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Chestnut shell-like $Li_4Ti_5O_{12}$ hollow spheres for high-performance aqueous asymmetric supercapacitors

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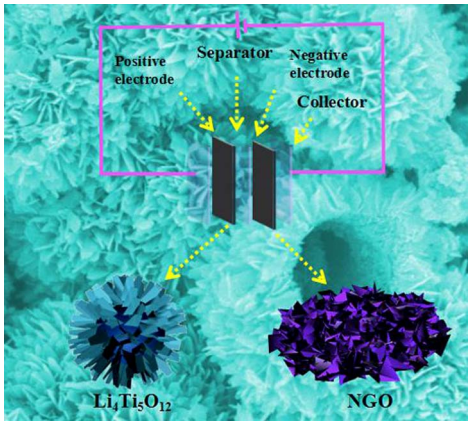
GRAPHICAL ABSTRACT



We have successfully synthesized 3D Li4Ti5O12 hollow sphere for high-performance.

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ABSTRACT

As promising electrode materials in supercapacitor, metal oxides have attracted significant attention recently. At present, it is highly desirable but remains challenging to prepare three-dimensional (3D) metal oxides hollow materials for further improving the performance of supercapacitors. Herein, 3D chestnut shell-like $Li_4Ti_5O_{12}$ hollow sphere is successfully fabricated by using an effective hydrothermal strategy. Owing to the unique structural feature and the desirable chemical composition, $Li_4Ti_5O_{12}$ hollow sphere displays a remarkable capacitance of 653.22 F/g at 1 A/g and keeps 88.56% over 4000 cycle. Furthermore, one aqueous asymmetric supercapacitor (ASC) is constructed based on $Li_4Ti_5O_{12}$ and N-doped graphene oxide (NGO) which is synthesized by a facile burning method. The $Li_4Ti_5O_{12}$//NGO ASC shows an energy density of 26.15 Wh/kg at power density of 799.83 W/kg, and yet keeps 14.45 Wh/kg even at 8.01 kW/kg. This strategy may offer a versatile idea of tailoring new type of 3D metal oxides hollow materials and opens the possibility for using in high energy storage device.

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1. Introduction

With notable characteristics of high power density (> 10 kW/kg), long cycle stability (> 10^5), low maintenance cost and fast charging-discharging rate [1–3], supercapacitors are ideal for high-power applications such as electrical vehicles, cranes and stand-by power systems [4,5]. Usually, supercapacitor is mainly divided in two categories: electric double layer capacitor (EDLC) and pseudocapacitor [6]. Particularly, pseudocapacitors possess ability to store more power than EDLCs on account of near surface redox reactions [7]. Many materials have been explored as pseudocapacitive materials for high performance. Especially, the transition metal oxides with binary (Co_3O_4, Fe_2O_3 and WO_3) [8–10] and ternary ($NiCo_2O_4$, $ZnCo_2O_4$ and $CuFe_2O_4$) [11–13] compositions are widely studied due to good cycling stability and specific electrical conductivity. In particular, ternary composition (such as the faradic lithium/sodium-intercalation electrodes Na_xMnO_2, $Li_4Ti_5O_{12}$ and $LiMn_2O_4$) [14–16] has been recognized as promising electrode materials due to better electrochemical activity and bigger capacity [11]. Recently, many researchers reported that the hybrid energy-storage system composed of supercapacitors and lithium ion batteries (LIBs) has been employed to complement both of their disadvantages. It improves the power density and cycle performance of LIBs through battery stress relaxation by rapid power capture and delivery of supercapacitors. Thereinto, as one zero-strain insertion material, $Li_4Ti_5O_{12}$ exhibits excellent Li^+ insertion and extraction reversibility and exhibits excellent structural stability in the course of charge/discharge [17]. Nevertheless, matter most for $Li_4Ti_5O_{12}$ is barely satisfactory power properties which come from inferior diffusion coefficient of lithium ion (< 10^{-6} cm^2/s) and poor conductivity (< 10^{-13} S/cm) [18,19].

People has realized packaging original two-dimensional nanoflakes in three-dimensional hierarchical structures with superior robustness will efficiently retain the individuing nanoflakes with mainly exposed surface area, therefore coming true the full advantages of three-dimensional nanomaterials. Moreover, hierarchical hollow constructions with well-defined interior space, light density and shell permeability attract great attention because of particular construction-dependent characteristics. For supercapacitor electrode, hollow micro/nanostructures is highly desirable due to the apparent structural advantages which guarantee the sufficient contact area among active sites and electrolyte and provide a reduced ion/electron diffusion path.

Asymmetric supercapacitor (ASC) well integrates good qualities of Li-ion battery and supercapacitor, exhibiting high energy density [20–23]. Carbon materials have been widely used in ASC as the negative electrode due to the good conductivity, big surface area and outstanding chemical stability [24,25]. Among them, graphene is an important representative. Heteroatom doping of graphene (Gr) with B, N, P and S elements has been recognized as an efficient method to adjust and control its surface chemistry and the electronic properties [26]. Thereinto, N element doping has been widely used due to its approximate atomic radius and valence electrons with C.

In this work, a high-performance ASC is developed with chestnut shell-like $Li_4Ti_5O_{12}$ hollow sphere and N-doped graphene (NGO). The $Li_4Ti_5O_{12}$ hollow sphere is fabricated by using an effective hydrothermal strategy and NGO is synthesized by a simple burning method. The $Li_4Ti_5O_{12}$ hollow sphere exhibits remarkable specific capacitance (653.22 F/g on 1 A/g) with good cyclic stability (retaining 88.56% over 4000 cycles at 5 A/g). NGO as a supercapacitor electrode also displays big specific capacitance (238.90 F/g on 1 A/g) and good cycling stability (keeps 92.94% of its original capacity after 2000 cycles at 2 A/g). One asymmetric supercapacitor is then developed by using $Li_4Ti_5O_{12}$ as positive electrode and NGO as negative material. The $Li_4Ti_5O_{12}$//NGO ASC shows good performances with the specific capacitance of 73.56 F/g and energy density of 26.15 Wh/kg at 799.83 W/kg. Importantly, it yet exhibits a high energy density of 14.45 Wh/kg even at 8.01 kW/kg. The excellent electrochemical performances suggest $Li_4Ti_5O_{12}$-NGO ASC is meetly desired for progressive energy storage device.

2. Experimental

2.1. Preparation of chestnut shell-like $Li_4Ti_5O_{12}$ hollow spheres

Chestnut shell-like $Li_4Ti_5O_{12}$ hollow sphere was prepared by a simple hydrothermal method. First, 1.35 g of $LiOH{\cdot}H_2O$, 4 mL of 30% H_2O_2 and 2.25 mL of Titanium isopropoxide ($C_{12}H_{28}O_4Ti$) were dissolved in 70 mL water and stirred for 30 min. Afterwards, this mixture was transferred into an autoclave and kept at 150 °C for 6 h. Subsequently, white precipitates were obtained by centrifuging, washing and drying. In the end, the products were annealed at 500 °C for 4 h to obtain $Li_4Ti_5O_{12}$ hollow spheres. Compared with other $Li_4Ti_5O_{12}$ reports on similar structure by using hydrothermal method [27,28], the outstanding innovations of this work are more simpler operation, far less time consuming and higher output.

2.2. Preparation of N-doped graphene oxide

Graphene oxide was prepared according to reference [29]. The NGO was fabricated by burning in an open condition. Firstly, 100 mg graphene oxide was put onto a watch glass. Afterwards, 3 mL Triethylamin (TEA) was added by syringe. The mixture was then set fire to. After the burning stopped, the black NGOs were collected. The photograph of the preparation process of NGO is shown in Fig. S1.

2.3. Characterization

X-ray powder diffraction (Shimadzu XRD-7000) was used to characterize the crystalline phase of samples. Raman spectra was recorded on a Renishaw Raman system model 1000 spectrometer (Gloucestershire, UK). The products morphologies were observed by scanning electron microscopy (SEM) with a JSM-6510 (JEOL Ltd., Japan) at 20 V–30 kV and a transmission electron microscopy (TEM, JEM-2100F). N_2 adsorption/desorption isotherms were recorded on an ASAP2020 surface area and porosity analyzer (Micrometrics Instrument Corporation). X-ray photoemission spectroscopy (XPS) was carried out on a Thermo Scientific K-Alpha spectrometer. Electrochemical measurements were tested on a CHI660E electrochemical workstation (Shanghai Chenhua).

2.4. Electrochemical tests

The electrochemical property is studied in a three-electrode and two-electrode systems. The electrochemical test of individual electrode was carried out in a three-electrode system with 2 mol/L potassium hydroxide as electrolyte with a platinum counter electrode and saturated calomel reference electrode. The working electrode is prepared by using active material, carbon black and polytetrafluoroethylene in a mass ratio of 80:10:10. The porosity and thickness of the purchased nickel foam are 95% and 1.6 mm, respectively. The mass loading of active materials on each nickel foam current collector was in the range of 2–3 mg. The slurry was pasted on a foam nickel substrate (1 × 1 cm^2) and pressed into sheets under 15 MPa then dried at 60 °C overnight. The specific capacitance (F/g) was calculated by Eq. (1) [30]:

$$Cm = \frac{2im\int Vdt}{V^2|_{ViVf}} = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where i_m (A/g) is the current density, $\int Vdt$ is the integral area of discharge process; V is the potential window between V_i and V_f; I represents the discharge current; m is the mass of the total active material; Δt is discharge time; ΔV is the potential window. The front formula can be simplified as the behind formula. Since the pseudocapacitive