Constructing T-Nb$_2$O$_5$@Carbon hollow core-shell nanostructures for high-rate hybrid supercapacitor

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HIGHLIGHTS

- T-Nb$_2$O$_5$@porous carbon core-shell hollow nanostructures are synthesized.
- Li$^+$ intercalation in T-Nb$_2$O$_5$@porous carbon nanostructures are capacitive behavior.
- Higher rate-capability of T-Nb$_2$O$_5$@ carbon with mesoporous shells are achieved.
- A high-performance hybrid supercapacitor device is successfully constructed.

GRAPHICAL ABSTRACT
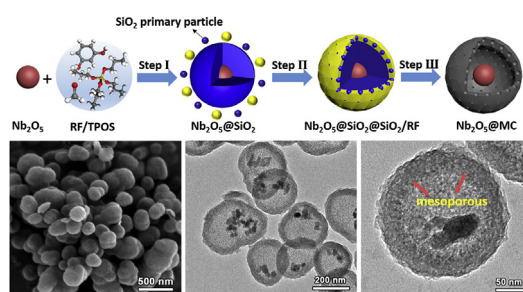
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ABSTRACT

Orthorhombic (T-) Nb$_2$O$_5$ is an intercalation pseudocapacitive material that possesses fast Li$^+$ diffusion pathways in its bulk crystalline structure. Herein, hollow core-shell nanostructures made up of T-Nb$_2$O$_5$ nanoparticles confined within porous carbon shells are constructed for further boosting its high-rate Li-insertion/extraction capability. By using different silica template precursors, carbon shells with mesoporous channels or relatively dense structure could be created, both of the T-Nb$_2$O$_5$@carbon hollow core-shell nanostructures demonstrate significant improvement on the rate capability compared to the T-Nb$_2$O$_5$ nanoparticles. Furthermore, it is found that the carbon shells with accessible mesopores of ~6 nm could provide a higher specific surface area and larger Li$^+$ diffusion channels, and thus the T-Nb$_2$O$_5$@mesoporous carbon (Nb$_2$O$_5$@MC) hollow core-shell nanostructures show better high-rate properties with a capacity of 173 C g^{-1} at a current density of 50 A g^{-1}. When paired up with mesoporous carbon hollow nanospheres (MCHS) cathode, the Nb$_2$O$_5$@MC//MCHS hybrid supercapacitor could deliver both ultrahigh power density and high energy density (~16 kW kg^{-1} with an energy density of 12 Wh kg^{-1}), which is attractive for a wide range of power delivery applications.

1. Introduction

Supercapacitor, a high power-density device, is generally classified into electric double-layer capacitor (EDLC) and pseudocapacitor depended on the types of charge storage mechanism [1]. For EDLC, the charges store at the electrode/electrolyte interface by electrostatic interactions in conductive carbonaceous materials [2], while pseudocapacitor stores charges through fast and reversible oxidation/reduction (Faradaic) reactions at the electrode/electrolyte interfaces or near the surface of the electrode [3]. Recently, Bruce Dunn [4,5] discovered that Nb$_2$O$_5$ crystals exhibited a typical intercalation pseudocapacitive behavior in their bulk phases. This is attributed to the unique orthorhombic (T-) Nb$_2$O$_5$ crystalline structure which could offer two-dimensional Li$^+$ transport pathways with almost no kinetics limitations

from solid-state diffusion [6–8]. Therefore, the high pseudocapacitance could be achieved due to the full utilization of whole bulk of T-Nb_2O_5 nanocrystals for capacitive energy storage [9].

It was reported that T-Nb_2O_5 could deliver a high specific capacitance even at high rates (nearly $400\,F\,g^{-1}$ being stored reversibly within $12\,s$ [4]), however, this result only relies on small mass loading. When T-Nb_2O_5 nanocrystals are fabricated into a relatively thick electrode, their bulk resistivity ($\sim 3 \times 10^4\,\Omega\,cm^{-1}$ at $300\,K$) would lead to inferior rate capability due to the sluggish mobility of electrons [10–13]. Carbon as a common material is widely used in nanocomposites to raise the conductivity and resultant pseudocapacitive properties of the semi-conductive metal oxides [14–17]. Very recently, many nanostructured T-Nb_2O_5/carbon composite materials, including Nb_2O_5/graphene [18–20], Nb_2O_5/carbide derived carbon [21], and Nb_2O_5/CNT [22], etc. [23–25], have been fabricated to address these issues. Synergistic effects between carbon and Nb_2O_5 crystals, such as facilitating electron and proton conduction, minimizing the particle size, and preventing particles from agglomerating could be the reasons for these composites with improved electrochemical performance.

The construction of core-shell nanostructure is an effective method to achieve better electrochemical performance for electrode materials [26–29]. Generally, the internal core is active component with functional properties, while the outer shell usually acts as a protection layer to prevent the active core from being affected by the outside environmental or brings new physical and chemical properties [30]. In addition, the aggregation of active core is possible to alleviate, allowing high transport rates for ions and electrons. More recent studies confirmed that higher rate capability and improved cycling stability could be achieved for supercapacitors using core-shell nanostructure electrodes [31,32]. Furthermore, porous carbon shell with hollow structure could provide high surface area and rapid ion diffusion channels, achieving further improvement in rate capability [33–35]. Therefore, Nb_2O_5 nanoparticles combined with porous carbon shell into a hollow core-shell structure should offer highly electrochemical capacitive properties by taking advantages of both components.

In this work, we present a facile one-pot synthesis for constructing hollow core-shell nanostructures made up of T-Nb_2O_5 nanoparticles confined within porous carbon shell. By using different silica template precursors, including tetrapropyl orthosilicate (TPOS) and tetrapropyl orthosilicate (TEOS), mesoporous carbon shell or relatively dense carbon shell could be created. As mesoporous channels could provide low resistant pathways for mass diffusion and transport compared to dense structure, the Nb_2O_5@mesoporous carbon hollow core-shell nanostructures (Nb_2O_5@MC) show much better electrochemical performance, with an initial reversible specific capacity of $410\,C\,g^{-1}$ at $1\,A\,g^{-1}$ and a unprecedented rate capability of $173\,C\,g^{-1}$ at $50\,A\,g^{-1}$. Furthermore, we demonstrate the suitability of Nb_2O_5@MC as anode material to pair up with the mesoporous carbon hollow nanospheres (MCHS) cathode for hybrid supercapacitors in order to achieve high energy and power densities simultaneously. This hybrid supercapacitor approach is able to fill the gap between batteries and conventional capacitors without sacrificing power delivery, which is attractive for a wide range of power delivery applications.

2. Experimental

2.1. Materials synthesis

2.1.1. T-Nb₂O₅ nanoparticles

Nb_2O_5 nanoparticles were prepared by the decomposition of niobic acid according to previous report [36]. In a typical synthesis, $0.5\,g$ Nb_2O_5 powder was dissolved in hydrofluoric acid (HF, 40%) in a water bath at $80\,°C$ for $6\,h$. Subsequently, the pH of the solution was tuned to 9.0 by adding aqueous ammonia solution ($NH_3\cdot H_2O$, 25%) so that a white precipitate of niobic acid ($Nb_2O_5\cdot nH_2O$) was obtained. After that, the resulting precipitate was collected by centrifugation, washed with water and dried in an oven at $80\,°C$ overnight. Finally, direct carbonization of Nb_2O_5 nanoparticles in N_2 flow at $700\,°C$ for $3\,h$ resulted in the formation of T-Nb_2O_5 nanocrystals.

2.1.2. Nb₂O₅@Carbon and Nb₂O₅@Mesoporous carbon hollow core-shell nanostructures

For the preparation of Nb_2O_5@mesoporous carbon (denoted as Nb_2O_5@MC), $150\,mg$ as-prepared Nb_2O_5 nanoparticles were dispersed in a $450\,mL$ solution consisting of ethanol, distilled water and ammonia water with a volume ratio of 7: 1: 3. After $1\,h$ sonication, TOPS ($2.5\,mL$), resorcinol ($0.5\,g$), and formaldehyde ($0.7\,mL$, 37 wt %) were added to the solution with continuous stirring at $40\,°C$ for $24\,h$. The precipitates were separated by centrifugation, washed several times with distill water, and dried at $80\,°C$ overnight. The dried solids were heat-treated in an N_2 flow at $700\,°C$ for $3\,h$ with a heating rate of $3\,°C$ min^{-1}. Finally, the silica in the carbonized samples was removed by NaOH etching ($4\,M$), leaving the hollow core-shell nanostructures with Nb_2O_5 core and carbon shell.

The synthesis procedure of Nb_2O_5@carbon hollow core-shell nanostructure (denoted as Nb_2O_5@C) is almost the same to that for Nb_2O_5@MC, except that $2.5\,mL$ TPOS is replaced by $1.9\,mL$ TEOS.

2.2. Material characterization

The size and morphology of the samples were investigated by a field emission scanning electron microscope (SEM, FEI-3000) and a transmission electron microscope (TEM, JEOL, 2100 F). X-ray diffraction (XRD, Rigaku/max 2550 diffractometer with Cu Kα ($0.15406\,Å$) radiation, $40\,kV/20\,mA$ current) was adopted to confirm the crystal structure of the samples. The carbon content of the samples was analyzed by thermogravimetric analysis (TGA, TA Instrument Q600 Analyser) from room temperature to $800\,°C$ at a rate of $10\,°C\,min^{-1}$ in air flow. The Brunauer-Emmett-Teller (BET) surface area was recorded by a Quadrasorb SI analyser using the standard N_2 adsorption and desorption isotherm measurements at $77\,K$. The total pore volume was calculated using a signal point at a relative pressure of 0.985, while the pore size distribution was derived from the desorption branch using Barrett-Joyner-Halenda (BJH) or QS-DFT model.

2.3. Electrochemical measurements

The electrode slurry was composed of active materials, carbon black (Timical super C65) and polyvinylidene fluoride (PVDF) binder at a weight ratio of 8: 1: 1 with N-methylpyrrolidone (NMP) solvent. After stirring for $6\,h$, the resulting slurries were uniformly casted onto a piece of Cu foil and dried in an oven at $80\,°C$ under vacuum overnight. Finally, the electrodes were obtained by punching them into small rounds with a diameter of $12\,mm$ and a thickness of $90\,\mu m$ (excluding Cu foil). In addition, the mass loading of the prepared electrodes was carefully controlled within the range of 1.2–$1.4\,mg\,cm^{-2}$.

The porous carbon counter electrodes were prepared by mixing the activated carbon (MSP-20) or MCHS (85 wt %) with carbon black (10 wt %) and polytetrafluoroethylene (PTFE, 5 wt %). Then the slurry was well ground in the ethanol to form a homogeneous paste. The paste was roll-pressed into a film with a controllable thickness, and then punched into an electrode with a diameter of $12\,mm$. All the electrodes were dried at $110\,°C$ for $12\,h$ in a vacuum oven.

The electrochemical tests were carried out using a three-electrode setup, where the obtained hollow core-shell nanostructures were used as the working electrodes, overcapacitive activated carbon and lithium foil were used as the counter and reference electrode, respectively. 1 M $LiPF_6$ dissolved in 1:1 v/v mixture of ethylene carbonate/diethyl carbonate (EC/DEC) was employed as the electrolyte. The separator was a microporous membrane (Celgard 2400). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted on a PCI-4/300 potentiostat (Gamry, USA), galvanostatic