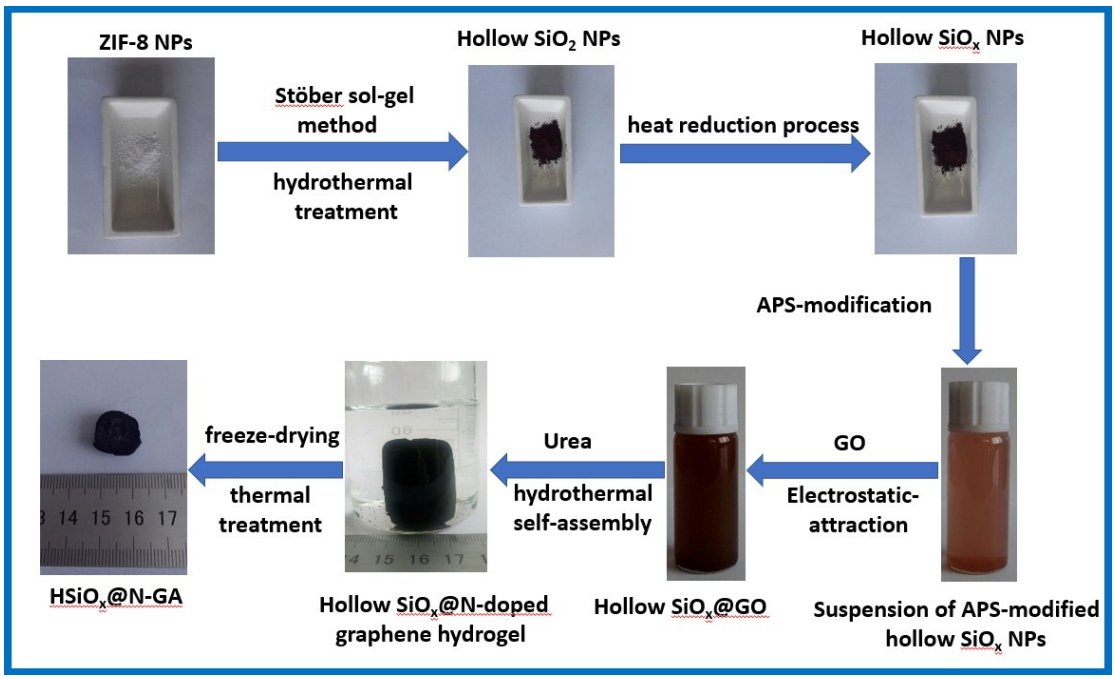

Fig. S1† The photograph illustration of the preparation process of $HSiO_x$@N-GA. Hollow SiO_x nanoparticles were synthesized with method of MOF-templet inducting, including fabrication of ZIF-8, Stöber sol-gel synthesis, hydrothermal treatment and heat reduction process. Hollow SiO_x@GO, which existed in the form of stable and uniform suspension, was obtained by the electrostatic-attraction between APS-modified hollow SiO_x nanoparticles and GO. Hollow SiO_x@N-doped graphene hydrogel was prepared by hydrothermal self-assembly with urea. After the freeze-drying and thermal treatment process, a monolithic hybrid aerogel ($HSiO_x$@N-GA) was obtained.

S2. Morphology information of the as-prepared hollow SiO_x nanoparticles

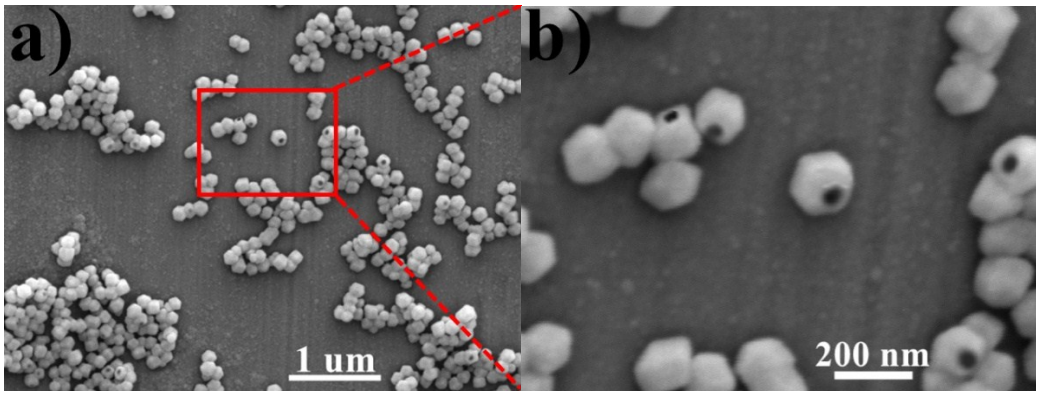

Fig. S2† (a) Low-magnification, (b) high-magnification SEM images of the as-prepared hollow SiO_x nanoparticles, showing hollow SiO_x nanoparticles exhibited the uniform sodalite zeolite-type structure-rhombic dodecahedral shape, as well as obvious irregular aggregation between hollow SiO_x nanoparticles, and average size of hollow SiO_x nanoparticles was ranged 100-160 nm; (b) is corresponding to the red-rectangle area in (a).

S3. Morphology information of the as-prepared $HSiO_x$@N-GA at low magnification

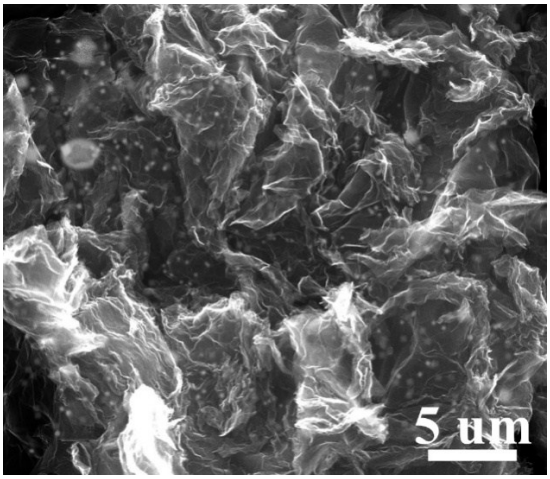

Fig. S3† SEM images of $HSiO_x$@N-GA at low magnification, showing hollow SiO_x nanoparticles were wrapped in the interior and surface of porous N-GA network.

S4. Morphology information of the as-prepared N-GA

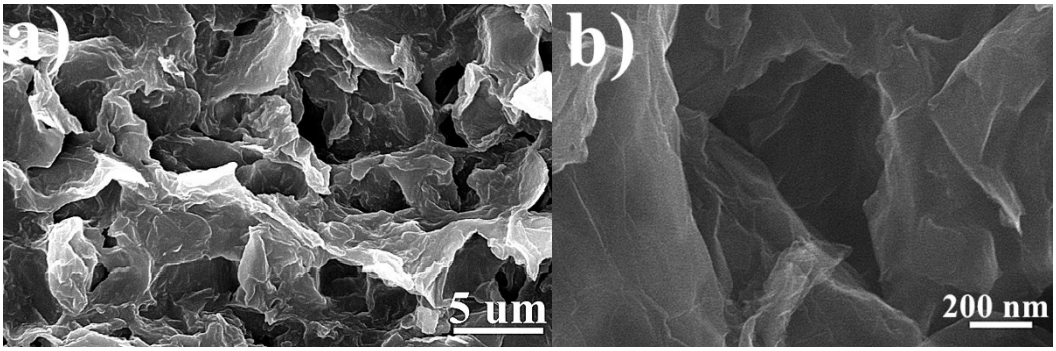

Fig. S4† SEM images of N-GA, showing fully interconnected, porous 3D graphene frameworks with randomly opened macro-/mesoporous structure.

S5. Nitrogen isothermal adsorption-desorption measurement of $HSiO_x$@N-GA, hollow SiO_x nanoparticles and N-GA.

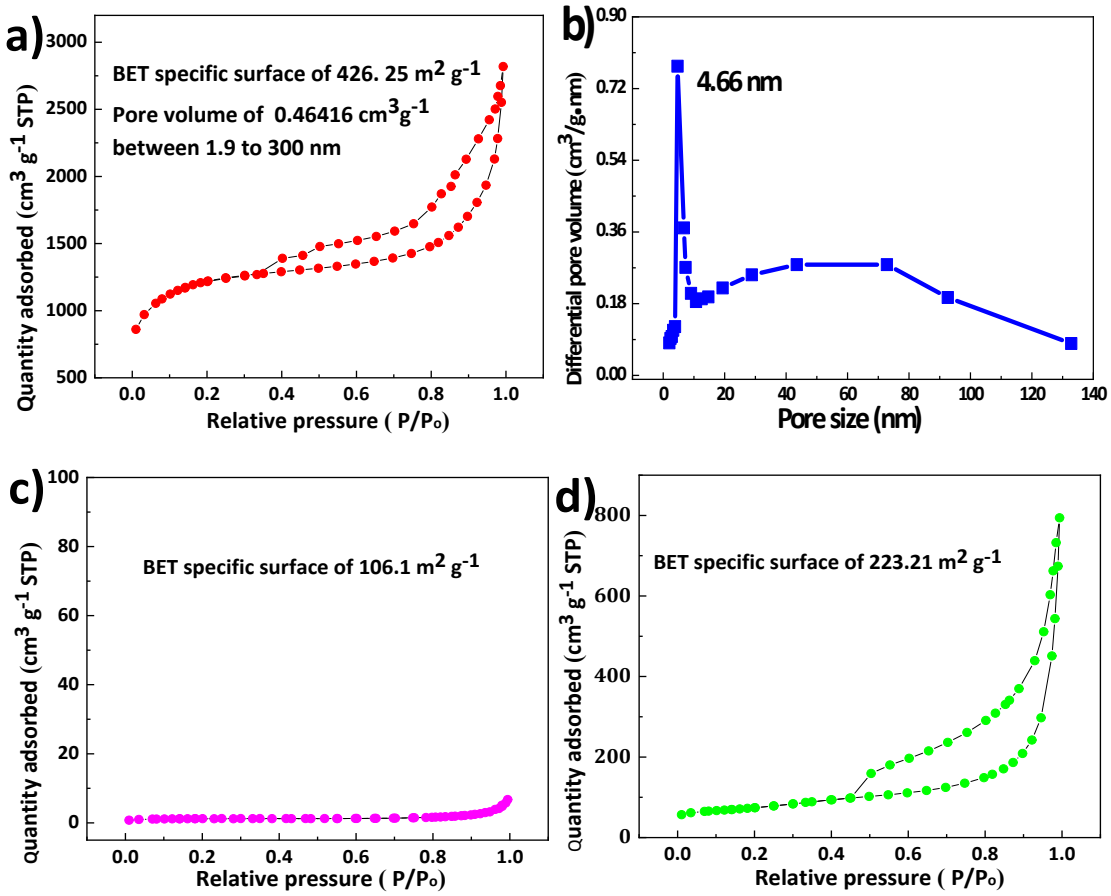

Fig. S5† (a) Nitrogen adsorption-desorption isotherm plot of $HSiO_x$@N-GA at 77 K; (b) BJH adsorption pore size distribution profiles of $HSiO_x$@N-GA; (c and d) Nitrogen adsorption-desorption isotherm plots of hollow SiO_x nanoparticles and N-GA at 77 K.

S6. Electrochemical performance of hollow SiO_x nanoparticles.

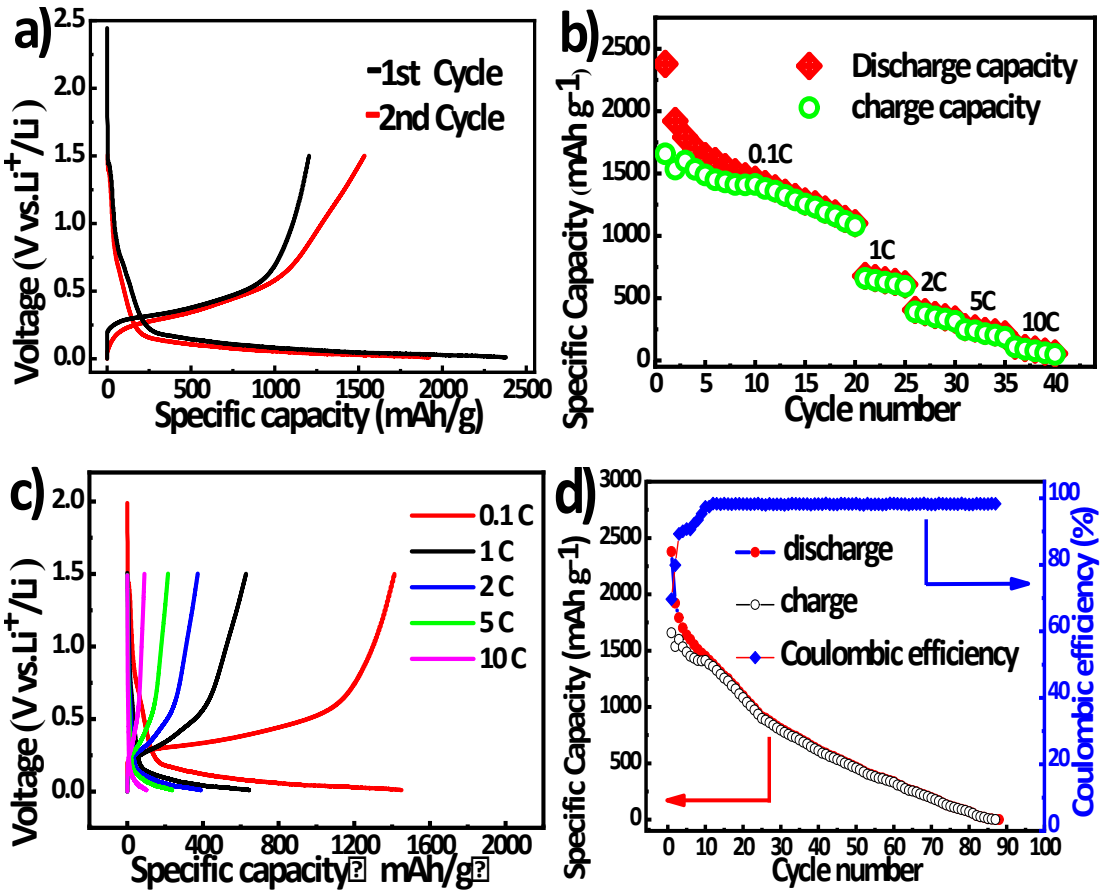

Fig. S6† Electrochemical properties of hollow SiO_x nanoparticles: (a) discharge and charge profiles for the initial two cycles at 0.1 C. The first discharge and charge capacities are 2380 and 1204 mA h g^{-1} with an initial Coulombic efficiency of 50.6%. The capacity is based on total anode mass of hollow SiO_x nanoparticles. (b) rate performance cycled from 0.1 C to 10 C. (c) discharge and charge profiles at current rates ranging from 0.1 C to 10 C and (d) cycling performance at 0.1 C and Coulombic efficiency. Hollow SiO_x nanoparticles anode was un-rechargeable under a current rate of 0.1C after 87 cycles, suggesting an inferior cycling performance.

S7. Electrochemical performance of N-GA.

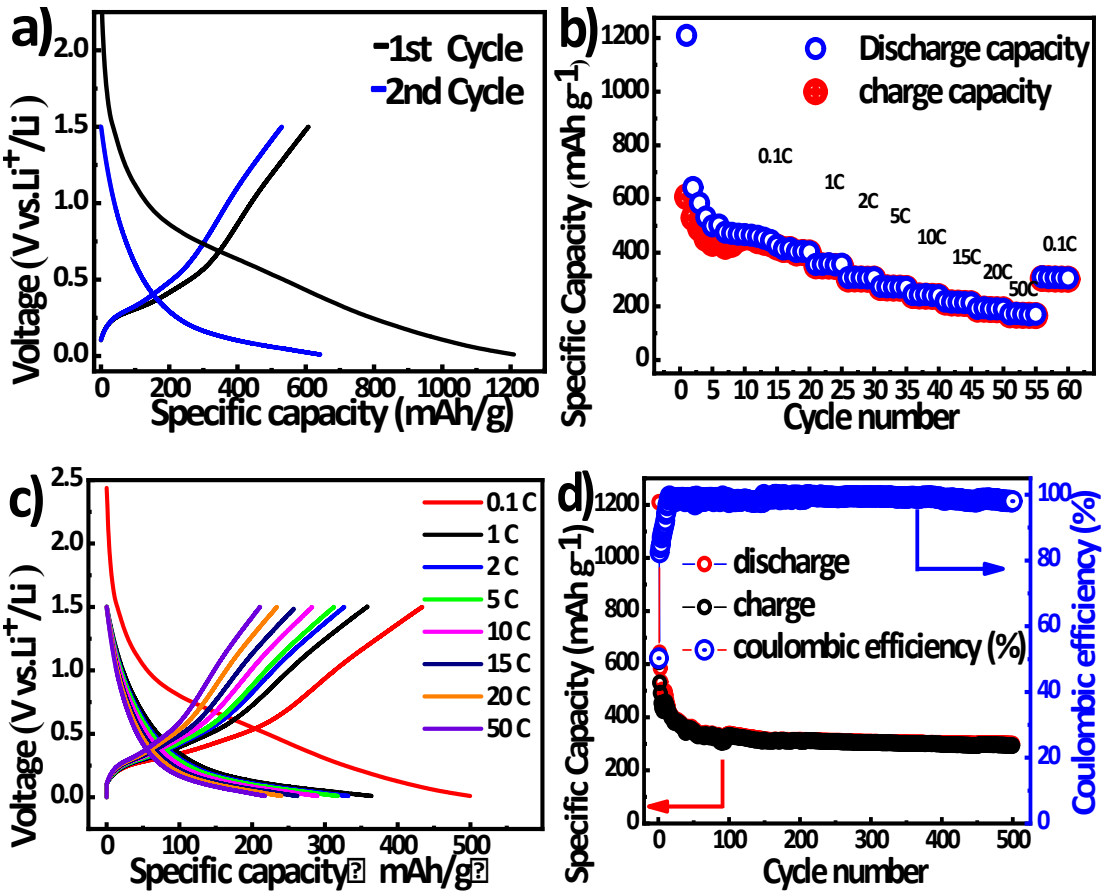

Fig. S7† Electrochemical properties of N-GA: (a) discharge and charge profiles for the initial two cycles at 0.1 C. The first discharge and charge capacities are 1209.5 and 608.1 mA h g^{-1} with an initial Coulombic efficiency of 50.27%. The capacity is based on total anode mass of N-GA. (b) rate performance cycled from 0.1 C to 50 C. (c) discharge and charge profiles at current rates ranging from 0.1 C to 50 C and (d) cycling performance at 0.1 C and Coulombic efficiency. N-GA exhibits a charge capacity of 293 mAh g^{-1} under a current rate of 0.1C after 500 cycles, suggesting a common cycling stability.

References:

[1] Liu He, Lu Li, Lingyu Zhang, Shuangxi Xing, Tingting Wang, Guangzhe Li, Xiaotong Wu, ZhongminSu and Chungang Wang, *CrystEngComm*, 2014, **16**, 6534.

[2] W. Li, Y. H. Deng, Z. X. Wu, X. F. Qian, J. P. Yang, Y. Wang, D. Gu, F. Zhang, B. Tu and D. Y. Zhao, *J. Am.Chem. Soc.*, 2011, **133**, 15830.

[3] X. Q. Zhang, H. Ren, T. T. Wang, L. Y. Zhang, L. Li, C. G. Wang and Z. M. Su, *J. Mater. Chem.*, 2012, **22**, 13380.

[4] SangKyu Lee, SeungMin Oh, Eunjun Park, Bruno Scrosati, Jusef Hassoun, MinSik Park, YoungJun Kim, Hansu Kim, IliasBelharouak and YangKook Sun, *Nano Lett*. 2015, **15**, 2863-2868.

[5] W.B. Luo, S.L. Chou, Y.C. Zhai and H.K. Liu, *J. Mater. Chem. A*, 2014, **2**, 4927-4931.

[6] Z. Xiong, L. L. Zhang, J. Ma and X. S. Zhao, *Chem. Commun.*, 2010, **46**, 6099-6101.

[7] W. Wei, S. Yang, H. Zhou, I. Lieberwirth, X. Feng and K. Müllen, *Adv. Mater.*, 2013, **25**, 2909-2914.

[8]YaJun Chao, Xianxia Yuan and ZiFeng Ma, *Electrochimica Acta.,*2008, **53**, 3468-3473.