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Boosting long-cycle-life energy storage with holey graphene supported $TiNb_2O_7$ network nanostructure for lithium ion hybrid supercapacitors

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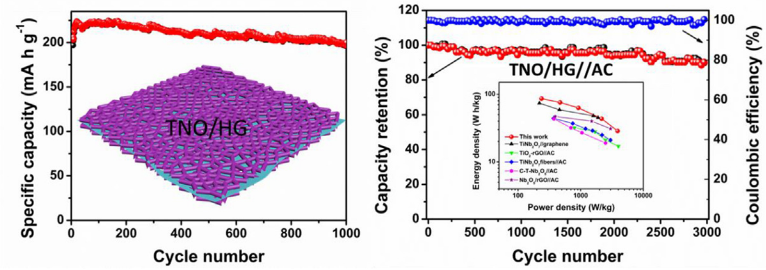
HIGHLIGHTS

- A novel composite of $TiNb_2O_7$ network nanostructure and holey graphene was fabricated.
- The long-term life with 91.5% capacity retention after 1000 cycles was obtained.
- The Li-HSC device exhibits high energy density and excellent cycling stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite many efforts devoted to explore novel electrode materials for lithium ion hybrid supercapacitors, the obtainable long-life cycling of existing anode materials are still inadequate for promising applications. This report demonstrates a new nanocomposite with $TiNb_2O_7$ network nanostructure in situ anchored onto the holey graphene, which is designed as anode material for lithium ion hybrid supercapacitors. Impressively, electrochemical analyses show that the good rate performance (capacity retention of 73.5% from 0.05 to 5 A g^{-1}) and long cycle life up to 1000 cycles at 1 A g^{-1} (a capacity retention of 91.5%) are attained. Furthermore, the lithium ion hybrid supercapacitor device consisting of this nanocomposite and activated carbon exhibits excellent cycling stability (90.2% of initial capacity after 3000 cycles), high energy density of 86.3 W h kg^{-1} (at 237.7 W kg^{-1}) and high power density of 3.88 kW kg^{-1} (at 28.7 W h kg^{-1}). This study ascribes the unprecedented performance to the high conductive holey graphene with abundant mesopores, the uniformly distributed $TiNb_2O_7$ network nanostructure and the synergetic effect between them. Based on these findings, the presented nanocomposite has great potential in high performance lithium ion hybrid supercapacitors.

1. Introduction

As the two mainstream and cost-effective energy storage devices, in the past decades supercapacitors (SCs) and lithium ion batteries (LIBs) have been explored for wide range of energy applications, from mobile devices to hybrid electric vehicles (HEVs) [1–4]. The SCs can provide high power (up to 10 kW kg^{-1}) and long cycle life resulting from fast non-faradaic surface reactions, but suffer from limited energy densities [5–7]. On the other hand, the LIBs can deliver high energy densities (130–200 W h kg^{-1}) owing to faradaic lithium insertion reactions, while they generally have low power densities and poor cycle life [8–11]. Therefore, in order to fulfill the necessary demands of electronic devices and HEVs, new electrochemical energy storage devices combining the advantages of SCs and LIBs are attracting great interests.

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In principle, a novel energy storage system, lithium ion hybrid supercapacitors (Li-HSCs) use lithium-insertion-type anode and non-faradaic capacitor-type cathode in a lithium-salt-containing electrolyte [12,13]. The combination of two type electrodes can effectively overcome the energy densities limitation of conventional electrochemical capacitors and the poor power densities in LIBs.

One of the major problems for Li-HSCs is the imbalance in the kinetics between two electrodes because the lithium-intercalation process is far more sluggish than the non-Faradaic capacitive reaction [11]. Therefore, it is important to explore novel anode materials with higher power capability to balance the kinetics between two type electrodes. Recently, spinel $TiNb_2O_7$ with unique ion-intercalation pseudocapacitance has been proposed as alternative candidate of high power anode material for Li-HSCs [7,12]. Due to the five electron transfer reaction with multiple redox couples of Nb^{5+}/Nb^{4+}, Nb^{4+}/Nb^{3+}, Ti^{4+}/Ti^{3+}, the $TiNb_2O_7$ has a high theoretical capacity of ~387 mA h g^{-1}, which surpasses that of $Li_4Ti_5O_{12}$ (175 m A h g^{-1}), TiO_2 (335 mA h g^{-1}) and Nb_2O_5 (200 mA h g^{-1}) [14–17]. Furthermore, the high working voltage (~1.6 V *vs.* Li^+/Li) of $TiNb_2O_7$ can effectively prohibit the formation of SEI layer and lithium dendrites, resulting in the higher rate and safer operation than other anode materials [18]. However, it suffers from the intrinsic low ionic and electronic conductivity, which restricts the electrochemical kinetics, leading to limited rate capability [19]. One of reported approaches to overcome this hurdle is compositing $TiNb_2O_7$ with conductive carbon materials [12,18,20–22]. For instance, Wang et al. prepared $TiNb_2O_7$@carbon composite through an electrospinning method followed by carbon coating, which exhibits high specific capacity of 280 mA h g^{-1} at 0.2 A g^{-1} and a capacity retention of ~80% after 100 cycles [12]. Ashish et al. reported the $TiNb_2O_7$ nanoparticles (25–30 nm)/graphene hybrid with great rate capability and capacity retention of 76% over 300 cycles at 1C [18]. Li et al. fabricated the layered $TiNb_2O_7$/graphene composite by direct dispersion and blending. The combined advantages of these two components improved the rate capability (around 180 mA h g^{-1} at 100 C rate) and cycling performance (200 mA h g^{-1} during 70 cycles at 0.2 A g^{-1}) [20]. The nano-$TiNb_2O_7$/carbon nanotube nanocomposite was prepared through direct mixing, reported by Lin and co-workers. This composite presents a large reversible specific capacity (~346 mA h g^{-1} at 0.1 C), prominent rate capability (163 mA h g^{-1} at 30 C) and a capacity retention of 97.6% after 100 cycles [22]. However, the limited long-term cycling of these composites still restricts their promising application in Li-HSCs energy storage. Recently, the graphene with open porous structure can significantly improve specific surface area and ion diffusion, boosting the capacity, rate capability and cycle life [23,24].

Here, we report a novel $TiNb_2O_7$/holey graphene (TNO/HG) nanocomposite with superior rate capability and long-term cycling performance for Li-HSCs. This nanocomposite was synthesized through in situ anchoring $TiNb_2O_7$ network nanostructure onto the holey graphene via facile wet chemical route. The highly conductive graphene with abundant mesopores and the uniformly distributed $TiNb_2O_7$ network nanostructure greatly facilitate rapid ions and electrons transport, thus improving sufficient utilization of electrochemical active sites. More significantly, the TNO/HG nanocomposite exhibits outstanding rate performance (capacity retention of 73.5% from 0.05 to 5 A g^{-1}) and great cycling stability (a capacity retention of 91.5% after 1000 cycles at 1 A g^{-1}). Moreover, a Li-HSC device with TNO/HG nanocomposite and activated carbon as anode and cathode respectively shows excellent cycling stability (90.2% of initial energy after 3000 cycles) and high energy density of 86.3 W h kg^{-1} (at 237.7 W kg^{-1}). These impressive electrochemical performances have rarely been reported to our knowledge, confirming its potential application in Li-HSCs energy storage.

2. Experimental

2.1. Synthesis of HGO

Graphene oxide (GO) was synthesized using modified Hummers method reported [25], and the holey multi-layer graphene oxide (denoted as holey graphene oxide and HGO) was prepared by a brief approach. Firstly, the GO aqueous disperse of 1 mg mL^{-1} was obtained via ultrasonication for 1.5 h. Then 6 mL of 30% H_2O_2 aqueous solution was added into 40 mL of 1 mg mL^{-1} GO aqueous dispersion, followed by heated at 90 °C under stirring for 2 h. Finally, The HGO was obtained after rinsing with deionized water to remove residual H2O2 and freeze-drying under vacuum.

2.2. Synthesis of TNO/HG, TNO/G and TNO

The HGO of 10 mg was redispersed in 40 mL ethanol by ultrasonication 1.5 h. Then, 0.4 mmol of $NbCl_5$ and 0.2 mmol of tetrabutyl titanate ($Ti(OC_4H_9)_4$) were dissolved into the solution, in turn. After stirring 2 h, a solution of 20 mL ethanol containing 0.5 mL oleylamine was added dropwise. After another 0.5 h, the mixture was transferred into 100 mL Teflon-lined autoclave, then kept at 200 °C for 24 h. The obtained products were centrifuged and washed using ethanol and deionized water to remove residual oleylamine and ions, and then freeze-dried. The $TiNb_2O_7$/holey reduced multi-layer graphene oxide (denoted as $TiNb_2O_7$/holey graphene and TNO/HG) was finally annealed at 900 °C under N_2 atmosphere for 2 h. For comparison, the pristine $TiNb_2O_7$ and $TiNb_2O_7$/reduced multi-layer graphene oxide (denoted as $TiNb_2O_7$/graphene and TNO/G) were synthesized by not adding HGO and replacing HGO with GO.

2.3. Material characterization

As-prepared samples were investigated using field-emission scanning electron microscope (FE-SEM, Titan G2 60-300) and transmission electron microscope (TEM, JEOL JEM-2100; HRTEM, Tecnai G2 F30). The crystal structure of samples were determined by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with Cu Kα radiation (λ = 1.5406 Å). The Raman spectra were obtained on Renishaw Invia Raman Microscope with 514.5 nm laser. The nitrogen adsorption-desorption isotherm and Barret-Joyner-Halenda (BJH) pore size distribution were measured by a Quantachrome Instruments, 2000-08. The thermogravimetric analysis (TGA) was carried out using TG instrument DGT-60 (Shimadzu, Japan) in air. X-ray photoelectron spectrometer (XPS) analysis was collected on a Thermo ESCALAB 250 with monochromatic Al Kα radiation.

2.4. Electrochemical characterization

For the half-cell tests, coin-type cells (CR2016) were assembled by sandwiching polypropylene membrane (Celgard 2400) between working electrodes and lithium metal foils in argon-filled glove box. The working electrodes were fabricated using the typical slurry-coating technique. In detail, the active material (80%), conductive super-P (10%) and polyvinylidene fluoride (PVDF, 10%) were thoroughly mixed and stirred in N-methyl-2-pyrrolidone (NMP) to form homogeneous slurry, which was then coated onto Cu foil (14 mm), followed by drying in vacuum at 105 °C for 10 h. The electrolyte was 1 M $LiPF_6$ in dimethyl carbonate, ethylene carbonate and diethyl carbonate (1:1:1, in volume percent). The average loading of active material was ~1 mg/cm^2. Galvanostatic charge-discharge measurements were conducted within the potential range of 1–3.0 V on battery test instruments (Land CT2001). The cyclic voltammetry (CV) and electrochemical impedance spectroscopies (EIS) were measured by CHI760C electrochemistry station (Chenhua, Shanghai, China). The EIS was performed at the open-circuit voltage (OCV) with frequency ranging from 100 kHz to 0.01 Hz.

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