

Changes of microstructures and lithium-ion storage performance induced in quadrangular carbon nanotubes by heat treatment

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Introduction

In our previous reports, a kind of quadrangular carbon nanotubes (CNTs) was prepared in large-scale.¹ This kind of CNTs was named as q-CNTs. Because of their special morphology and microstructures including quadrangular cross section, as well as one open end and “herringbone”-like walls, q-CNTs should have broad potential applications in many fields, including drug delivery, conductive and high-strength composites, field emission displays and radiation sources, hydrogen storage media, and supercapacitor. Preliminary investigation revealed that the unique nanostructures of q-CNTs can be favorable to lithium-ion diffusion, so q-CNTs exhibit excellent high-rate performance (a high-reversible capacity of 181 mAhg^{-1} at the current density of 1000 mA g^{-1} (ca. 3 C)) when used as the anode materials for lithium-ion batteries. However, the first cycle efficiency of q-CNTs electrode (40 %) is still lower than the values of commercial graphite materials. This is a general drawback for carbon nanomaterial electrodes.³² High-temperature heat treatment (or graphitization) is an effective way to improve the first cycle efficiency of carbon materials, because the defects and impurities such as metal nanoparticles can be removed.² Therefore, it is very important to investigate the changes of morphology and microstructures of q-CNTs after high-temperature heat treatment.

Here, q-CNTs are transformed to graphitized q-CNTs (gq-CNTs) by heat treatment at 2800°C . The morphology and structure of gq-CNTs were characterized by scanning electron microscope (SEM), transmission electron microscope (HRTEM), and x-ray diffraction (XRD) measurements. The electrochemical performance of gq-CNTs used as anode materials were also investigated. Compared with q-CNTs, the gq-CNTs still keep the high-rate performance and simultaneously possess higher first cycle efficiency, indicating that gq-CNTs should be a promising candidate for new generation anode materials in lithium-ion secondary batteries.

Experimental

Synthesis of quadrangular carbon nanotubes and traditional carbon nanotubes: 1,2,4,5-Tetramethylbenzene (durene, $\text{C}_{10}\text{H}_{14}$) was chosen as the carbon source and ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) as the metal precursor. The q-CNTs were prepared by the co-carbonization of durene (10 g) and ferrocene (25 g) at 520°C for 3 h. The synthesis procedure in detail can be seen reference.¹ The gq-CNTs were obtained by the graphitization of q-CNTs at 2800°C .

Characterization: The high-resolution transmission electron microscope (HRTEM) measurement was carried out with a JEOL JEM-3010 F microscope operating at 300 kV. The scanning electron microscope (SEM) observation was conducted on a Hitachi S-4700 field emission scanning electron microscope (FESEM). X-

ray diffraction (XRD) measurements were performed with a Rigaku D/max-2500B2+PCX system using $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) over the range of $5\text{-}90^\circ (2\theta)$ at room temperature.

Electrochemical measurements: The electrochemical experiments were conducted in a two-electrode system described elsewhere.³ Working electrode was prepared by mixing active mass (q-CNTs or gq-CNTs, 80 wt.%), acetylene black (10 wt.%) and poly(vinylidene difluoride) (PVDF, 10 wt.%) and Lithium sheet was used as both reference and counter electrodes. One molar LiPF_6 solution in a ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 volume) was used as electrolyte. The cells were galvanostatically discharged and charged in the voltage range from 0.01 to 2.50 V versus Li/Li^+ at various current densities.

Results and Discussion

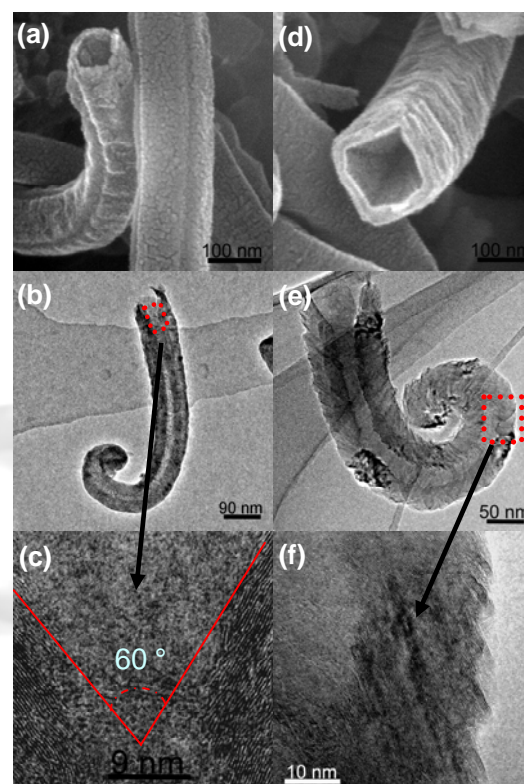


Fig. 1 (a) SEM, (b) TEM, and (c) HRTEM images of as-prepared q-CNTs, and (d) SEM, (e) TEM, and (f) HRTEM images of gq-CNTs.

Fig. 1a shows that the cross section of as-prepared CNTs is quadrangular, the bodies are also tetrahedral and its one end is open, which is quite different from the commercial CNTs with circular cross section. In further, it can be seen clearly that q-CNTs body is made up of four planes and the edge of both intersecting planes can be observed clearly. Fig. 1b shows TEM image of an as-prepared q-CNT. It also reveals that one end is open and the other one is closed, consisting with the SEM observation. The HRTEM image (Fig. 1c) shows that the wall of the q-CNT consists of stacked graphene nanosheets rather than the concentric graphene cylinders. These graphene nanosheets form “herringbone”-like nanostructure rather than “Russian Doll”-like concentric nanostructure of commercial CNTs. Although the herringbone-like CNTs have previously been reported, their cross sections are circular rather than polygonal,

because they are composed of conical graphene cups.¹ Here, q-CNTs consist of square pyramid graphene cups, formed by four trapezoidal graphene nanosheets (Fig. 2c). The average wall thickness of this q-CNT is ca. 40 nm. And the angle of graphene sheets is ca. 60°, as shown in Fig. 2b. Therefore, the average length along the “red line” (in Fig. 2b) of graphene nanosheets is very small and only ca. 80 nm.

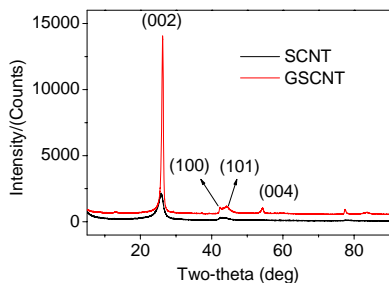


Fig. 2 XRD patterns of two CNTs.

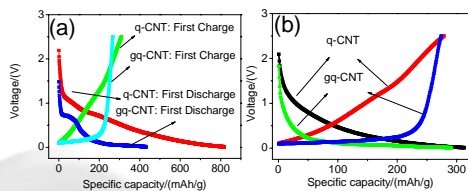


Fig. 3 a) the first and b) second discharge/charge curves for q-CNTs and Gq-CNTs.

After heat treatment at 2800 °C, the cross section of Gq-CNTs remains quadrangular (Fig. 1d). Its one end is still open (Fig. 1d and e). And the SEM image (Fig. 1d) also shows clearly the morphology of open end of Gq-CNTs is still square pyramid. In further, HRTEM image (Fig. 1f) shows that the wall of Gq-CNTs remains “herringbone”-like nanostructure. These results reveal that Gq-CNTs also consist of stacked graphene cups, which keep square pyramid nanostructure in spite of a high-temperature annealing at 2800 °C. Thus, the graphene nanosheets forming the Gq-CNTs are still very small. It also confirms fully that as-prepared quadrangular carbon nanotubes possess a higher thermal stability. HRTEM measurements also exhibit that the most prominent feature change in Gq-CNTs is that the formation of loops between adjacent active plane ends of both the inner and outer surfaces. These loops are energetically stable and should be one of the reasons for maintaining of quadrangular cross section of Gq-CNTs at high temperature.

The structural changes of q-CNTs after the heat treatment are also investigated by XRD measurements (Fig. 2). It can be seen that the (002) peak present at a higher angle and its intensity sharpen largely, indicating higher degree of graphitization after 2800 °C heat treatment. Interestingly, the peak intensity of (100) plane is still very low, indicating that in-plane domain size (L_a) of the graphitic sp^2 sheets of q-CNTs remains very small after heat treatment, which consists with the HRTEM observation. The changes in microstructures of q-CNTs may result in the variations of electrochemical performance when they are used as anode materials for lithium-ion batteries.

Fig. 3a shows the first charge/discharge profiles for q-CNTs before and after heat treatment. From Fig.3a, the first discharge

specific capacity (C_1) and reversible capacity (C_{rev}) of q-CNTs at a current density of 50 $mA g^{-1}$ are 969 and 348 $mAh g^{-1}$, respectively. Therefore, the first cycle efficiency of q-CNTs electrode is ca. 40 %, which is still lower than the values of commercial graphite materials. After heat treatment, q-CNTs exhibits lower C_1 (431 $mAh g^{-1}$) at the same current density. The lower C_1 should be related with the less defects in Gq-CNTs. However, the C_{rev} of Gq-CNTs is still up to 268 $mAh g^{-1}$, so the first cycle efficiency (62 %) is improved obviously. In addition, compared with the q-CNTs, the obviously lower voltage plateau for the intercalation/deintercalation of lithium ion in Gq-CNTs can be seen in the discharge/charge curves (Fig. 3a and b) and voltage hysteresis is decreased. Because of maintaining of quadrangular cross section of Gq-CNTs, smaller graphene nanosheets, and “herring-bone” like wall, Gq-CNTs, Gq-CNTs also possess better high-rate performance. At the current density of 1 A/g, the reversible capacity of Gq-CNTs is still up to ca. 100 mAh/g after 30 cycles. This value is little lower than that of as-prepared q-CNTs (ca. 134 mAh/g at the same current density after 30 cycles), which may be attributed to that the formation of loops induce the decrease of effective diffusion channels of lithium ions. Even so, the Gq-CNTs is more suitable for practice application in anode materials because of its higher first cycle efficiency, lower voltage hysteresis, and better high-rate performance.

Conclusions

In summary, q-CNTs are transformed to graphitized q-CNTs (Gq-CNTs) by heat treatment at 2800 °C. SEM measurements show that Gq-CNTs still possess quadrangular cross section as the same as that of q-CNTs. HRTEM and XRD measurements reveal that the crystallization degree of Gq-CNTs is much higher than that of q-CNTs. HRTEM measurements also exhibit that the most prominent feature change in Gq-CNTs is that the formation of energetically stable loops between adjacent active plane ends of both the inner and outer surfaces. When used as the anode materials for lithium-ion batteries, compared with q-CNTs, the Gq-CNTs still keep the high-rate performance, and simultaneously possess higher first cycle efficiency, obviously lower voltage plateau and lower voltage hysteresis, indicating that Gq-CNTs should be a promising candidates for new generation anode materials in lithium-ion secondary batteries.

Acknowledgments. This work was supported by the National Natural Science Foundation of China (50572003 and 50972004), State Key Basic Research Program of China (2006CB9326022006), and Foundation of Excellent Doctoral Dissertation of Beijing City (YB20081001001).

References

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