



# Porous structured niobium pentoxide/carbon complex for lithium-ion intercalation pseudocapacitors



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## ABSTRACT

A facile soft-templated synthesis of the niobium pentoxide/carbon (Nb<sub>2</sub>O<sub>5</sub>/C) from the polymerization of resorcinol with formaldehyde under the hydrothermal condition is introduced. This material has been characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and energy dispersive spectrometer (EDS) techniques. The carbon is well-dispersed in the nanostructure along with Nb<sub>2</sub>O<sub>5</sub> and the material is porous. The intimate contact between Nb<sub>2</sub>O<sub>5</sub> and carbon improves its conductivity. The electrochemical studies revealed that the porous Nb<sub>2</sub>O<sub>5</sub>/C displayed good pseudocapacitive response. The specific capacitance of the Nb<sub>2</sub>O<sub>5</sub>/C was 387 F g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and 210 F g<sup>-1</sup> at 5 A g<sup>-1</sup>. The Nb<sub>2</sub>O<sub>5</sub>/C exhibits superior cycling performance, which can remain about 96% of its initial capacitance after 1000 cycles at 5 A g<sup>-1</sup>.

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## 1. Introduction

Due to people's concerns about energy issues, more and more attention has been paid to supercapacitors. Supercapacitors have high power supply and relative long cycle life, which make them as supplementary to batteries and a newly promising class of energy storage devices [1–5]. Of many kinds of supercapacitors, attention on Li ion capacitors (LICs) has been escalating due to their high energy density since proposed in 2001 [6,7]. Benefits are not only more energy density from Faradaic lithium-intercalation electrodes, but also high power density and excellent cycling stability from non-Faradaic capacitive electrodes [8]. These high performance lithium ion hybrid electrochemical supercapacitors (Li-HEC) possess higher power supply than the rechargeable battery and higher energy capacitance than supercapacitors [6,9–16]. Therefore, Li-HEC is the most promising device which could bridge the gap between the Li-ion batteries and electric double-layer capacitors (EDLCs) and turn out to be an ultimate power supply in the near future [7,17].

Dunn et al. [18] have found a new class of pseudocapacitor materials arising from the reversible Li<sup>+</sup> intercalation into orthorhombic phase (designated as T-Nb<sub>2</sub>O<sub>5</sub>). The Li<sup>+</sup> intercalation could not only happen at the surface, but also in the bulk of crystals, and the overall kinetics are not limited by diffusion [19].

Intercalation and extraction process can be described by the following equation [20]:



When  $x = 2$ , theoretical capacitance is acquired, up to 360 F g<sup>-1</sup> [18,21]. T-Nb<sub>2</sub>O<sub>5</sub> has the unique open channels to facilitate Li<sup>+</sup> transport [22]. No kinetic limit from the solid-state diffusion is found in the crystal of T-Nb<sub>2</sub>O<sub>5</sub> during the bulk intercalation process [23,24]. T-Nb<sub>2</sub>O<sub>5</sub> is a promising pseudocapacitor material due to its higher theoretical capacitance, an excellent rate performance and a stable cyclic life. However, there are some limitations imposed on the application of Nb<sub>2</sub>O<sub>5</sub>, for example, its low conductivity. Nb<sub>2</sub>O<sub>5</sub> is a semiconductor with a bandgap of ~3.4 eV, and poor conductivity ( $3 \times 10^{-6}$  S cm<sup>-1</sup>) [25–27]. Many contributions have been devoted to overcome the influences of its poor conductivity. One method is the modification of morphology of the material to have a facile access to the electrolyte. Kong et al. [28] synthesized the mesoporous Nb<sub>2</sub>O<sub>5</sub> from a cellulose nanocrystal template. Kong synthesized Nb<sub>2</sub>O<sub>5</sub> core-shell microspheres with high rate performance [29]. Wei et al. synthesized Nb<sub>2</sub>O<sub>5</sub> nanobelts with thickness and width in nanometers [30]. Le Viet et al. synthesized Nb<sub>2</sub>O<sub>5</sub> nanofiber by electrospinning [31]. Liu et al. [32] synthesized Nb<sub>2</sub>O<sub>5</sub> nanosheets through hydrothermal reaction. The other is the combination of Nb<sub>2</sub>O<sub>5</sub> with conductive carbon materials, such as carbide-derived carbon (CDC) [33], carbon [34,35] and graphene [25,36,37], etc. Kong et al. [29] synthesized the carbon wrapped Nb<sub>2</sub>O<sub>5</sub> nanoparticles. Wang et al. [38] synthesized the

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composite of Nb<sub>2</sub>O<sub>5</sub> grown on carbon nanotubes (CNTs). Wang et al. [39] tried to physically mix the Nb<sub>2</sub>O<sub>5</sub> nanoparticles and CNTs during the electrode slurry preparation. The introduction of CNTs could enable fast electron transport and effectively improve rate capability. However, the physical mixing is more like increasing the amount of conductive agent, which could not have a quite good contact between CNTs and Nb<sub>2</sub>O<sub>5</sub>. Besides, carbon materials are more likely to aggregate during the hybrid process. Additional functioning steps are needed to get a well dispersion of carbon materials in composites [17]. Hence challenge still remains that developing a general and effective chemical approach to construct conductive T-Nb<sub>2</sub>O<sub>5</sub>/C composites.

The multi-dimensional carbon material has been considered a promising candidate to combine with Nb<sub>2</sub>O<sub>5</sub> to obtain high active material mass loading, sufficient electronic conductivity and direct exposure of the active sites to the electrolyte. Recently, Long et al. [19] reported a free-standing T-Nb<sub>2</sub>O<sub>5</sub>/graphene composites with ultrahigh gravimetric/volumetric capacitance of 625.5 F g<sup>-1</sup> and 961.8 F cm<sup>-3</sup> at 1 mV s<sup>-1</sup>, respectively. Lee, et al. [35] prepared the T-Nb<sub>2</sub>O<sub>5</sub>/CNTs nanocrystals with the core-shell structure, which exhibited a reversible specific capacity of ~180 mAh g<sup>-1</sup> at 0.05 A g<sup>-1</sup>. Ordered mesoporous phenolic resins from the reaction of resorcinol with formaldehyde are widely used as support materials in the field of catalysis, electrodes and adsorbents [40]. There are many synthesis methods, like evaporation-induced self-assembly (EISA), a two-phase system based pathway and hydrothermal [41–43]. Phenolic resins via a soft-templated hydrothermal method are of convenience compared with time-consuming EISA. Briefly, traditional hard template strategy involves synthesis of hard template, repetitive filling of the pores with carbon precursor, pyrolysis at a high temperature, and removal of the hard template. Due to the multi steps involved and low yield of the carbon, this method is complicated with no commercial value. The other attracting strategy is the soft template approach, which helps to synthesize phenolic resins with nano-scale properties. The added template controls the polymerization of phenolic resin and helps to form nano-scale pores and tunnels, which provides the active sites for materials.

Herein, we introduce a facile one-step soft-templated hydrothermal synthesis of the composites of Nb<sub>2</sub>O<sub>5</sub>/carbon. All the precursors and the template were put into the autoclave and the composites were synthesized after carbonation in nitrogen. Nb<sub>2</sub>O<sub>5</sub> nanoparticles are intimately loaded upon the carbon materials, which helps enhance the conductivity of Nb<sub>2</sub>O<sub>5</sub>. The electrochemical tests show that the composite has a quite good performance as supercapacitor electrodes. The in situ hybrid needs no pre-functionalization for carbon materials before the combination. The straightforward synthesis approach is able to obtain the porous Nb<sub>2</sub>O<sub>5</sub>/C composites, which greatly improve the utilization of active T-Nb<sub>2</sub>O<sub>5</sub> nanocrystals. The Nb<sub>2</sub>O<sub>5</sub>/C has a high specific capacitance, 387 F g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and 210 F g<sup>-1</sup> at 5 A g<sup>-1</sup>. It also exhibits superior cycling performance with no obvious drop after 1000 cycles at 5 A g<sup>-1</sup>.

## 2. Experimental

### 2.1. Chemicals

Niobium(V) oxalate hydrate (Nb(HC<sub>2</sub>O<sub>4</sub>)<sub>5</sub>·xH<sub>2</sub>O) were purchased from Alfa Aesar. Soft template poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer Pluronic F127 (PEO<sub>106</sub>-PPO<sub>70</sub>-PEO<sub>106</sub>, M<sub>w</sub> = 12600) was got from Sigma-Aldrich. Other chemicals were bought from Sino-pharm Chemical Reagent Co., Ltd. All chemicals were used without further purification.

### 2.2. Preparation of Nb<sub>2</sub>O<sub>5</sub>/C samples

Nb<sub>2</sub>O<sub>5</sub>/C composite was synthesized by a templated hydrothermal synthesis as follow: 3.78 g F127, 0.62 g niobium oxalate hydrate and 60 mg resorcinol were dissolved in sequence in 60 mL DI water with sonication. After the formation of transparent solution, ~1 mL formaldehyde (35%wt) solution was added into the solution. The resultant homogeneous solution was dumped into a 100 mL Teflon-lined autoclave and then moved into an oven at 150 °C for 10 h. The orange-red particles were collected by filtration, rinsed several times with DI water and ethanol, and dried in air at 80 °C for 12 h. The as-made particles was calcined at 350 °C and 600 °C for 2 h successively at a heating rate of ~2 °C min<sup>-1</sup> under a nitrogen atmosphere. By adding resorcinol to control the amount of carbon content in product, the content of carbon in Nb<sub>2</sub>O<sub>5</sub>/C was 10%.

### 2.3. Preparation of Nb<sub>2</sub>O<sub>5</sub> samples

3.78 g F127, 0.62 g niobium oxalate hydrate was dissolved in 60 mL DI water under ultrasonication for ~30 min. Then ~1 mL HCl solution (2 M) was added into the transparent solution. The as-made solution was put into a 100 mL Teflon-lined autoclave and heated at 150 °C for 10 h. The white precipitation was collected and washed with DI water and ethanol. The white powders were dried at 80 °C for 12 h in air before calcined at 600 °C for 2 h in air.

### 2.4. Fabrication of coin capacitors

The as-synthesized Nb<sub>2</sub>O<sub>5</sub>/C powders were mixed with 5% polyvinylidene fluoride (PVDF) N-methyl-2-pyrrolidinone (NMP) solution and stirred overnight. Nb<sub>2</sub>O<sub>5</sub>/C powders and PVDF were in an 8:1 wt ratio in the slurry. The as-made slurry was dispersed on the copper foil and dried at 110 °C for 12 h. The coated foils were packed into CR 2016 cells in the argon-filled glove box, with the as-synthesized materials as working electrodes and lithium foils both as the reference electrodes and the counter electrodes. The electrolyte used was 1 M LiPF<sub>6</sub> in EC/DMC (V/V, 1:1). The mass loading of the Nb<sub>2</sub>O<sub>5</sub>/C electrodes is ~5 mg/cm<sup>2</sup> and the thickness is ~25 μm.

As for Nb<sub>2</sub>O<sub>5</sub> samples, the mass ratio of the acetylene black in use is based on the carbon ratio of Nb<sub>2</sub>O<sub>5</sub>/C composites. The determination of the weight ratio of carbon in Nb<sub>2</sub>O<sub>5</sub>/C is based on the weight loss after the re-calcination of as-prepared particles at 600 °C in air.

### 2.5. Characterization

The X-ray powder diffraction (XRD) measurements were carried out on Bruker D8 advance (Bruker, Cu K $\alpha$  radiation, Germany). The galvanostatic charge–discharge test was carried out using Land CT2001A Cell Testing system (Wuhan Land Electronics). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed/conducted on a CHI 660D electrochemical workstation (Chenhua Instruments, China) The transmission electron microscope (TEM) images were got from JEOL JEM-2100F field emission electron microscope. Energy dispersive spectrometer (EDS) analysis was performed on X-Max (Oxford instruments, UK).

## 3. Results and discussion

### 3.1. Material characterization

The synthesis procedures of the samples and the possible mechanism are demonstrated in Fig. 1.

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