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Ultrafine tin oxide on reduced graphene oxide as high-performance anode for sodium-ion batteries

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ABSTRACT

Na-ion Battery is attractive alternative to Li-ion battery due to the natural abundance of sodium resource. Searching for suitable anode materials is one of the critical issues for Na-ion battery due to the low Na-storage activity of carbon materials. In this work, we synthesized a nanohybrid anode consisting of ultrafine SnO_2 anchored on few-layered reduced graphene oxide (rGO) by a facile hydrothermal route. The SnO_2/rGO hybrid exhibits a high capacity, long cycle life and good rate capability. The hybrid can deliver a high charge capacity of 324 mAh $g_{SnO2}{}^{-1}$ at 50 mA g^{-1}. At 1600 mA g^{-1} (2.4C), it can still yield a charge capacity of 200 mAh $g_{SnO2}{}^{-1}$. After 100 cycles at 100 mA g^{-1}, the hybrid can retain a high charge capacity of 369 mAh $g_{SnO2}{}^{-1}$. X-ray photoelectron spectroscopy, ex situ transmission electron microscopy and electrochemical impedance spectroscopy were used to investigate the origin of the excellent electrochemical Na-storage properties of SnO_2/rGO.

1. Introduction

Li-ion batteries are currently dominant power sources for portable electronic devices and show promising applications in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1–4]. One of the concerns on Li-ion batteries is the limited lithium reserves [5] for large-scale energy storage like grid and EVs/HEVs [6–8]. Na-ion batteries thus become a hot topic in view of more affluent Na resources [9–13]. Developing suitable anode materials is one of the critical issues for Na-ion batteries since graphite is inert toward electrochemical Na storage [14], in contrast to the case for Li-ion batteries. The diffusion rate of Na ions in electrode is smaller than that of Li ions due to the large size [15]. Compared with graphite, hard carbons [16–19] and transition metal oxides [20–23], based on absorption and conversion mechanism, respectively, exhibit much higher Na-storage activity. Similar to Li, Na can form alloys with some elements, such as Sb [24–28], P [29–31], Ge [32,33] and Sn [34–40], delivering a high Na-storage capacity.

Among various candidates, Sn-based materials receive a special attention because metallic Sn can yield a capacity as high as 847 mAh g^{-1} by forming a Na-rich $Na_{15}Sn_4$ composition [41], in addition to its low cost and environmental friendliness. However, an extremely large volume expansion of 520% occurs during the conversion from Sn to $Na_{15}Sn_4$ [34], leading to particle pulverization/exfoliation and rapid capacity fading. A support thus is necessary to buffer the volume changes and to fix/disperse the pulverized particles. Graphene is considered as an ideal support because of its large specific surface area [42], high mechanical strength [43], and superior electronic conductivity [44]. Besides, graphene itself exhibits a reversible Na-storage performance [45]. The work by Qu et al. showed that the electrochemical performance of SnS_2 can be considerably enhanced by forming a SnS_2/reduced-graphene-oxide (SnS_2/rGO) hybrid which could maintain a capacity of 500 mAh g^{-1} after 400 cycles at 1 A g^{-1} [40].

In this work, we prepared a SnO_2/rGO nanohybrid by a facile hydrothermal route. Ultrafine SnO_2 nanocrystals (below 10 nm) are uniformly anchored on wrinkled, few-layered rGO sheets, forming a unique hybrid nanostructure. The SnO_2/rGO hybrid can yield a high Na-storage capacity and sustain long-term cycling. The origin of the excellent electrochemical performance of SnO_2/rGO was systematically studied by X-ray photoelectron spectroscopy (XPS), ex situ transmission electron microscopy (TEM) and electrochemical impedance spectroscopy (EIS). The results showed that a combination of the buffering, conducting and dispersing effects of

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rGO as well as the formation of an effective surface protection film underlie the excellent electrochemical performance of SnO_2/rGO.

2. Experimental

2.1. Preparation of SnO_2/rGO

Graphite oxide (GO, 25 mg), prepared by a modified Hummers method [46], was uniformly dispersed in deionized (DI) water (30 mL) by ultrasonic treatment. Then, a mixed aqueous solution (40 mL) of $SnCl_2{\cdot}2H_2O$ (90 mg) and $NH_4{\cdot}H_2PO_4$ (6.6 mg) was added slowly to the above solution with stirring. $NH_4{\cdot}H_2PO_4$ was used as the surfactant to control the particle size of SnO_2. After intensive stirring at 80 °C for 6 h, the mixed solution was transferred to a Teflon-lined stainless steel autoclave (100 mL) and heated in an electric oven at 220 °C for 48 h. The product was collected by centrifugation, washed with DI water and absolute ethanol repeatedly, and dried at 60 °C under vacuum overnight. For comparison, a SnO_2/carbon-nanotube (CNT, Shenzhen Nanotech Port Co., Ltd) composite was also prepared with a similar route by replacing GO with CNT during the synthesis and the content of CNT in SnO_2/CNT is controlled at a similar value as rGO in SnO_2/rGO. Bare SnO_2 was prepared with a similar route without the addition of GO in the precursors. Bare rGO was also prepared by reducing GO at 220 °C for 48 h in DI water via a hydrothermal route.

2.2. Materials characterization

The phases of the hydrothermal products were analyzed by X-ray diffraction (XRD) on a Rigaku D/Max-2550pc powder diffractometer equipped with Cu Kα radiation ($\lambda = 1.541$ Å). XPS of the products were measured on a KRATOS AXIS ULTRA-DLD spectrometer with a monochromatic Al Kα radiation ($h\nu = 1486.6$ eV). Thermogravimetric (TG) analysis of SnO_2/rGO was carried out on a DSCQ1000 instrument from 28 to 800 °C at a ramp rate of 10 °C min^{-1} in air. N_2 absorption/desorption isotherms were recorded on an AUTOSORB-1-C apparatus. The morphologies of the products were observed by field-emission scanning electron microscope (SEM) on a FEI-sirion microscope, TEM and high-resolution TEM (HRTEM) on a JEM 2100 F microscope. The cycled electrodes were also characterized by XPS and TEM.

2.3. Electrochemical measurements

The electrode slurry was made by mixing 75 wt% active material (SnO_2/rGO, SnO_2, or rGO), 15 wt% acetylene black, and 10 wt% polyacrylic acid (PAA) binder in a water/ethanol mixture (1:1 in volume) with magnetic stirring for 2 h. PAA instead of PVDF was used as binder since it shows amorphous and cross-linking characters that enable strong and uniform binding of the active particles and it has low swellability in carbonates and high elastic modulus that enable effective suppression of the electrodes collapse [47,48]. The working electrodes were made by coating the slurry onto Al foil (not react with Na) followed by drying at 100 °C under vacuum overnight. CR2025-type coin cells were assembled in an Ar-filled glove box using Na foil as the counter electrode and glass fiber (Whatman GF/D) as the separator. The electrolyte was 1M $NaPF_6$ dissolved in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume). Fluoroethylene carbonate (FEC) was used as the electrolyte additive. The volume ratio of FEC/EC + DEC is 5%. The cells were galvanostatically cycled at various current densities between 0.005 and 3.0 V (vs. Na/Na^+) on a Neware battery tester (Shenzhen, China). Unless otherwise stated, for SnO_2/rGO, the specific capacity was calculated based on the mass of SnO_2 and the specific current was based on the total mass of SnO_2 and rGO, where 1 C is defined as 667 mA g^{-1} based on the formation of a maximum $Na_{15}Sn_4$ composition. EIS measurements were conducted on a Princeton Applied Research VersaSTAT3 electrochemistry workstation by applying an ac voltage of 10 mV amplitude over the frequency range 10^{-3}–10^6 Hz at desodiation states. Before the EIS tests, the

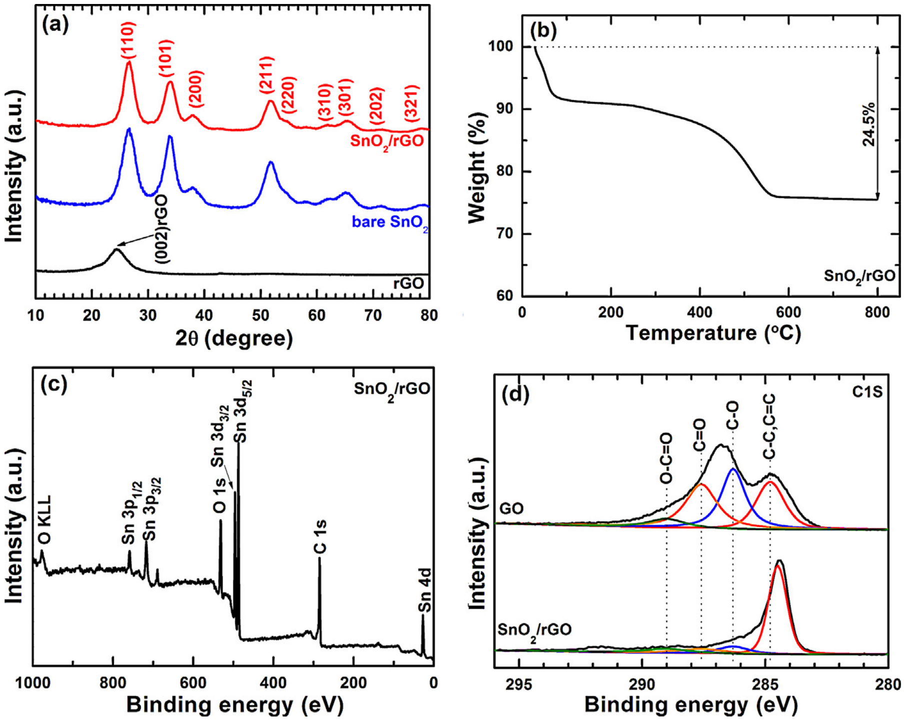

Fig. 1. (a) XRD patterns of SnO_2/rGO, SnO_2 and rGO, (b) TG curve of SnO_2/rGO, (c) XPS survey of SnO_2/rGO, and (d) C1s XPS of GO and SnO_2/rGO.