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A supercritical ethanol route for one-pot synthesis of tin sulfide–reduced graphene oxides and their anode performance for lithium ion batteries

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ABSTRACT

A simple, green, and ultra-fast one-pot supercritical ethanol (scEtOH) route was developed to synthesize tin sulfide–reduced graphene oxides (SnS–RGOs) by the simultaneous reduction of GO and the heterogeneous nucleation and growth of SnS nanosheets on the basal plane of RGO. The SnS–RGO composites exhibited a mesoporous structure with porosity up to 63%. When tested as an anode in lithium-ion batteries, the SnS–RGO composite with 44 wt% SnS loading delivered high reversible capacity of 613 mAh g^{-1} at 50 mA g^{-1} after 100 cycles and high rate capacity of 198 mAh g^{-1} at a high charge-discharge rate of 1 A g^{-1}.

Introduction

The development of new electrode materials for large-scale lithium ion batteries (LIBs) has received considerable attention because of emerging energy storage applications such as electric vehicles and stationary energy storage systems [1,2]. Graphite — which is currently used as a commercial anode material for LIBs — is not suitable for large-scale applications because of its low theoretical capacity (372 mAh g^{-1}) and safety issues [3,4]. A wide variety of materials have been studied as potential alternative anode materials for LIBs, including silicon, metal oxides (e.g., Fe_3O_4, CuO, TiO_2, and MoO_2), and metal sulfides (e.g., MoS_2 and TiS_2). Tin sulfide is a promising next-generation anode material because of its high theoretical capacity, abundance in nature, low cost, non-toxicity, and good safety [5–12]. For example, tin monosulfide (SnS) exhibits high theoretical capacity of 782 mAh g^{-1} (based on 4.4 Li alloying reaction per SnS) and suffers less irreversible loss than tin oxides and tin phosphides [6,7]. In addition, because of its intrinsic high electronic conductivity (0.01–0.19 S cm^{-1}), SnS can deliver high capacities under fast charge-discharge conditions [12].

As with most alloying materials, the huge volume change of SnS during Li-ion insertion/extraction causes serious mechanical stress in the composite electrode, which leads to loss of electrical contact between the active material and the current collector, thus resulting in rapid capacity fading [8–11]. To overcome the volume change of SnS during the charge/discharge process, various methods have been proposed. These can be categorized into two approaches: tailoring particle size/morphology (e.g., 2D nanosheets [13], nanoflowers [14], nanorods [7], yolk-shell structures [15], and nanobelts [16]) and formation of carbon composites [17–19]. Recently, it has been demonstrated that incorporating SnS nanoparticles into graphene sheets could yield excellent electrochemical performance [6,8,11,20]. Graphene sheets can provide high electronic conductivity, large specific surface area, chemical stability, and excellent mechanical properties to accommodate the huge volume change of SnS and maintain the structural integrity of the electrode during the charge/discharge process. In addition, a SnS-graphene composite could exhibit a mutual symbiotic effect in which graphene could prevent the aggregation of SnS particles and SnS could prevent the restacking of graphene. This could enhance the cycling stability of SnS/graphene electrodes [8,11]. For example, the SnS-graphene composite that was prepared using a hydrothermal method delivered high reversible capacity of 613 mAh g^{-1} after 100 cycles

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at 500 mA g^{-1} with 55% initial Coulombic efficiency (CE) [11]. A SnS nanorods-RGO composite synthesized using a solvothermal method in *N,N*-dimethyl formamide exhibited reversible capacity of 602 mAh g^{-1} after 50 cycles at 160 mA g^{-1} [11]. Although excellent electrochemical properties were achieved, the methods for the synthesis of SnS-graphene composites were complicated multi-step processes requiring long reaction times (10–24 h) and the use of toxic organic solvents, which should be addressed more carefully.

Herein, we developed a simple, one-pot, green process to synthesize SnS-graphene composites using supercritical ethanol (scEtOH) in a very short time (10 min). Because of their unique physicochemical properties such as zero surface tension, low viscosity, high diffusivity, environmental benignity, high supersaturation ratio, and scalability, supercritical fluids are highly versatile and effective media for synthesizing various types of nanomaterials [21]. For example, various types of cathode (e.g., $LiCoO_2$ [22], $LiFePO_4$ [23–26], and $LiFeSiO_4$ [27]) and anode nanomaterials ($Li_4Ti_5O_{12}$ [28–30]) have been synthesized in supercritical water. When supercritical alcohols are used, nanostructured materials that could exhibit high electrochemical performance (e.g., hierarchical nano/mesoporous particles and nanosheets) could be produced; for example, various types of nanostructured electrode materials including $LiFePO_4$ [31], $LiMSiO_4$ (M = Fe, Mn) [32], $Li_4Ti_5O_{12}$ [33–36], TiO_2 [37], MoO_2 [38], ZnO [39], MoS_2 [40], and $NaFeO_2$ [41] were produced in supercritical alcohols. In addition, the unique deoxygenation ability associated with supercritical alcohols has been used to synthesize hydrogen-enriched RGO with high electrochemical performance [42,43]. A new approach for synthesizing metal oxide- or metal sulfide-graphene composites in supercritical alcohols has been proposed. Simultaneous one-pot reduction of graphene oxide (GO) to RGO and heterogeneous nucleation and growth on the basal plane of RGO could produce highly dispersed and tightly anchored metal oxide nanoparticles on RGO sheets. Various types of composite electrode materials (SnO_2–RGO [44], Fe_3O_4–RGO [45], TiO_2–RGO [46], MoO_2–RGO [47], and MoS_2–RGO [48,49] with enhanced electrochemical performances (relative to their bare particles) have been synthesized in supercritical alcohols.

In this study, SnS–RGO composites were synthesized by the simultaneous reduction of GO to RGO and deposition of SnS nanosheets on the surface of RGO in scEtOH without using an additional sulfurization step. When tested as an anode in LIBs, the SnS–RGO composite with 44 wt% SnS loading exhibited high reversible capacity (613 mAh g^{-1} at 50 mA g^{-1} after 100 cycles), excellent high rate performance (198 mAh g^{-1} at 1 A g^{-1}), and good capacity recovery after ultrafast charge-discharge. The physicochemical and electrochemical properties of SnS–RGO composites with different SnS loadings were examined and compared with those of bare SnS particles.

Experimental

Materials

Tin(II) acetate (purity ≥ 99.0%), thioacetamide (purity ≥ 99.0%), and natural graphite flakes (size <45 μm, purity ≥ 99.99%) were purchased from Sigma Aldrich (USA). HPLC-grade ethanol was purchased from Honeywell Burdick and Jackson® (USA). Distilled and deionized (DDI) water was prepared using an AQUAMax™-Basic 360 water purification system equipped with a 0.22 μm filter (Young Lin Instrument Co., Ltd. South Korea). Poly(vinylidenedifluoride) (PVDF, Kurelha Chem. Co., Japan), acetylene black (DENKA Co. Ltd., Japan), and 1-methyl-2-pyrrolidinone (NMP, purity ≥ 98%, Alfa Aesar, MA, USA) were used as received.

Synthesis of SnS–RGO composites

Graphene oxide (GO) was prepared from the oxidative treatment of natural graphite flakes using the modified Hummer's method [50,51]. The detailed procedure for GO synthesis is described elsewhere [52,53]. The GO was dispersed in ethanol at a concentration of 0.0149 mg mL^{-1}. Known amounts of tin(II) acetate and thioacetamide were charged into the GO suspension (24 mL). The mixture was stirred for 30 min and sonicated for 30 min. The suspension was then loaded into an SUS 316 reactor (11 mL inner volume). The reactor was sealed tightly and placed in a molten salt bath (salt weight ratio KNO_3:$NaNO_3$:$Ca(NO_3)_2$ = 46:24:30) at a steady temperature of 400 °C. After 10 min reaction time, the reactor was quenched in a cold-water bath. The SnS–RGO composite particles synthesized were purified by washing several times with ethanol to remove residual organic species. The particles were then filtered and dried in a vacuum oven at 80 °C for 12 h. The SnS loading in the composite was controlled by adjusting the tin(II) acetate and thioacetamide concentrations in ethanol, as listed in Table 1.

Characterization

Functional groups of the samples synthesized were characterized using a NICOLET iS10 Fourier-transform infrared (FT-IR) spectrometer (Thermo Electron Co. USA). The crystal structures and phase purities of the samples were examined using a D/Max–2500 V/PC Rigaku X-ray diffractometer (XRD, Japan) with Cu–K_α radiation generated at 40 kV and 50 mA. The diffraction patterns were measured in the 2θ range 10–90°. The thermal stabilities of the SnS–RGO composites and the SnS loadings in the composites were analyzed using a Q50 thermogravimetric analyzer (TGA, TA Instruments, USA) at temperatures ranging from 30 to 700 °C at a heating rate of 10 °C min^{-1} and air flow rate of 60 mL min^{-1}. The morphologies of the samples were observed using a JEOL

Table 1
Crystal parameters and textural properties of SnS, RGO, and SnS–RGO composites.

Sample code	Sn precursor conc. (g mL^{-1})	S precursor conc. (g mL^{-1})	SnS content[a] (wt%)	BET surface area (m^2 g^{-1})	Average pore size diameter (nm)	Total pore volume (cm^3 g^{-1})	Porosity[b] (%)
Bare SnS	0.04736	0.03307	100	3.76	15.3	0.014	6.9
GO	–	–	–	25.3	8.1	0.051	9.3
RGO	–	–	–	205.0	22.1	1.130	69.4
SnS–RGO-1	0.04736	0.03307	75	37.1	21.1	0.196	46.3
SnS–RGO-2	0.01184	0.00827	44	147.8	13.5	0.498	63.0

[a] Estimated using TGA (see Fig. 3).
[b] Estimated under the assumption that the density of graphene is 2 g cm^{-3} and the density of SnS is 5.22 g cm^{-1}.

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