# Hairy graphite of high electrochemical performances prepared through in-situ decoration of carbon nanotubes

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ABSTRACT

A hairy graphite is synthesized through a modified chemical vapor deposition (CVD) method, in which 2,3-dipicolinic acid and $Ni(NO_3)_2$ are employed as the carbon source and the catalyst precursor, respectively. Under $Ar/H_2$ (95:5) reducing atmosphere at 900 °C, $Ni(NO_3)_2$ is reduced to nickel nanoparticles and 2,3-dipicolinic acid is pyrolyzed into carbon fragments. With the catalysis of nickel nanoparticles, carbon nanotubes (CNTs) are in-situ grown on the graphite surface through realignment of the carbon fragments. The hairy pattern of geometry of the graphite@CNT composite not only improves the mechanics and conductivity of the electrode, but also has more room to accommodate the volume change of the graphite particle upon prolonged electrochemical cycles. A superb rate performance and prolonged cycle life are obtained. The simple and effective strategy for integration of graphite with in-situ grown CNTs is very useful for boosting its electrochemical properties.

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## 1. Introduction

Rechargeable lithium-ion batteries (LIBs) represent an excellent choice for electric vehicles (EVs) and energy storage systems (ESS) [1–3]. One of the major challenges in the development of LIBs is the long-term cycling capability (3000–5000 deep charge-discharge cycles with 10–15 year calendar life). To attain this goal, much effort has been made in fabricating and optimizing active materials [4–8]. Graphite is widely adopted as the anode material of commercial LIBs due to its high specific capacity, low working potential close to that of lithium metal, low cost, and environmental friendliness [9,10]. However, graphite anode-based LIBs always exhibit considerable capacity fade during long-term cycling, posing a great challenge for EV and ESS applications. One of the important reasons is the mechanical failure of the graphite electrode laminate. Upon electrochemical cycling, graphite undergoes more than 10% volume change (expansion/contraction) with lithium insertion and extraction. As the result, cracks are easily to be induced within the electrode laminate, leading to physical and electrical disconnection between neighboring graphite particles and electrochemical deterioration of the electrode [11–13].

In our previous studies [12], we have correlated the mechanics of graphite laminate with its long-term cycling performance and the results show that volume change of the active material translates into the electrode laminate deformation. From this point of view, developing graphite electrode laminate of high breaking stress and low Young's modulus helps to prolong its cycle life. So far, attempts to improve the mechanics and electronic conductivity of graphite material in Li-ion industry are focused on developing new binders or conductive additives, such as introducing styrene-butadiene rubber (SBR), using 3-D cross-linked binder [14,15], and developing 3-D conductive networks [16], etc. Establishing inherent physical connection between graphite particles must contribute to significant mechanical improvement of the electrode. However, up to today, this work has rarely been reported.

Since 1991, CNTs have aroused wide attention as it is known to be one of the strongest fibers and possess excellent mechanical and electrical properties [17–19]. CNTs can reinforce some forms of matrix owing to their unique mechanics and electronic conductivity. Composite materials with CNTs always demonstrate high performance and multi-function. Moreover, CNTs are able to develop continuous conductive networks at a low percolation threshold and improve long-term conductivity of the composite [20,21]. Many researches have shown that addition of CNTs greatly reduces the cell resistance and improve the electrochemical performance of electrode materials [22,23]. In-situ growth of CNTs is one of the most effective routes for improving the mechanics and conductivity of graphite material. Zhao et al. [24,25] investigated the CNTs grown in the pores of expanded graphite by CVD method and explored the optimum catalyst concentration. Feng et al. [26]

prepared a sandwich structure graphite consolidated composite (GCC) by the intercalation of CNTs at the interlayer of expanded graphite using CVD and discovered that bending strength of the CNT/GCC blocks was remarkably increased. However, as far as we know, boosting the electrochemical performances of graphite anode through *in-situ* growth of CNTs has never been reported.

In this work, robust CNTs were in-situ grown onto a graphite surface with a modified chemical vapor deposition (CVD) method. Different with the traditional CVD method using gaseous carbon source such as methane and ethane, 2,3-dipicolinic acid is adopted as the carbon source in this study. With this method, morphology and amount of CNTs can be easily controlled by adjusting the temperature, deposition time, and catalyst content [24,27,28]. The unique hierarchical hairy structure contributes to a significant improvement of the mechanics of the graphite laminate. We herein elucidate the effects of the in-situ growth of CNTs on graphite surface in comparison with the bare graphite and CNT blended graphite. In-depth physical and electrochemical analyses confirm the electrochemical improvement of the hairy graphite@CNT composite is attributed to the inherent CNT connections between the neighboring graphite particles.

## 2. Experimental

### 2.1. Preparation of the hairy graphite@CNT composite

Natural graphite (NG) with an average particle size of $\sim$25 $\mu$m was purchased from Beterui New Energy Materials Group Co. Ltd., Shenzhen, China, and used as the anode material. *In-situ* growth of CNTs was realized through a modified CVD method, in which nickel nitrate ($Ni(NO_3)_2$, AR grade) and 2, 3- dipicolinic acid ($C_7H_5NO_4$, 98% purity) were chosen as the catalyst and the carbon source, respectively. Fig. 1 shows the schematic of the preparation route for the hairy graphite@CNT composite. Firstly, the NG (2.4 g) was dispersed in alcohol (50 ml). Nickel nitrate aqueous solution was added dropwise. Molar ratio between carbon and nickel was set at 400:1, 200:1 and 100:1, respectively. The solution was then heated under vigorous magnetic stirring until the solvents were completely evaporated. The obtained sample was further dried at 110 °C under vacuum for 10 h to remove the trace water. The

dried mixture, NG@Ni(NO$_3$)$_2$, was spread out into a quartz boat. The boat was then transferred to the right side of a tube furnace with bi-temperature zones. Meanwhile, another quartz boat filled with 2, 3- dipicolinic acid (2 g) was put at the left zone of the furnace. Under the protection of Ar/H$_2$ (95:5) atmosphere, the furnace was heated at a rate of 3 °C min$^{-1}$ and held at 900 °C for 4 h. After cooling down to room temperature, the resulting CNT decorated graphite was treated with 10%wt HNO$_3$ for 2 h to remove the trace Ni nanoparticles dispersed on the graphite surface. This is followed by thorough washing untill pH-value of the solution gets to *ca.* 7. Finally, the obtained hairy graphite@CNT composite was dried at 110 °C for 10 h under vacuum. As a reference, the bare NG underwent the same process but in absence of Ni catalyst.

### 2.2. Physical and electrochemical characterizations

For preparing graphite electrode laminate, slurries of 88.8% graphite, 3.2% conductive additive (either Super P conductive carbon or CNTs) and 8% Polyvinylidene difluoride (PVDF) in N-methylpyrrolidone (NMP) solvent were prepared. The slurry was thoroughly homogenized using a high shear homogenizer (Fluko FA25, Germany) at 4000 rpm for 15 min until a viscous and uniform slurry was obtained. Electrode laminates were prepared by casting the slurries onto a copper foil (15 $\mu$m-thick, 99.99% purity) by doctor blade method. For comparison, the electrodes made with the bare graphite and super P carbon additive, and the bare graphite blended purchased CNTs were prepared, which were denoted as the bare graphite and NG + CNT mixture, respectively. All the electrodes were cast to have approximately the same mass loading of active material (around 2.9 mg cm$^{-2}$). They were completely dried at 120 °C for 10 h under vacuum prior to use.

To determine the electronic conductivity and mechanical properties of the electrode laminates, the electrode film was peeled off from the Cu substrate. The conductivity measurements were performed by using a four-point probe apparatus (ST2263, Suzhou Jingge Electronic Co., Ltd). Breaking stress and Young's modulus of the electrode laminates were measured by using a force measurement system (TY8000, Jiangsu Tianyuan testing equipment Co., Ltd). A stretching speed of 0.00125 mm s$^{-1}$ was applied. Determination for each sample was repeated 3 times.



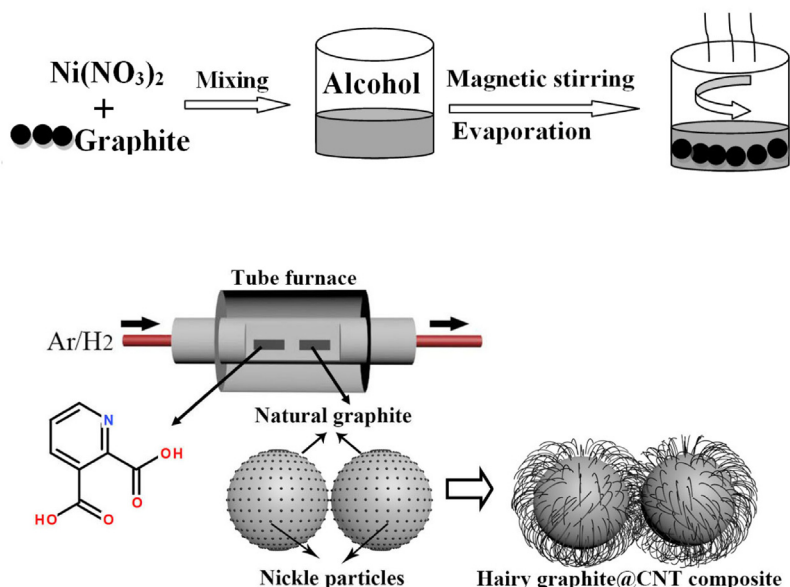**Fig. 1.** The overall preparation route of the hairy graphite@CNT composite through a modified CVD method.