Supplementary Information for

Nitrogen doped graphene nanoribbons for high performance lithium ion batteries

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Experimental materials

Melamine and anhydrous ferric chloride were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Concentrated nitric acid (65-68%) was purchased from Tianjin Kermel Chemical Co., Ltd (Tianjin, China). Commercial multi-walled carbon nanotubes (length $<2\mu$ m, diameter 20-40nm, purity>95%) were purchased from Nanotech Port Co., Ltd (Shenzhen, China). All the chemicals were analytical grade reagents and were used without any purification.

Experimental procedure

1. Synthesis of iron filled nitrogen doped carbon nanotubes

The floating catalyst chemical vapor deposition (FCCVD) method was used to synthesize Fe@CN_x-CNTs. Anhydrous ferric chloride was employed as catalyst precursor and filled iron source. Melamine was used as carbon and nitrogen source. Reaction process was carried out in a quartz tube inserting into tubular furnace with diameter 40mm and length 600mm. Same mass of FeCl₃ and melamine was separately put into two porcelain boats (length 80mm) then pushed them into the quartz tube side by side until reached the entrance of furnace. Before the furnace was heated, argon was introduced into the reaction system at a flow rate of 400sccm for 30min to displace the air in the tube. Then the FCCVD system was heated to 800°C at a rate of 10°C/min. In the experiment, melamine and FeCl₃ would evaporate together as temperature of tube entrance could exceed 400°C(higher than their boiling points, 300°C for melamine and 315°C for FeCl₃) while the central area of the tube reached 800°C. Then Ar flow was adjusted to 200sccm so catalyst and carbon source could mix evenly and carbon nanotubes would grow when mixture got central of the tube. The whole evaporation process lasted for about 30min. After that the system cooled down to room temperature in the protection of Ar gas.

2. Formation of nitrogen doped graphene nanoribbons

100mg Fe@CN_x-CNTs was added into 100ml nitric acid then ultra-sonicated for 5min to form a homogenous suspension. The mixture was heated in a round-bottom flask equipped with a reflux condenser and magnetic stirrer immersed in an oil bath at 120°C. The reflux time lasted for 4 or 10h. After that the mixture was poured into 500ml de-ionized water and filtered. Then the resulting black solid was carefully washed until a neutral pH was achieved. The finally products were dried under vaccum at 80°C for 12h.

For comparison, we also carried the KMnO₄/H₂SO₄ oxidation as reported by Kosynkin and coworkers¹. In detail, 150 mg Fe@CN_x-CNTs was added into 30ml concentrated sulfuric acid with continuous stirring for 2 h then treated them with 750 mg KMnO₄. The mixture was kept for 1 h at room temperature then heated to 60 °C for another 1h. The resulted yellow green solution was diluted by de-ionized water containing 10 ml H₂O₂ solution (30 wt%). The final samples were obtained after centrifugation and washing process and their characterizations were shown in Fig. S8.

Characterization

The morphology of products was characterized by scanning electron microscopy (SEM, JMS-6360 LV) and transmission electron microscopy (TEM, JEM-2000EX). The crystalline phases of the products were examined using Rigaku D/MAX-2400 diffractometer (XRD) equipped with a rotating anode and a CuK α radiation source (λ =0.15418 nm). X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo ESCALAB 250 spectrometer employing an Al-K α X-ray source. Thermal stability of the samples was assessed by thermal gravimetric analysis (TGA, TA-Q50) in air with temperature range from 30 °C to 800 °C at a heating rate of 10 °C min⁻¹.

Electrochemical measurements

At first, slurry was prepared by mixing 70% active electrode material (N-GNRs), 20% acetylene black, 10% polyvinylidene fluoride (PVDF) binder. Then working electrodes were fabricated by slurry casting on a Cu foil. The electrodes were dried under vacuum at 120°C overnight. Coin type cells were assembled in a glove box under argon atmosphere (water and oxygen concentration less than 0.1 ppm). It consisted of a prepared electrode, polypropylene separator, and lithium foil as the counter electrode. The electrolyte used in this experiment was 1 M LiPF₆ salt dissolved in ethylene carbonate (EC), diethyl carbonate (DEC) in a 1:1 volume ratio. The galvanostatic charge/discharge tests were carried out on a Land CT2001A battery test system between 0.01-3.0 V using 2016 coin-type cells.



Fig.S1 XRD patterns of (a) pristine Fe@CN_x-CNTs, (b) N-GNRs. It can be seen that iron nanowires filled into the CNTs are mainly α -Fe and Fe₃C phase and most of them dissolved into nitric acid solution after 10h reflux, thus only graphite peak (002) can be observed in sample N-GNRs.



Fig. S2 TG and differentiate curves (DTG) of (a) pristine $Fe@CN_x$ -CNTs, (b) P-CN_x-CNTs (Partially unzipped N doped CNTs obtained by reflux in concentrated nitric acid for 4h), and (c) N-GNRs.

The TG plot of Fe@CN_x-CNTs shows a slight weight increase at around 420 °C then the weight decrease dramatically resulting from the oxidation of CNTs. A stable weight percentage of 52.9% (It represents the weight of residual iron oxide and the content of iron is 37.0% by calculation) was achieved at 700°C. As reported, the weight loss rate of ferromagnetic metal filled CNTs always gets slower with the increasing of temperature since the tube walls which protect metal filled inside will be firstly destroyed then metal oxide will be formed.² Theoretically, there will be a point of inflection exists in TG curve. However, the TG curve of Fe@CN_x-CNTs is smooth, which means that the iron and iron carbide filled inside are oxidized by air together with the tube walls. This is an interesting phenomenon and needs further investigation. DTG plot derived from TG exhibits one single peak located at 545°C for the pristine samples. While the partially opened CNTs/N-GNRs exhibit three independent peaks located at 250°C/220°C, 489°C/454°C and 585°C/582°C. The first peak corresponds to the pyrolysis of oxygen-containing functional groups.³ The second peak ascribes to N-GNRs which have large surface area and contain abundant edges leading to less thermal stability than CNTs.⁴ The last peak attributes to residual CNTs which are not fully unzipped. From Figure S2 (b) and (c), we can clearly see that the peaks of N-GNRs get larger with the increment of oxidation time in nitric acid. And the content of N-GNRs is dominant in the materials based on their weight loss.



Fig.S3 SEM (a) and TEM (c, d) images of flat N-GNRs and partially opened N doped CNTs after reflux in concentrated nitric acid for 10h (Fig. S3(b) is the diameter distribution of N-GNRs based on SEM). SEM (e, f) and TEM (g, h, i) images of P-CN_x-CNTs or curved N-GNRs obtained after oxidation in concentrated nitric acid for 4 h (e, g-i) or through oxidation in diluted nitric acid (40 wt%) for 10 h (f). The SEM and TEM images of d-i all display partially opened CNTs and clearly exhibit the transformation of CNTs into GNRs.



Scheme S1 Schematic of the unzipping process (black balls represent carbon atoms, green balls represent nitrogen atoms and blue balls represent oxygen atoms). I : The pair of carbonyl groups were introduced into the C-C bonds of tube walls and broke them. II : Juxtaposition of the buttressing ketones distorted the neighbor parallel bonds making them more prone to be attacked and once an opening started further opening enhanced.¹ III: N-GNRs formed after relief of the bond angle strain.

Based on the characterizations we suggest that the special structure (thin wall, big diameter and iron filling) and nitrogen doping are the main factors leading to easily unzipping of $Fe@CN_x$ -CNTs. Thin walled CNTs with big diameters are easier to be longitudinal unzipped because of their abundant defects compared with the smaller ones.⁵ The role of iron fillingis is very complicated. Take into consideration of the structures of pristine samples, we believe that the high iron filling ratio prohibits the formation of bamboo compartments during CNTs growing process. And the iron may also promote the nitric acid oxidation process which has been observed in H₂O₂ or air oxidation experiments.⁶ There are at least two roles for N atoms in unzipping CNTs. Firstly, nitrogen doping introduces defects into the tube walls which makes them favor formation of vacancies and oxygen-containing functional groups. Moreover, nitrogen atoms exhibit high charge density and oxidant ion could be attached to the N-doped sites.⁷ As reported, the C=N bond of pyridinic nitrogen could be oxidized to C-O-N bond and further oxidized to C=O group which were also confirmed by XPS in our experiment.⁵ So nitrogen atoms are favorable factors for oxidation and nitrogen doped sites are preferential sites for initial unzipping. A comparative experiment using KMnO₄/H₂SO₄ solution as oxidant has also been done, but only few GNRs and many graphite fragments were observed (as the following Fig. S7). This demonstrates that $Fe@CN_x$ -CNTs could be easily oxidized and unzipped while moderate oxidation is more favorable to keep the integrity of the ribbon structures.



Fig. S4 (a) SEM and (b) TEM images of commercial CNTs after reflux for 10h in concentrated nitric acid (labeled as A-CMCNTs). The images reveal that the commercial CNTs still keep tube structures without longitudinal cutting along the tube walls.



Fig. S5 Cycling performance of pristine $Fe@CN_x$ -CNTs, commercial CNTs and P-CN_x-CNTs obtained by oxidation in nitric acid for 4 h, current density: 0.1 A g⁻¹.

A discharge capacity of 445 mAh g⁻¹ was obtained for Fe@CN_x-CNTs, higher than the 347 mAh g⁻¹ of commercial CNTs after 100 cycles. As the iron filled in the tube cavities cannot contribute to the lithium storage, so nitrogen doping is the main reason for their higher capacity compared with that of the commercial ones. The lithium storage ability of sample was further improved after partially unzipping of CNTs and a high capacity of 613 mAh g⁻¹ was achieved for P-CN_x-CNTs after 100 cycles.



Fig. S6 Galvanostatic charge-discharge profiles of (a) Fe@CN_x-CNTs, (b) P-CN_x-CNTs, (c) N-GNRs, (d) Commercial CNTs and (e) A-CMCNTs electrodes at a current density of 0.1 A g^{-1} between 0.01-3.0 V versus Li⁺/Li.

The Fig.S6 (a-c) clearly demonstrates that the capacity increases with the post-treatment time in nitric acid. The first cycle discharge capacity of Fe@CN_x-CNTs is 645 mAh g⁻¹ and improve to 788 mAh g⁻¹ or 1173 mAh g⁻¹ after reflux for 4h or 10 h, respectively. Similarly, for the commercial CNTs and A-CMCNTs, the specific capacity grows from 663 mAh g⁻¹ to 1010 mAh g⁻¹ after acid treatment process ((d) and (e)). The reason may be ascribed to that the oxygen-containing functional groups introduced into the carbon matrix induced the formation of a much more stable, chemically bonded SEI layer.⁸ The N-GNRs shows much more higher reversible capacity than the A-CMCNTs for the first and following cycles. The discharge and charge capacity of N-GNRs after 100 cycles shows higher values than that of the 50 cycle, while the A-CMCNTs show a capacity decrease during cycling. The results confirm that nitrogen doping and edge effect are beneficial to improving the capacity and cycling stability of carbon materials. And more graphene edges in GNRs would provide more Li⁺ storage sites.



Fig. S7 (a) SEM and (b) TEM images of samples obtained by heating $Fe@CN_x$ -CNTs in KMnO₄/H₂SO₄ solution using the method reported by Kosynkin and co-workers.¹

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