Electrochimica Acta 148 (2014) 73–78

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Synergistic performance of porous laminated tungsten disulfide/copper oxide/single-wall carbon nanotubes hybrids for lithium ions batteries

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ARTICLE INFO

Article history:
Received 1 October 2014
Received in revised form 10 October 2014
Accepted 10 October 2014
Available online 17 October 2014

Keywords:
tungsten disulfide/copper oxide/single-wall carbon nanotubes hybrid
lithium ions battery
lamellar
porous thin films

ABSTRACT

A novel ternary tungsten disulfide (WS_2)/copper oxide (CuO)/single-wall carbon nanotubes (SWCNT) porous laminated hybrids are fabricated with the aid of electrostatic interaction and vacuum filtration. In which, the layered WS_2 sheets are spaced by high electrochemical active CuO nanosheets and conductive SWCNT and form a unique sandwich-like porous structures. When used as a lithium ion batteries anode, it demonstrates high reversible specific capacity of 962.4 mA h g^{-1} at 0.1 A g^{-1} after 100 cycles and excellent rate capability, a reversible specific capacity of 418.1 mA h g^{-1} even at a high rate current density of 2 A g^{-1}. The unique assembled WS_2/CuO/SWCNT porous hybrids not only show the improved electrical conductivity, but also provide efficient charge transport channels for electrolyte penetration and sustain for the volume variation during the lithiation and delithiation. These synergistic effects significantly improve the electrochemical performances. The synthesis approach presented here would be extended to the other layered-based composites for energy applications.

1. Introduction

For now, rechargeable lithium ions batteries (LIBs) are the dominant power source for popular consumer electronics and considered as the most promising power sources for portable electronic devices and vehicles. Various electrode materials with large reversible capacity, long cycle life and charge/discharge rate have been extensively investigated [1–4]. In recent years, two-dimensional inorganic materials, such as graphene, MoS_2, WS_2 and Ti_3C_2 have been investigated as anode materials for LIBs because of their unique layered crystal structure, which are prefer ions and molecules intercalation [5–9].

As a typical layered transition metal dichalcogenide, tungsten disulfide (WS_2) has been extensively studied in many applications such as photosensor device, catalyst, field-effect transistor, and many others [10–13]. Recently, different morphologies and sizes of WS_2 were investigated as anodes materials for LIBs [14–16]. However, the stacking between nanosheets and low electronic conductivity usually lead to a rapid decay of capacity and poor rate capability. Therefore, introducing a conductive spacer between WS_2 nanosheets is an efficient strategy to avoid the aforementioned disadvantages [17]. Exfoliation of crystal into monolayer or few-layers is one of the most efficient route to shorten diffusion pathways and add diffusion channels for electrolyte penetration when used as anodes in LIBs [18]. Wang et al. reported layered MoS_2 intercalated by single-wall carbon nanotubes (SWCNT) can improve both stability and discharge capacity [19]. Recently, a new composite consisting of graphene, poly ethylene oxide and exfoliated MoS_2 was designed by Xie's group, which showed high sepcific capacity and excellent high-rate performance for reversible Li^+ storage [18]. Compared with the mechanical mixture, our group recently developed a facile electrostatic-assisted self-assembly method to obtain CuO/reduced graphene oxide (rGO) porous layered structure [20,21]. The unique sandwiched porous structures provide plenty of paths for electrolyte-ion access to the surface of the CuO and rGO sheets, lead to enhance the electrochemical performance. However, all of these 2D

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http://dx.doi.org/10.1016/j.electacta.2014.10.037
0013-4686/

dimensional related electrodes are binary composites. In order to further improve their performance, making ternary composites electrodes might be a novel strategy due to the synergistic effects.

In this study, we fabricated a novel ternary WS_2/CuO/SWCNT porous hybrids anode for LIBs by electrostatic-assisted self-assembling and vacuum filtration process. Highly positively charged CuO nanosheets easily assembled with negatively charged WS_2 nanosheets and SWCNTs into flocculent networks. The layered porous film composed of WS_2/CuO/SWCNT was obtained by filtering the above flocculent suspension on a PC support. When used as anodes in LIBs, in the unique structure, CuO nanosheets not only acted as the interlayer spacer between the WS_2 nanosheets but also as an active material (the theoretical capacity of CuO is about 674 mA h g^{-1}, higher than 433 mA h g^{-1} of WS_2 based on 4 mol of Li^+ insertion), both of which were beneficial to enhance the specific capacity. The intercalated SWCNT networks increased the conductivity of the electrode and provided rapid charge transfer during the electrochemical reaction. Due to these synergistic effects, thus, the WS_2/CuO/SWCNT hybrids electrode exhibited high reversible specific capacity of 962.4 mA h g^{-1} at 0.1 A g^{-1} after 100 cycles. Even at a high rate current density of 2 A g^{-1}, the electrode still showed a remarkable reversible specific capacity of 418.1 mA h g^{-1}, which was higher than the theoretical capacity (372 mA h g^{-1}) of graphite.

2. Experimental Section

2.1. Materials

WS_2 particles, n-butyl lithium and n-hexane were purchased from Alfa Aesar, J&K and Acros, respectively. Copper nitrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) and aminoethanol (AE) were purchased from Sigma-Aldrich. SWCNT were derived from Carbon Nanotechnologies. Polycarbonate (PC) membranes with pore size of 200 nm were used to filter the mixture composites. Deionized water (18.2 MΩ) produced by a Millipore Direct-Q System was used throughout all experiments.

2.2. Synthesis of WS_2 nanosheets

The WS_2 particles were exfoliated as presented previously [22]. Briefly, 500 mg WS_2 powder was dispersed in 10 mL of n-butyl lithium under stirring for 48 h in a N_2-filled glove box. Then wash the suspensions several times using n-hexane. The obtained powder was dispersed in *ca.*200 mL deionized water under the ultrasonication for 2 hrs. Excess lithium hydroxyl was removed by centrifuging. The concentration of diluted WS_2 nanosheets suspension is about 1.5 mg/mL.

2.3. Synthesis of CuO nanosheets

According to the previously reported method [21], a certain volume of 1.6 mM AE aqueous solution was mixed with an equal volume of 2 mM $Cu(NO_3)_2$ aqueous solution with stirring for 1 minute, then keep the mixture at 25 °C for 24 hrs. The colloidal mesoporous CuO nanosheets with a concentration of *ca.* 0.053 mg/mL were obtained.

2.4. Synthesis of SWCNT dispersion

100 mg of SWCNT was added to 50 mL of 6 M nitric acid at 80 °C for 24 hrs. Then wash the black solution with deionized water until the solution reached pH 6.5. Finally, the oxidized water-soluble and negatively charged CNTs were dispersed in water by sonification to give a concentration of 1 mg/mL [22].

2.5. Synthesis of ternary laminated WS_2/CuO/SWCNT porous hybrids

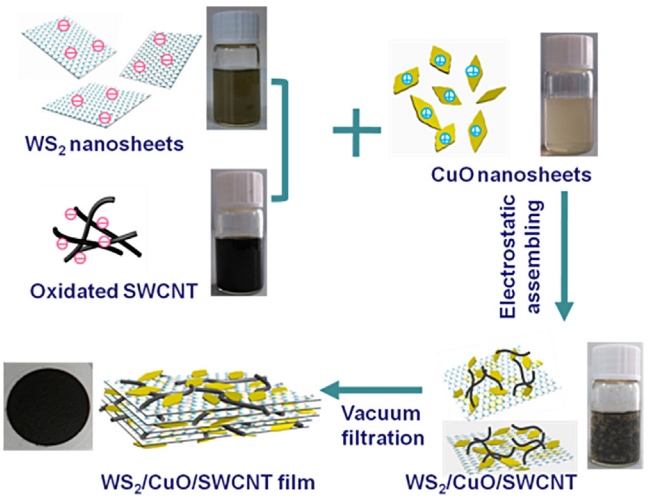
20 mL negatively charged WS_2 nanosheets and a certain amount of SWCNT dispersions were mixed together under vigorous stirring. Then, 187.5 mL CuO nanosheets colloidal was added into the above mixture. Since the CuO nanosheets were highly positively charged, they quickly assembled with the negatively charged WS_2 nanosheets and SWCNTs into a flocculent suspension within a few minutes. Subsequently, the WS_2/CuO/SWCNT lamellar film was prepared by filtering the mixture through a PC membrane. Three WS_2/CuO/SWCNT hybrid lamellar films with mass ratios of WS_2 to CuO to SWCNT of 3:1:1 (50 mg), 3:1:2 (60 mg) and 3:1:4 (80 mg) were prepared, and named as WCS-1, WCS-2, and WCS-4, respectively. The synthesis process is schematically illustrated in Scheme 1. WS_2/CuO composites (mass ratios of WS_2 to CuO is 3:1, 40 mg) were also prepared for comparison. The active mass in electrodes were 0.88 mg, 1.08 mg, 1.18 mg and 0.80 mg for WCS-1, WCS-2, WCS-4 and WS_2/CuO under 0.1 A g^{-1}, the active mass of WCS-2 was 0.96 mg for the test of rate capability.

2.6. Electrode preparation and electrochemical characterization

The electrode was prepared by mixing WS_2/CuO/SWCNT hybrid lamellar films, carbon black and polyvinylidene fluoride at a weight ratio of 8:1:1 using N-methyl-pyrrolidinone as solvent. Then the slurry was pasted onto pure Cu foils. After evaporation of the solvent and drying, the prepared electrode was incorporated into a coin-type cell with lithium foils as both counter and reference. The electrolyte employed in the cell was 1 M $LiPF_6$ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. The galvanostatic (GV) charge-discharge performances of the cell were tested in the voltage range of 0.01–3.0 V under a constant current density of 0.1 A g^{-1} by EQ-BST8-WA battery-test system, cyclic voltammetry (CV) was recorded by a CHI 660D electrochemical workstation in the voltage range 0.01–3.0 V with a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) results were obtained from a frequency range of 100 kHz to 1 Hz.

2.7. Characterization

The crystallinity of the composite is obtained by X-ray diffraction (XRD) at room temperature using an X'Pert PRO (PANalytical, Netherlands) instrument with Cu *Kα* radiation.



Scheme 1. Schematic illustration of the preparation process of porous WS_2/CuO/SWCNT lamellar film.