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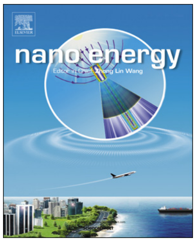

RAPID COMMUNICATION

Orthorhombic niobium oxide nanowires for next generation hybrid supercapacitor device

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Abstract

Energy storage device with high energy density at high power density is of particular importance for various applications, such as hybrid vehicles. Next generation high performance hybrid supercapacitor using organic electrolyte is able to provide high operation voltage as well as enhanced energy density. However, the energy density at high power density is usually low, partly due to the slow electrode kinetics at high current densities. In this contribution, we report a facile preparation method for orthorhombic phase niobium oxide (T-Nb_2O_5) nanowire structure with ultra-thin carbon coating, which shows stable high rate Li^+ storage ability. A prototype of 3 V hybrid supercapacitor is fabricated using carbon coated T-Nb_2O_5 as anode and commercially available activated carbon as cathode. This hybrid device shows high energy density of 43.4 Wh kg^{-1} and a high power density of 7.5 kW kg^{-1} with excellent stability.

Introduction

Supercapacitors are a kind of electrochemical energy storage devices, which have attracted much attention due to their high power delivery ability. Electric double layer capacitors (EDLCs) have already been utilized in various applications, such as trucks, buses, elevators as well as heavy duty constructions and railways in powering forklifts and yard cranes [1]. However, the energy density is expected to elevate to double or triple times to 20–30 Wh kg^{-1} at a certain power density for various emerging applications so as to penetrate a larger energy storage market. In order to achieve enhanced energy density of supercapacitor, elevated operation potential window is highly demanded, as $E=0.5CV^2$. Though numerous efforts have been spent on developing aqueous electrolyte based hybrid supercapacitor device, the water decomposition will limit the operation window of device less than 2 V. Therefore, organic electrolyte based non aqueous hybrid (asymmetric) supercapacitor is of great interest for its large operation window (>2.5 V).

Lithium ion insertion metal oxide with fast charge storage ability is an ideal choice to develop the hybrid supercapacitor with carbon electrode [2]. They are qualified to provide large amount of charge storage as well as large operation window of

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hybrid device. V_2O_5, [3] $Li_4Ti_5O_{12}$ [4] and B-TiO_2 [5] have been explored as electrode materials for non-aqueous hybrid supercapacitors. Generally, the charge storage of these materials contains both instant capacitive (EDLC and pseudocapacitive) charge storage (surface reaction) and diffusion controlled battery-type charge storage (bulk reaction, diffusion controlled). However, due to the low Li^+ diffusion constant in the bulk, the rate capability of these materials is not satisfactory. As a result, the energy densities of those hybrid devices at high power densities are still not satisfactory. For example, though Chen et al. successfully achieved an energy density of 40 Wh kg^{-1}@ 210 W kg^{-1} in a V_2O_5-CNT//Activated Carbon device, the energy density only remains 7 Wh kg^{-1} @ 6.1 kW kg^{-1}. The low energy density at high power densities would not be favorable for heavy duty or high power delivery operations. In order to achieve better energy density at high power densities, fast electrochemical reaction kinetics of Li^+ diffusion is highly desirable for non-aqueous hybrid supercapacitor.

Recently, orthorhombic phase Nb_2O_5 (T-Nb_2O_5) nanocrystals are found to exhibit fast pseudocapacitive Li^+ storage based on an unique intercalation pseudocapacitance. [6,7] The Li^+ diffusion is proved to have fast kinetics in the bulk material without inducing any phase change [6]. However, the capacities of T-Nb_2O_5 nanocrystals are only around 140~150 mAh g^{-1} [6,7], even they have high surface areas. Considering the theoretical capacity of 200 mAh g^{-1} for T-Nb_2O_5, there is plenty of room for improvement in capacity. Besides, the report on Nb_2O_5 based non-aqueous hybrid supercapacitor is still scarce. Wang et al. reports a pseudo hexagonal Nb_2O_5-CNT composite for hybrid supercapacitor [8]. The energy density drops from 33.4 Wh kg^{-1} to 4 Wh kg^{-1} when the power density increases to 4 kW kg^{-1}. The poor performance is largely caused by the non-optimum phase of Nb_2O_5. On the other hand, one dimensional nanomaterials are of great interest for fully harnessing the merit of materials in energy storage applications. The short ion diffusion length, facile electron conduction channel as well as ease of electrolyte diffusion would greatly benefit the electrochemical process [9,10]. It is therefore invaluable to synthesize one dimensional T-Nb_2O_5 nanowire to harness its potential for hybrid supercapacitor applications.

Currently, there are limited attempts on the controlled synthesis of Nb_2O_5 nanowire with different phases. Most methods are based on the chemical etching of Nb metal as starting material. For example, the high temperature annealing of Nb sheet under O_2 atmosphere at 1000 °C yields M-Nb_2O_5 (monoclinic) nanowire [11], or under Ar at 900 °C produces tetragonal Nb_2O_5 nanowire [12]. The long time etching in NH_4F gives H-Nb_2O_5 (pseudo-hexagonal, main product) nanorods with mixed phases [13]. Another method is electrospinning using niobium ethoxide as precursor followed by heat treatment, which produced different phases of Nb_2O_5 (including T-Nb_2O_5) [14]. However, the stability of T-Nb_2O_5 is very poor. The capacity degrades 30% in just 40 cycles at 0.05 A g^{-1}.

Here, we develop an oxalate coordination chemistry route to synthesize ultra-thin H-Nb_2O_5 (pseudo-hexagonal) nanowires using low cost $NbCl_5$ as starting material. The ultra-thin nanowires can be transformed into T-Nb_2O_5 nanowires through heat treatment at 600 °C. In addition, a few nanometers thin carbon coating is achieved as the shell of T-Nb_2O_5 nanowire by the carbonization of polydopamine. The carbon coated T-Nb_2O_5 nanowire shows a high rate charge/discharge performance and high rate cycling stability as Li^+ ion storage electrode. The capacity reaches 186.8 mAh g^{-1} @ 0.5 C, while it preserves 140.1 mAh g^{-1} @ 25 C. Meanwhile, the capacity can maintain 82% after 1000 cycles at 5 C. A high performance prototype of 3 V hybrid supercapacitor is fabricated with pseudocapacitive carbon coated T-Nb_2O_5 nanowire and activated carbon. The fast Li^+ storage of T-Nb_2O_5 as well as the fast EDLC of activated carbon ensures high energy density delivery at high power density.

Material and methods

Synthesis of Nb_2O_5 nanowires and T-Nb_2O_5 nanowires

All chemicals were purchased from Sigma and were used as received. Briefly, 0.218 g $NbCl_5$ (0.8 mmol) was added into 20 ml DI water under vigorous stirring to give a white floc. Oxalic acid dehydrate (0.5 g, 4 mmol) was added into the suspension till it became transparent. Finally, 0.28 g hexamethylenetetramine (HMTA, 2 mmol) was added into the above solution. The solution was transferred into a 40 ml Teflon lined autoclave and kept at 180 °C for 14 h. After that, the samples were collected by centrifuge and were washed with DI water for several times. The samples were dried in oven at 60 °C. T-Nb_2O_5 nanowires were achieved by annealing the sample at 600 °C for 3 h. For the growth of Nb_2O_5 nanowires on different substrates, silicon and carbon nanofiber substrates were placed in the autoclaves without any special treatment.

Synthesis of polydopamine derived carbon coated T-Nb_2O_5

15 mg dopamine hydrochloride was dissolved in a 15 ml pH 8.5 buffer of Tris containing 50 mg T-Nb_2O_5 sample. The mixture was allowed to stir at room temperature for 48 h. After that, the product was collected by centrifuge and was washed by DI water for several times. The sample was dried in the oven at 60 °C. To carbonize the polydopamine, the dried sample was placed in a tube furnace and heat at 600 °C under constant Ar flow for 3 h.

Structure characterizations

The products were characterized using X-ray powder diffractometry (XRD; Shimadzu XRD-6000, Cu Ka radiation) at a scan rate of 2° min^{-1}, scanning electron microscopy (FESEM; JEOL, JSM-7600 F) and transmission electron microscopy (TEM; JEOL, JEM-2100 F). N_2 adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements using TriStar II surface area and porosity analyzer.

Electrochemical characterization

Activated carbon was purchased from XinSen Carbon Industry Co., Ltd, with a BET surface area of 2084.15 m^2 g^{-1}. The working electrode was prepared by mixing 80 w.t% active material, 10 wt.% carbon black, and 10 wt.% polyvinylidene fluoride (PVDF) in NMP. The mixture was then stirred overnight