



# The creation of hollow walls in carbon nanotubes for high-performance lithium ion batteries

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## ARTICLE INFO

### Article history:

Received 18 October 2017

Received in revised form

13 February 2018

Accepted 10 March 2018

Available online 12 March 2018

## ABSTRACT

Although high mechanical and electronic properties have made carbon nanotube (CNT) a promising active material for lithium ion batteries, the relatively low theoretical specific capacity ( $372 \text{ mAh g}^{-1}$ ) of CNT has hindered its application. Here we have developed a general and efficient template strategy in synthesizing a new family of CNTs with controllable hollow walls and explored their promising applications in LIBs. The hollow structure formed between CNT core and nitrogen-doped graphene shell can be effectively used for lithium storage, and a reversible specific capacity of  $635 \text{ mAh g}^{-1}$  was achieved as anode material in LIB. Interestingly, the hollow structure has been further incorporated with silicon to offer even higher specific capacity of  $930 \text{ mAh g}^{-1}$  with good cyclic stability.

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## 1. Introduction

Modern electronics have witnessed the emergence of various energy storage devices that are widely used in our daily life [1–4]. Particularly, lithium ion batteries (LIBs) have attracted broad interests from both academy and industry due to the demonstrated high performances [5–7]. Among a broad range of active materials, carbon nanotube (CNT) has been mostly explored as a promising one due to its high mechanical and electronic properties [8–10]. However, based on the lithium storage mechanism, i.e., one lithium atom for six carbon atoms, a relatively low specific capacity is available for CNTs, which largely hinders their applications as high-performance anode materials for LIBs [11–16].

The specific capacity of CNTs may also be affected by its morphology [17–20], and the design of hollow structures in their walls is expected to obviously enhance their energy storage capability because the resulting hollow space may store more charges and greatly increase stability by accommodating large volume variation during charge and discharge. It is necessary while remains challenging to synthesize such CNTs with hollow walls based on the available synthetic approaches.

In this Communication, we have developed a general and efficient template strategy in synthesizing a new family of CNTs (Fig. 1a) with controllable hollow walls and explored their promising applications in LIBs. The hollow structure formed between CNT core and nitrogen-doped graphene shell can be effectively used for lithium storage, so the novel CNTs (denoted as HNCNTs) showed a reversible specific capacity of  $635 \text{ mAh g}^{-1}$  as anode material in LIB. In addition, the hollow structure also provided ideal platform for incorporation of active materials such as silicon, so the silicon volume change can be well accommodated during charge and discharge, which produced even much higher specific capacity of  $930 \text{ mAh g}^{-1}$  with good cyclic stability.

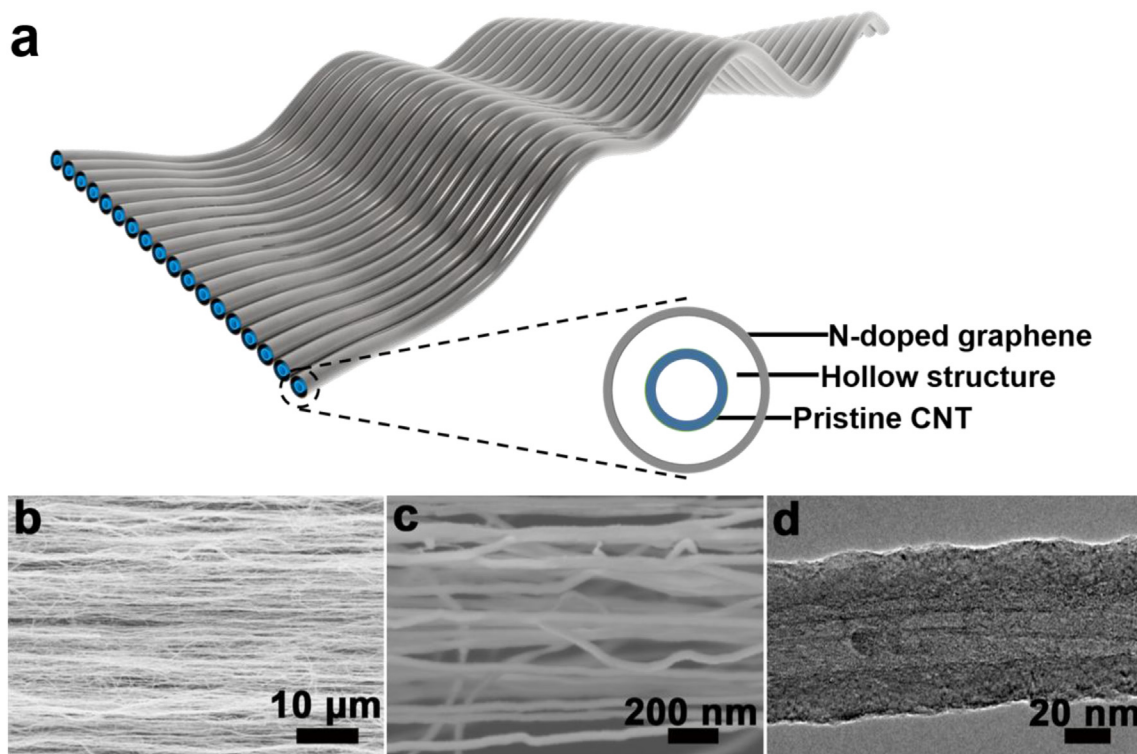
## 2. Experimental section

The synthesis of spinnable CNT arrays was discussed previously [21] and further summarized in the Supporting Information. Aligned CNT sheets were dry-drawn from spinnable CNT arrays and transferred to a curved polytetrafluoroethylene board that was kept suspending. After the deposition of  $\text{Al}_2\text{O}_3$  on both sides of a CNT sheet by electron beam evaporation, nitrogen-doped graphene layers were grown on the outer surface of  $\text{Al}_2\text{O}_3$  layer through chemical vapor deposition. The  $\text{Al}_2\text{O}_3$ -coated CNT sheet was first transferred to a silicon wafer with two ends fixed, then the chemical vapor deposition process was applied with Ar (110 sccm) and  $\text{H}_2$  (10 sccm) as the carrying gas. When the temperature reached  $1060 \text{ }^\circ\text{C}$ , Ar (40 sccm) and  $\text{CH}_3\text{CN}$  were further introduced

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**Fig. 1.** (a) Schematic illustration to the structure of the aligned HNCNTs. (b) Scanning electron microscope (SEM) image of an aligned CNT sheet. (c) SEM image of a nitrogen-doped graphene/ $\text{Al}_2\text{O}_3$ /CNT film. (d) Transmission electron microscope (TEM) image of nitrogen-doped graphene/ $\text{Al}_2\text{O}_3$ /CNT after HF etching. Thickness of  $\text{Al}_2\text{O}_3$  in c and d, 10 nm. (A colour version of this figure can be viewed online.)

to the tube furnace, and the reaction time was controlled from 5 to 30 min to synthesize nitrogen-doped graphene shells with different thicknesses. The obtained samples were then immersed in HF (10 vol%) for 24 h to thoroughly remove the  $\text{Al}_2\text{O}_3$  layer. The obtained samples were then washed with deionized water for three times and dried in vacuum oven at 80 °C for 24 h. In the case of Si-incorporated HNCNTs, Si was deposited on both sides of the CNT sheet before the deposition of  $\text{Al}_2\text{O}_3$ . HCl instead of HF was used to etch  $\text{Al}_2\text{O}_3$  layer. All the other experimental conditions were kept the same to the HNCNTs.

### 3. Results and discussion

Spinnable CNT arrays were synthesized *via* chemical vapor deposition using  $\text{Fe}/\text{Al}_2\text{O}_3$  as catalysts. The as-synthesized CNTs were multi-walled with an average diameter of ~15 nm. Aligned CNT sheets could be then continuously drawn from aligned CNT arrays (Fig. 1b), followed by deposition of  $\text{Al}_2\text{O}_3$  onto their surfaces through electron beam evaporation. Another nitrogen-doped graphene layer was then grown onto the surface also by chemical vapor deposition but at a higher temperature of 1060 °C (Figs. 1c and S1). Based on the XPS test, the atomic content of nitrogen was ~5% as shown in Fig. S1. The graphitization of the re-grown layer can be confirmed by high-resolution TEM image (Fig. S2). Both  $\text{Al}_2\text{O}_3$  and nitrogen-doped graphene layers were coaxially deposited on CNTs, which was verified by energy-dispersive X-ray spectroscopy (Fig. S3). On the basis of aligned CNT templates, the resulting nitrogen-doped graphene/ $\text{Al}_2\text{O}_3$ /CNT also demonstrated high alignment confirmed by the dependence of electrical resistance on angle (Fig. S4). The  $\text{Al}_2\text{O}_3$  layer was further thoroughly etched by HF solution to produce the hollow structure between CNT and nitrogen-doped graphene layer (Fig. 1d). Fig. S5 shows the

nitrogen-doped graphene sheet peeled off the HNCNT, and it was flexible with well-maintained structure.

The parameters of the hollow structure can be well controlled by varying the thicknesses of  $\text{Al}_2\text{O}_3$  and nitrogen-doped graphene layers (Fig. 2a). For instance, the size of the hollow structure was varied from 10 to 30 nm by controlling the thickness of  $\text{Al}_2\text{O}_3$  from 10 to 30 nm (Fig. 2b–d and S6). As the lengths of HNCNTs were hundreds of micrometers, it remained challenging to accurately measure the specific surface area and pore distribution by the traditional method of measuring the typical nitrogen adsorption-desorption isotherms [22]. After etching the  $\text{Al}_2\text{O}_3$  layer, the CNT template was observed randomly distributing within the interspace. In addition, the thickness of the nitrogen-doped graphene layer can also be tailored, e.g., from 20 to 100 nm by increasing the re-growth time from 5 to 30 min (Fig. 2e and f, S7 and S8). It should be noted that occasionally more than one CNT had been bundled together within the nitrogen-doped graphene layer (Fig. S9). Besides, some cross-structured HNCNTs were also observed due to the crossed CNT templates (Fig. S10). Interestingly, more sophisticated hybrid structures can be synthesized on the basis of similar strategies. For instance, the deposition and growth of  $\text{Al}_2\text{O}_3$  and nitrogen-doped graphene layers were repeatedly performed to form a Matryoshka-like structure. Both the  $\text{Al}_2\text{O}_3$  and nitrogen-doped graphene layers had a thickness of ~20 nm, contributing to a total diameter of about 200 nm for the hybrid structure (Fig. S11), which was a magnitude larger than that of bare CNT. After complete removal of  $\text{Al}_2\text{O}_3$ , two hollow layers formed: one between CNT and the inner nitrogen-doped graphene layer, and the other sandwiched between two nitrogen-doped graphene layers (Fig. 2g).

The electrochemical properties of HNCNTs were investigated by assembling coin cells with lithium wafers as counter electrodes. It was found that the samples with 30 nm of  $\text{Al}_2\text{O}_3$  layer and 5 min of

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