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# A flexible 3D nitrogen-doped carbon foam@CNTs hybrid hosting $TiO_2$ nanoparticles as free-standing electrode for ultra-long cycling lithium-ion batteries

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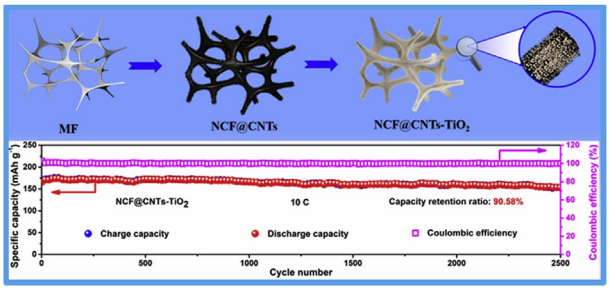
## HIGHLIGHTS

- A flexible 3D free-standing NCF@CNTs-$TiO_2$ electrode is prepared by a facile approach.
- Low-cost commercial melamine foam is used as the starting material of carbon skeleton.
- The electrode has a 3D interconnected conductive network with high surface area.
- Excellent long-term cycling lithium storage capability is demonstrated.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Free-standing electrodes have stood out from the electrode pack, owing to their advantage of abandoning the conventional polymeric binder and conductive agent, thus increasing the specific capacity of lithium-ion batteries. Nevertheless, their practical application is hampered by inferior electrical conductivity and complex manufacturing process. To this end, we report here a facile approach to fabricate a flexible 3D N-doped carbon foam/carbon nanotubes (NCF@CNTs) hybrid to act as the current collector and host scaffold for $TiO_2$ particles, which are integrated into a lightweight free-standing electrode (NCF@CNTs-$TiO_2$). In the resulting architecture, ultra-fine $TiO_2$ nanoparticles are homogeneously anchored in situ into the N-doped NCF@CNTs framework with macro- and meso-porous structure, wrapped by a dense CNT layer, cooperatively enhances the electrode flexibility and forms an interconnected conductive network for electron/ion transport. As a result, the as-prepared NCF@CNTs-$TiO_2$ electrode exhibits excellent lithium storage performance with high specific capacity of 241 mAh $g^{-1}$ at 1 C, superb rate capability of 145 mAh $g^{-1}$ at 20 C, ultra-long cycling stability with an ultra-low capacity decay of 0.0037% per cycle over 2500 cycles, and excellent thermal stability with ~94% capacity retention over 100 cycles at 55 °C.

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## 1. Introduction

Recently, lithium ion batteries (LIBs) have been the subject of great attention owing to their high energy density and long cycling performance [1–4]. With the increasing demand for flexible electronic equipment, soft batteries as the energy sources have become the focus of research. In conventional LIB anodes, the preparation of electrodes will undergo a serial mixing process [5–7], in which the agglomeration phenomenon often occurs, cutting off the diffusion pathways for Li ions and electrons [8]. In addition, the electrically insulating components, such as the polymeric binder, conducting additive, and current collector (copper foil with 8–9 mg $cm^{-2}$), account for nearly 85%–90% of the total electrode mass, leading to a low specific mass capacity [8,9] and increasing the manufacturing complexity and production costs. Hence, finding how to design a lightweight electrode with high specific capacity plays a vital role in the development of integrated LIB electrodes.

To address the above issues, free-standing electrodes have stood out in recent years, owing to the elimination of additional conductive additives and binders [10–13], which improves the gravimetric capacity and gravimetric energy storage of batteries [8]. Due to the nature of their soft, flexible, and stretchable substrate materials, the corresponding electrodes are believed to be suitable for widespread application. To date, sponges, carbon cloth, and filter paper have been usually used to support the active materials for preparing free-standing electrodes [14]. Even so, the sponges, owing to the absence of a robust framework, are easily destroyed, and the corresponding fabrication process is often very complex [11,15]. In comparison, carbon cloth is too heavy [10,15–17]. Moreover, the filter paper, with its insufficient electrical conductivity, cannot completely optimize the performance of the active materials [18]. Hence, how to simplify the fabrication process, reduce the production cost, and improve the electrical conductivity of the matrix still remain the most important challenges for the development of a flexible electrode. In this regard, flexible three-dimensional (3D) N-doped carbon foam (NCF) obtained by the simple carbonization of cheap melamine foam (MF) probably represents a promising next-generation material for free-standing electrodes owing to its natural low cost, high conductivity, and mechanical flexibility, which will contribute to excellent electrochemical performance of the active materials [9,14,19,20].

Among the various anode materials, titanium dioxide has been intensely studied for the LIBs [21,22] because of its low cost, excellent electrochemical activity, and high safety [2,23–25]. Nevertheless, its poor electronic conductivity and sluggish lithium ion diffusion are the main obstacles to realizing practical applications of $TiO_2$-based anodes [26–28]. Therefore, many conductive fillers such as carbon nanotubes (CNTs) [29,30] or graphene [13,31] have been introduced to overcome the poor electronic conductivity of $TiO_2$. With the introduction of conductive agents, enhanced specific capacity and cycling stability are obtained. For instance, Tang et al. adopted a two-step method to form anatase/rutile $TiO_2$ nanocrystals anchored on CNTs. Such $TiO_2$/CNTs nanocomposites exhibited superior lithium storage properties with ultra-high rate capability and good cycling properties, as the $Li^+$ transport can be dramatically enhanced by the specific nanostructure, hierarchical pores, and sufficient conductivity [32,33]. Although much progress has been obtained for $TiO_2$ anode by the addition of the conductive carbon matrix to improve its structural integrity and conductivity [34], or accelerate its $Li^+$ transport, most of the reported $TiO_2$ anode materials are powdery and thus cannot be directly used as flexible free-standing electrodes to meet the urgent demand for soft electronic equipment.

Here, we have designed and fabricated a lightweight, flexible 3D free-standing electrode configuration that is composed of N-doped carbon foam@CNTs (NCF@CNTs) hosting $TiO_2$ nanoparticles (NPs), namely, NCF@CNTs-$TiO_2$. Building such a 3D free-standing electrode structure begins by engineering a highly conductive and flexible 3D NCF@CNTs architecture as an advanced current collector by a liquid phase immersion/adsorption approach combined with pyrolysis of commercial low-cost MF. The 3D NCF@CNTs can be used as an ideal host matrix for $TiO_2$ NPs loaded on sites through a facile tetrabutyl titanate (TBOT) hydrolysis and annealing process, in which ultra-fine $TiO_2$ NPs are generated and homogeneously anchored into the porous NCF@CNTs framework. In the resultant hybrid, the 3D carbon foam matrix has superior mechanical flexibility and robustness, directly transforming the NCF@CNTs-$TiO_2$ into a free-standing electrode without requiring additional binders and conductive agents. Moreover, the N-doped carbon foam skeleton with dense CNT wrapping layers cooperatively forms an interconnected 3D conductive network for fast electronic/ionic transport, so as to enhance the electrochemical reaction kinetics of the hosted $TiO_2$ NPs. In addition, the high surface area of NCF@CNTs-$TiO_2$ combined with its unique macro- and meso-porous structure can also facilitate electrolyte penetration with improved ion accessibility. Accordingly, the as-prepared NCF@CNTs-$TiO_2$ hybrid as a flexible 3D free-standing electrode not only exhibits remarkable specific capacity (241 mAh $g^{-1}$ at 1 C) and superb rate capability (145 mAh $g^{-1}$ at 20 C), but also possesses ultra-long cycling life (ultra-low capacity decay of 0.0037% per cycle over 2500 cycles) and excellent thermal stability (~94% capacity retention over 100 cycles at 55 °C). Hence, NCF@CNTs-$TiO_2$ holds great potential as an advanced free-standing electrode for developing high energy density and high power density LIBs.

## 2. Experimental section

### 2.1. Preparation of NCF and NCF@CNTs

The MF was washed thoroughly using deionized water and ethanol, and then dried at 80 °C in an oven overnight. The cleaned MF was soaked in a 3% (mass ratio of the CNTs to water) CNT solution. Then, the foam was moved and rolled five times until the CNTs solution was absorbed uniformly. After rolling, the foam was dried in an oven at 80 °C overnight. Subsequently, the foam was calcined at 800 °C for 1 h with a heating rate of 5 °C $min^{-1}$ in Ar atmosphere to obtain NCF@CNTs. The NCF can be obtained by directly carbonizing the cleaned MF. Then, the NCF and NCF@CNTs were punched into disks with a diameter of 12 mm.

### 2.2. Preparation of the NCF-$TiO_2$ and NCF@CNTs-$TiO_2$ electrodes

$TiO_2$ NPs were tightly and uniformly anchored on the NCF and NCF@CNTs by a hydrolysis method, as reported previously [7,18]. In a typical process, 20 mL of ethanol, 2 mL of acetic acid ($CH_3COOH$), and 3 mL of tetrabutyl titanate (referred to as TBOT) were added into a beaker and intensively stirred to obtain a transparent homogeneous solution. Then NCF or NCF@CNTs foam discs were immersed in the solution for 2 h to allow for sufficient wetting. After the wetting, the discs were taken out of the solution and put onto filter paper to remove the redundant solution on the surfaces of the NCF or NCF@CNTs. Afterwards, as illustrated in Fig. 1, the materials were immersed in boiling water for 3 h to complete the hydrolysis of TBOT. After cooling down to room temperature, the discs were washed with deionized water five times and dried in an oven at 80 °C overnight. After that, the as-prepared electrodes were obtained by calcining them at 600 °C in Ar atmosphere for 3 h with a heating rate of 2 °C $min^{-1}$. The obtained samples are referred to as NCF-$TiO_2$ and NCF@CNTs-$TiO_2$, respectively. For comparison, pristine $TiO_2$ was also prepared using the same hydrolysis process without the addition of NCF or NCF@CNTs foam discs.

### 2.3. Materials characterization

The structure and phase analyses were conducted by X-ray diffraction (XRD, Philips X'pert TROMPD, Cu Kα radiation, λ = 1.54178 Å). Raman spectra were collected on a Raman spectrophotometer (Horiba