An interlayer nanostructure of rGO/Sn₂Fe-NRs array/rGO with high capacity for lithium ion battery anodes

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ABSTRACT An interlayer nanostructure of rGO/Sn₂Fe-NRs array/rGO was synthesized via a versatile integration of Sn₂Fe nanorods (NRs) array in between reduced graphene oxide (rGO) nanosheets. Impressively, as an anode material for lithium ion batteries, the as-prepared nanocomposites deliver a high specific capacity of 690 mA h g⁻¹ at a current density of 0.5 C (500 mA g⁻¹), and 582 mA h g⁻¹ at 1 C (1000 mA g⁻¹) with exceptional rate capability and cycling stability over 600 cycles. These significantly improved electrochemical properties benefit from the high structural stability and electrical conductivity of rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures. It is demonstrated that the designed interlayer nanostructures are outstanding architectures for lithium ion battery anodes.

Keywords: interlayer nanostructures, rGO/Sn₂Fe-NRs array/rGO, anodes, capacity, high density

INTRODUCTION

Lithium ion batteries (LIBs) are key enabling technology of electrical vehicles and portable electronic devices, as well as mainstream solutions to the stationary storage of renewable energy [1–6]. As LIBs anode materials, nanoalloys with high specific capacity often undergo large volume expansions during charging/discharging process, which leads to a poor cycling stability. Another major anode species, graphene, suffers from the low capacity and rapid decay caused by agglomeration. Thus, it is highly demanded to explore alternative anode materials that could endow LIBs with desirable electrochemical properties, especially high reversible stability, high specific capacity and high rate capability. Based on precedent research, nanoalloy/graphene nanocomposites are expected to exhibit improved cycling

stability by providing mechanical/structural integrity against changes in volume. Also they could potentially enhance the specific capacity of LIBs because they follow Li-storage mechanisms such as conversion and alloying reaction with Li [7,8].

The tin (Sn)-based LIBs anodes, cycling between Sn and Li_{4.4}Sn, exhibit an attractive theoretical specific capacity of 994 mA h g⁻¹ [9]. Moreover, Sn meets the major requirements for replacing the current graphite LIBs anodes owing to its high abundance and non-toxicity [10,11]. However, the specific capacity usually fades, because the volume of Sn increases by 260% upon its lithiation to Li_{4.4}Sn and the associated stress pulverizes the anode [12]. The fading has been extensively studied and overcome through alloying Sn with metal counterparts, as doping with an inert second component at an appropriate composition, including Mn, Ni, Co, etc., which could effectively absorb structural strain caused by the volume change [13,14]. Meanwhile, nanocomposite LIB anode materials based on two dimensional (2D) graphene layers have drawn much interest recently [15,16]. Graphene, as a substrate, accommodates volume changes and aggregation of active materials during reversible conversion reactions. Its superior electrical conductivity facilitates rapid and homogeneous lithium and electron transport to the active phase [17–19]. Furthermore, graphene itself is an ideal lithium storage material by offering sufficient defect sites for interfacial storage [20–22]. With multiple advantages of both materials above, the nanostructured Sn-nanoalloy/graphene composites with synergic effect are considered competent candidates for LIBs anodes. Earlier studies were established on nanoparticles (NPs) of

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SnFe, SnNi, etc. dispersing on graphene. Yet they are commonly flawed by the NPs agglomeration over charging-discharging cycles [23]. Therefore, it is significant to construct nanostructured Sn-nanoalloy/graphene composites with a stable and robust framework as well as a remarkable electrochemical performance.

We here designed a new interlayer nanostructure to achieve high electrochemical performance for LIB anodes. The reduced graphene oxide (rGO) nanosheets are engineered as the substrate and cover, while Sn_2Fe nanorods array (NRs array) as interlayer, which results in the formation of rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures. The nanostructures can promise the following advantages: 1) the top and bottom graphene layers serve as stable unfolded shells for fast electron transport; 2) Fe in Sn_2Fe NRs array, acting as electrochemical inert component, effectively accommodates the large volume expansion of Sn during the charging-discharging process; 3) the enclosed and ordered Sn_2Fe NRs array nanostructures exhibit a supreme structural and cycling stability by facilitating the electron transfer as well as providing free volume expansion space for Li^+ intercalation and deintercalation [24–28]; 4) one dimensional (1D) NRs are very conductive in the sense of directed transmission of electrons, thus enhancing the reversible capacity of the as-synthesized anode materials [29–34]; 5) the interlayer nanostructures empower the stability of integral structure while effectively hindering side reactions in LIBs, which further improves specific capacity in a high-rate charging-discharging process; moreover, such graphene covered interlayer nanostructures offer volume expansion space for Sn. The measurement results show that our interlayer nanostructures of rGO/ Sn_2Fe -NRs array/rGO achieve excellent electrochemical performance. The first cyclic charging-discharging specific capacity under a current density of 0.5 C reaches 1467 mA h g^{-1} . It maintains 690 mA h g^{-1} after 600 cycles. The capacity retention reaches 47%, while the as-synthesized materials at 1 C delivers 582 mA h g^{-1} after 600 cycles. It turns out that the newly interlayer nanostructures of rGO/ Sn_2Fe -NRs array/rGO are prospective as LIBs anode materials.

EXPERIMENTAL SECTION

Chemicals

Sodium hydroxide (NaOH, 99%) was purchased from Aldrich; sodium borohydride (NaBH_4 , 95%), stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%), stannous oxalate (SnC_2O_4 ,

99%), ferric acetate ($\text{C}_6\text{H}_9\text{FeO}_6$, 99%), triethylene glycol ($\text{C}_6\text{H}_{14}\text{O}_4$, 99%), and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC), and were used without further purification.

Synthesis of Sn_2Fe NRs

Sn_2Fe NRs were prepared by a facile hydrothermal method. Briefly, 1.5 mL of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol L^{-1}) and 3.5 mL of $\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$ (2 mmol L^{-1}) were dissolved in 8.6 mL of ethanol, followed by the addition of 0.18 g of 1-hexadecylamine (HDA) and 1 mL of NaOH (1 mmol L^{-1}). After continuous stirring for 1 h, 200 μL of hydrazine hydrates and 200 μL of formaldehyde were added to the solution. The as-obtained mixture was transferred into a 20-mL polytetrafluoroethylene (PTFE) lined stainless steel autoclave, which was subsequently heated at 180°C for 5 h with a heating rate of 1°C min^{-1} . The sample was then collected by centrifugation, and washed with ethanol and deionized water. Finally, the sample was vacuum dried at 60°C for 2 h.

Synthesis of rGO/ Sn_2Fe -seeds

In a typical procedure, 2.5 mL of graphene oxide (GO, 0.5 mg mL^{-1}) were first synthesized and purified by a modified Hummers method. 0.25 g of poly(vinyl pyrrolidone) (PVP) was dispersed in 12.5 mL of triethylene glycol, followed by the addition of the prepared GO, 0.3 mmol of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.15 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. After stirring for 0.5 h, 0.5 mmol of NaBH_4 was added. The mixture solution was transferred into a 20-mL PTFE lined-autoclave, then heated at 180°C and kept for 5 h. The rGO/ Sn_2Fe -seeds were collected by centrifugation, and washed with ethanol and deionized water for several times. Then the as-obtained products were vacuum dried at 80°C and used as seeds (nucleation centers).

Synthesis of Sn_2Fe -NRs array/rGO

To fabricate Sn_2Fe -NRs array/rGO, seed-mediated growth method was used. The as-obtained rGO/ Sn_2Fe -seeds were dispersed in 1.5 mL of tin (II) oxalate (0.01 mol L^{-1}) and 1.5 mL of ferric acetate (0.01 mol L^{-1}) ethanol solution, followed by the addition of 12.5 mL of ethylene glycol with continuous stirring for 0.5 h. The mixture solution was transferred into a 20-mL PTFE lined-autoclave, and heated at 180°C for 5 h. Then the Sn_2Fe -NRs array/rGO was collected by centrifugation, and washed with ethanol and deionized water for several times.

Synthesis of rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures

Typically, the as-obtained samples were dispersed in 2.5 mL

of GO (0.5 mg mL^{-1}). Then, 12.5 mL of ethylene glycol and 200 μL of hydrazine hydrate were added under continuous stirring for 0.5 h. The mixture solution was transferred into a 20-mL PTFE lined-autoclave, and heated at 180°C for 5 h. Finally, the interlayer nanostructures of rGO/Sn₂Fe-NRs array/rGO were collected by centrifugation, and washed with ethanol and deionized water for several times and dried at 60°C under vacuum.

Characterization

The morphology and structure were investigated by field-emission scanning electron microscopy (FE-SEM) (JEOL, S-4800, Japan), transmission electron microscopy (TEM) and high resolution TEM (HRTEM) (JEOL JEM-2100EX microscopy, Japan). Element analysis was carried out by selected area energy dispersive X-ray spectrometer (EDS) conducted at 20 keV on a TN5400 EDS instrument (Oxford). The powder X-ray diffraction (XRD) patterns were recorded by using a Bruker D8 (German) diffractometer with a Cu K α radiation source ($\lambda = 0.154056 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) measurements were performed on an RBD-upgraded PHI-5000C ESCA system (Perkin Elmer) using Al K α radiation ($h\nu = 1486.6 \text{ eV}$). The whole XPS spectrum (0–1100 eV) and the narrower, high-resolution spectra were all recorded using an RBD 147 interface (RBD Enterprises, USA) and Auger-Scan 3.21 software. Binding energies were calibrated using the containment carbon ($C_{1s} = 284.6 \text{ eV}$). Thermogravimetry (TG) analyses were carried out on thermogravimetric analyzer (Netzsch TGA 409) at the temperature from 30 to 800°C with the heating rate of $10^\circ\text{C min}^{-1}$ in air.

Electrochemical measurements

An electrode slurry was prepared by mixing active materials with conductive carbon black and poly(vinylidene fluoride) binder at a weight ratio of 8:1:1 in *N*-methyl-2-pyrrolidone (NMP) to obtain a uniform dispersion, followed by drop-casting onto copper foils and vacuum drying at 80°C overnight to form the anode. CR2016 coin batteries were assembled with lithium foils as the counter electrodes inside an Ar-filled glove box. A Celgard 2400 polypropylene membrane was used as the separator. The electrolyte was 1.0 mol L^{-1} LiPF₆ in a mixed solvent of ethylene carbonate and diethyl carbonate (EC/DEC, 1:1, *v/v*). The mass loading of active materials on each electrode was 0.18–0.19 mg cm^{-2} . Galvanostatic charging-discharging (GCD) tests were performed between 0.5 and 3 V by using a Neware (Shenzhen, China) battery test system. Cyclic voltammetry (CV, 0.1 mV s^{-1}) and electrochemical impedance spectroscopy (EIS, 0.01 Hz–100 kHz, 10 mV) measurements were conducted by using an electrochemical workstation (CHI 660E and Versa STAT4). The cells were charged-discharged at different current densities within 0.1–1.5 C. The specific capacities were calculated based on the mass of active materials.

RESULTS AND DISCUSSION

Fabrication mechanism

The schematic synthesis of fabrication process is shown in Scheme 1. The controlled synthesis of rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures was initiated by a heteroepitaxial growth of Sn₂Fe NRs arrays. Sn₂Fe NPs first

Scheme 1 The fabrication schematic of rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures.

nucleated on the surface of GO. With the reaction proceeding, Sn_2Fe NPs grew into the well-aligned NRs arrays as GO was reduced to rGO. Subsequently, another rGO layer was anchored on the other side of the Sn_2Fe -NRs array. At the first stage, driven by electrostatic attractions between metal ion precursors and deprotonated $-\text{OH}$, $-\text{COOH}$ and other oxygen-containing functional groups of GO, Sn^{2+} and Fe^{2+} ions were adsorbed and embedded on the surface of GO nanosheets. The *in-situ* reduction of GO and metal precursors were simultaneously triggered by heating at 180°C in triethylene glycol, resulting in the formation of the Sn_2Fe NPs dispersing on rGO sheets. These NPs acted as nucleation sites for further hierarchical assembly process into NRs, and were planted on the planar rGO substrates. In the Sn_2Fe NRs array growth process, the homogeneous nucleation of Sn_2Fe seeds requires higher activation energy than hetero-nucleation, because of lower interfacial energy and saturation ratio between Sn_2Fe crystals and solutions. Thus epitaxial crystal tends to grow from substrate-generated nuclei along the direction of crystallization with low activation energy. Finally, the newly added rGO layers were wrapped around Sn_2Fe -NRs array/rGO and arranged by the affinity between positive charged ions on Sn_2Fe NRs and deprotonated oxygen-containing groups ($-\text{OH}$, $-\text{COOH}$, etc.) of GO. The *in-situ* reduction triggered by heating, gave rise to the resultant interlayer nanostructures of rGO/ Sn_2Fe -NRs array/rGO. The reaction conditions including metal precursor concentrations, precursor/GO mass ratios, heating temperatures and heating time were investigated. The nanostructures with best morphology and electrochemical properties were synthesized at metal precursor concentration of 2 mmol L^{-1} , precursor/GO mass ratio of 20:1, heated at 180°C for 5 h (Supplementary information (SI), Figs S1–S4).

Morphology and structure

The fabrication of rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures was achieved through integrating the Sn_2Fe NRs array on rGO nanosheets before the coverage of rGO layer on the other side, as shown in Scheme. 1. Based on the morphology study of rGO/ Sn_2Fe -NRs array/rGO construction by SEM images taken stepwise (Figs 1a–f), it can be observed that the array-arranged Sn_2Fe NRs (each NR has a diameter of ca. 10 nm) grew uniformly on rGO substrates (Figs 1a–c).

Subsequently, NRs arrays were covered by another rGO layer on the top intimately (Figs 1d and e). In addition, Figs S3A demonstrates that the Sn_2Fe -NRs arrays indeed grew on the rGO substrate. Compared with the pure rGO (Fig.

1f), the morphology of rGO almost maintained during the incorporation of Sn_2Fe -NRs array. A distinct morphology of NRs arrays can also be observed in TEM image in Fig. 1g. In Fig. 1h, HRTEM image of the Sn_2Fe NRs presents the crystalline structure with lattice spacing of 0.206 and 0.256 nm corresponding to (202) and (211) facet, respectively. The selected area electron diffraction (SAED) pattern in Fig. 1i recorded from the Sn_2Fe NRs indicates (202) and (211) plane diffraction, which means that the Sn_2Fe NRs exhibit tetragonal polycrystalline structure.

Furthermore, the morphology optimization of Sn_2Fe nanoalloys was discussed in detail by varying Fe/Sn molar ratios. The SEM images, together with the corresponding EDS and XRD analysis, are exhibited in Fig. S5. The optimal rod-like SnFe nanostructures were formed at Fe/Sn molar ratio of 1:2. As an important parameter of electrodes performance, the Brunauer-Emmett-Teller (BET) surface area of rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures was measured by N_2 adsorption/desorption isotherms (Fig. S6), and summarized in Table S1. It shows that the as-synthesized interlayer nanostructures have a BET surface area of $116.30\text{ m}^2\text{ g}^{-1}$. The high BET surface area indicates that the nanostructures are capable to offer a large quantity of Li^+ binding sites, leading to a high charging/discharging cycle efficiency. From the adsorption and desorption curves, when the relative pressure (P/P_0) reaches the maximum, c.a. 92 mL, the total pore volume of the materials can be calculated with Equation of $92 \times 0.001547 = 0.14232\text{ mL}$ (0.001547 equals to the volume after 1 mL nitrogen gas cohesion). The measured total pore volume is 0.15 cm^3 , which is almost consistent with the calculated value. It can be clearly observed that the curve is classified as H3 hysteresis loop class, which was defined by International Union of Pure and Applied Chemistry (IUPAC). The classification indicates the materials show tablet slit structure space.

The EDS spectra of Sn_2Fe NRs, graphene and rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures together with their corresponding XRD patterns, Raman spectra and XPS analysis are presented in Fig. 2. In Fig. 2a, the EDS analysis of Sn_2Fe NRs (trace (1)) shows that the Fe/Sn atomic ratio is $\sim 1:2$, which is consistent with the composition of Sn_2Fe nanoalloy. The predominant carbon peak in EDS spectrum of graphene (Fig. 2a, trace (2)) reveals that GO was entirely reduced to rGO. The EDS spectrum of rGO/ Sn_2Fe -NRs array/rGO nanocomposites (trace (3)) shows the dominant elements C, Fe, and Sn are at an atomic ratio of 6:1:2. It conforms to the original inventory ratio. In Fig. 2b, the XRD pattern of Sn_2Fe NRs

Figure 1 SEM images of the Sn_2Fe -NRs array/rGO in different magnifications (a–c), interlayer nanostructures of rGO/ Sn_2Fe -NRs array/rGO (d, e) and graphene (f); TEM image of the Sn_2Fe -NRs array/rGO (g) for NRs array viewed in perpendicular (1) and inclination (2); HRTEM image of the Sn_2Fe -NRs array/rGO (h), and SAED pattern of Sn_2Fe -NRs array/rGO (i).

(trace (1)) shows three peaks of (211), (202) and (213), which can be indexed to tetragonal Sn_2Fe (JCPDS#65-0374). Trace (3) shows the obvious difference of peak positions from those in trace (2). Also intensities of peaks corresponding to (002), (211), (202) and (213) vary from those of Sn_2Fe NRs. Thus, the resultant rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures are composites of its counterparts (graphene, Sn_2Fe NRs). It should be noted that both the XRD patterns of Sn_2Fe NRs and rGO/ Sn_2Fe -NRs array/rGO show the evidence of peaks of tetragonal SnO_2 (Fig. S12), which potentially emerges from oxidation of trace amounts of Sn in Sn_2Fe by atmospheric oxygen. As the Raman spectra shown in Fig. 2c, the distinct changes among those of graphene, Sn_2Fe -NRs array/rGO and rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures exist obviously. The peak at 1345 cm^{-1} (D band) corresponds to the defects and disorders in the graphene atomic lattice, while the peak at 1589 cm^{-1} (G

band) corresponds to the vibration of sp^2 -bonded carbon atoms in 2D hexagonal lattice. The intensity ratios of D band to G band (I_D/I_G) are 0.87, 0.95 and 1.09, respectively, for graphene, Sn_2Fe -NRs array/rGO and rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures. An increasing ratio of I_D/I_G from bare graphene to rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures demonstrates more disordered carbon structure in the composite. That is caused by the insertion of Sn_2Fe NRs into rGO layers. Furthermore, it is assumed that a large number of defects or cavities may be generated on the surface of rGO, which serves as storage sites for lithium ions. Additionally, the compositions of Sn_2Fe and graphene in rGO/ Sn_2Fe -NRs array/rGO interlayer nanostructures were determined by TG analysis (Fig. S7). The composition of Sn_2Fe NPs in the composite can be calculated based on the Equation below: Sn_2Fe NPs (wt.%) = $100\% \times (\text{wt.}\% \text{ of composite at } 800^\circ\text{C}) / (\text{wt.}\% \text{ of } \text{Sn}_2\text{Fe} \text{ NPs at } 800^\circ\text{C})$. It is determined that the composite consists of

Figure 2 EDS (a) and XRD (b) for Sn_2Fe NRs (1), graphene (2), and $\text{rGO}/\text{Sn}_2\text{Fe}$ -NRs array/ rGO (3), respectively; Raman spectra (c) for graphene (1), Sn_2Fe -NRs array/ rGO (2) and $\text{rGO}/\text{Sn}_2\text{Fe}$ -NRs array/ rGO (3), respectively; XPS analysis of detail spectra of Sn 3d (d), separated analysis of Fe 2p (e) and C 1s (f).

about 22.8 wt.% graphene and 77.2 wt.% Sn_2Fe NPs.

In order to further identify and compare the chemical states of elements, XPS was applied to the architecture of $\text{rGO}/\text{Sn}_2\text{Fe}$ -NRs array/ rGO interlayer nanostructures (Figs 2d–f). Compared with the full spectrum of Sn_2Fe NRs, C 1s clearly appears in final nanostructures (Fig. S8). As shown in Fig. 2d, both Sn 3d_{5/2} and Sn 3d_{3/2} magnified spectra were split into three peaks at valence states of Sn^0 , Sn^{2+} and Sn^{4+} , respectively, due to the existence of Sn_2Fe , SnO and SnO_2 in

the structures, which were impossible to be ruled out from the samples, also partly testified by the XPS patterns. From magnified Fe 2p peaks shown in Fig. 2e, two peaks resulting from the 2p electrons multiple-splitting are 2p_{3/2} and 2p_{1/2} with binding energy (BE) values of 709.7 and 723.0 eV, implying for Fe^0 . In addition, the C 1s spectrum of Fig. 2f mainly indicates graphite carbon (282.2 eV), and C–OR (282.6 eV) and C=O (284.5 eV) remained after the functionalization. The signals of carbon in final nanostructures

are slightly shifted, however, with the same binding energy differences between peaks in references. The reason is suggested to be that the atomic environment of C is different from that in the pristine carbon materials, and the synergistic effect results in the signals shift of metallic bonding energy. All the above illustrate the formation process of rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures.

Electrochemical measurement for lithium ion batteries

Electrochemical performances were characterized for the interlayer nanostructures of rGO/Sn₂Fe-NRs array/rGO. CV was tested for the first three cycles with a sweep rate of 0.1 mV s⁻¹, a potential range from 3.00 to 0.01 V, *versus* Li/Li⁺ at room temperature. As depicted in Fig. 3a, three peaks center at 0.18, 0.86, and 1.30 V, respectively, in the first cathodic polarization process. The peak located at 0.86 V corresponds to the decomposition of electrolyte and the formation of solid electrolyte interphase (SEI) layer on the surface of electrodes. The peaks of 0.18 V and 1.30 V are caused by the intercalation of Li⁺ into the Sn₂Fe NRs array or graphene (alloying to Li_{4.4}Sn) and the formation of Li₂O and Li_xSnFe. As for the first anodic sweep, the peaks center at 2.03, 1.06, and 0.68 V, respectively, which indicate the de-alloying process of Li_{4.4}Sn as well as the oxidation from Li⁰ to Li⁺. In addition, as shown in the voltage range from at 0.24 V, the small peak at 0.24 V is associated to the decomposition of a small amount of SnO₂ and the formation of β phase Sn in Sn₂Fe. This peak was slightly shifted in subsequent scans and then stabilized at ~0.37 V because of several redox stages with various ions in the system [35]. It is noted that except for the first cycle, the CV curves of all the cycles overlap with each others well, indicating that the final composite exhibits a good reversibility of the discharge-charge cycle. As observed, the profiles of these curves are in accordance with those of Li-storage behavior of Sn₂Fe anodes calculated by the following Equations:

The GCD profiles of cycles for the as-synthesized anode materials at a current density of 0.5 C are shown in Fig. 3a. The plateaus in the range of 0.3–0.8 V correspond to the lithiation process while those of 0.5–2.1 V correspond to the delithiation process, which are consistent with the standard CV curves. In the 1st, 50th, 100th and 200th cycles, the discharge capacities reach 1467, 812, 764 and 742 mA h g⁻¹, respectively. Obviously, all of them are higher than those of bare Sn₂Fe NRs and Sn₂Fe-NRs array/rGO (Fig. S9). Furthermore, according to the molar ratio of

active materials (C:Sn=3:1, measured by EDS), it can be calculated that the theoretical capacity of the as-prepared nanocomposites is 1003 mA h g⁻¹. As observed in the GCD profiles of rGO/Sn₂Fe-NRs array/rGO at a current density of 0.1 C (Fig. S13), the discharge and charge capacities of rGO/Sn₂Fe-NRs array/rGO in the first cycle are 1519.2 and 917.6 mA h g⁻¹, respectively, corresponding to a Coulombic efficiency of 60.4%. The initial capacity loss (39.6%) could be mainly ascribed to the irreversible formation of SEI layer and inactive Li₂O component from surface-oxidized layer, which are also reflected in its CV curves. In addition, the rGO/Sn₂Fe-NRs array/rGO nanostructured electrode is tested at different charge and discharge rates both ranging from 0.1 C to 2 C, then back to 0.2 C in the rate capability tests (Fig. 3C). It exhibits the capacities of 1251.1, 899.8, 853.3, 796.6, 755.6, 726.0 and 682.5 mA h g⁻¹, respectively, which are much higher than those of Sn₂Fe-NRs array/rGO. Remarkably, the capacity of interlayer nanostructures remains at 890.7 mA h g⁻¹ when the current density returns to 0.2 C, showing outstanding rate capability compared to with that of Sn₂Fe-NRs array/rGO.

The improved electrochemical properties of rGO/Sn₂Fe-NRs array/rGO composites compared with those of bare Sn₂Fe NRs and Sn₂Fe-NRs array/rGO can also be verified by EIS in Fig. 3d. Each curve exhibits a semicircle in the high frequency region followed by a straight line in the low frequency region. From the bare Sn₂Fe NRs to rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures, the initial resistances exhibit a reducing trend (shrinking semicircles) in the high frequency region, which means that the as-synthesized interlayer nanostructures have much smaller interface impedance. As for the straight line in the low frequency region, the slope of the curve of rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures is the largest among the three systems, indicating the highest Li⁺ transfer rate of diffusion. In addition, the interface impedance and Li⁺ transfer rate of diffusion of interlayer nanostructures change little after 200 cycles, which further reveals a good charging/discharging stability of rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures. Thus, high capacity and long cycle life are realized in the rGO/Sn₂Fe-NRs array/rGO composites anodes.

Fig. 3e shows the cycling performance of the rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures, Sn₂Fe-NRs array/rGO, graphene and Sn₂Fe NRs at a current density of 0.5 C. It can be observed that the rGO/Sn₂Fe-NRs array/rGO composite anode delivers a capacity of 1467 mA h g⁻¹ from the very beginning of charging/discharging process. The capacity retains at 743 mA h g⁻¹ after 200

Figure 3 (a) CV curves of the rGO/Sn₂Fe-NRs array/rGO for the first three cycles at a scan rate of 0.1 mV s⁻¹. (b) GCD profiles in the potential range of 0.01–3.0 V (vs. Li/Li⁺) at a current density of 0.5 C; (c) rate performance of the rGO/Sn₂Fe-NRs array/rGO and Sn₂Fe-NRs array/rGO; (d) EIS of the rGO/Sn₂Fe-NRs array/rGO before and after cycling, Sn₂Fe-NRs array/rGO and Sn₂Fe NRs. (e) Cycling performance of the rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures, Sn₂Fe-NRs array/rGO, graphene and Sn₂Fe NRs at 0.5 C. (f) Cycling performance of the rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures at 0.5 C and 1 C.

cycles at a retention rate of 51%. They are obviously higher than those of the other three anode materials (607, 363 and 172 mA h g⁻¹). Interlayer nanostructured anode displays a slow decline of capacity, representing for a stable charging-discharging performance. The Coulombic efficiency of the four anodes maintains around 98% over cycles, which reveals that the as-synthesized anodes have a good charging-discharging stability. The cycling performance of interlayer nanostructures anodes at a current density of 0.5 C and 1 C are compared in Fig. 3f to further study its charging/discharging properties. Under a current density of 1 C,

the anode materials show a desirable stability, at a capacity of 582 mA h g⁻¹ over 600 cycles. Even under a high current density of 1.5 C, the rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures exhibit a better reversibility compared with Sn₂Fe-NRs array/rGO nanocomposite (Fig. S10). The capacity of rGO/Sn₂Fe-NRs array/rGO anode reaches 1037 mA h g⁻¹ while that of Sn₂Fe-NRs array/rGO is 824 mA h g⁻¹. Furthermore, the capacity of interlayer nanostructured anode still remains 333 mA h g⁻¹ with the measured Coulombic efficiency of nearly 99% after 200 cycles. Compared with previously reported graphene composite mate-

Table 1 Comparison of the long-life electrochemical performances of rGO/Sn₂Fe-NRs array/rGO as anode materials for LIB with previous works

Morphology	Parameters	Initial capacity (mA h g ⁻¹)	Cycled capacity (mA h g ⁻¹)
FeSn ₂ /graphene nanocrystals [36]	100 mA g ⁻¹ , 40 cycles	1418.0	401
SnCo/graphene nanoparticles [32]	1000 mA g ⁻¹ , 60 cycles	1117	571
Fe ₂ O ₃ /graphene nanorods [33]	100 mA g ⁻¹ , 30 cycles	1735	602
SnO ₂ /graphene nanorods [37]	100 mA g ⁻¹ , 25 cycles	1010	470
Carbon coated nanorods [34]	40 mA g ⁻¹ , 50 cycles	1246	473
rGO/Sn ₂ Fe-NRs array/rGO	500 mA g ⁻¹ , 600 cycles	1467	690

Scheme 2 Schematic of the rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures before (a) and after (b) electrochemical cycling for 200 cycles and (c) loss of activity for 600 cycles.

rials in Table 1, the constructed rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures exhibit enhanced capacity after long cycles under high current densities.

Scheme 2 elaborates the reversible lithiation/delithiation process over charging/discharging cycles. The corresponding morphology changes were observed after 200 and 600 cycles (Fig. S11). In the as-synthesized interlayer nanostructures, the significantly improved performance was attributed to the stable structural integrity and high electrical conductivity of rGO/Sn₂Fe-NRs array/rGO interlayer nanostructures. The results demonstrate that the resultant interlayer nanostructured electrodes exhibit excellent electrochemical properties with the outstanding cycling stability. In the as-synthesized structure, top/bottom graphene layers play a crucial role in electrons transport. The void space covers around the Sn₂Fe NRs and the interspace between NRs allows for expansion without deforming the overall morphology in lithiation/delithiation process, so that the SEI layers formed outside the NRs are not ruptured over cycles. Even after 200 cycles, the interlayer nanostructures still remain nearly the same morphology as before (Fig. S11B). It is observed that there is little agglomeration of morphology, thereby only little collapse of structure after 600 cycles (Fig. S11C).

CONCLUSIONS

In conclusion, the first reported interlayer nanostructures of rGO/Sn₂Fe-NRs array/rGO were constructed through a heteroepitaxial growth of Sn₂Fe NRs array on the substrate of rGO followed by the coverage of another rGO layer

on the top. Owing to the inhibition of side reactions by the compact structure, high electrical conductivity of bottom/top rGO and Sn₂Fe NRs arrays, the as-synthesized interlayer nanostructures of rGO/Sn₂Fe-NRs array/rGO deliver outstanding specific capacity of 690 mA h g⁻¹ over 600 cycles at a current density of 0.5 C. Furthermore, the nanostructure working as an LIBs electrode exhibit an exceptional stability under 1 C and 1.5 C. This unique structure can be further studied with other transition metal or alloy materials. It is believed that the interlayer nanostructures of rGO/Sn₂Fe-NRs array/rGO are of great potential to be incorporated into next-generation energy storage devices.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details are available in the online version of the paper.

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高容量rGO/Sn₂Fe-NRs阵列/rGO层间纳米结构锂离子负极材料研究

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摘要 基于阵列夹层纳米结构的稳定性和石墨烯的电子传递特性, 本文通过原位生长的层间组装过程, 获得了一类新型的rGO/Sn₂Fe-NRs阵列/rGO层间纳米结构复合材料. 该结构中, Sn₂Fe纳米合金棒阵列排布于rGO纳米层之间. 将此材料应用于锂离子电池负极, 可以促进电极反应中的物质传输, 并能有效避免副反应产生, 从而表现出优异的倍率性和循环稳定性, 并在高电流密度下保持高比容量. 在电流密度分别为0.5 C (500 mA g⁻¹)和1 C (1000 mA g⁻¹)时, 比容量分别达到690 mA h g⁻¹和582 mA h g⁻¹. 本工作对促进电化学性能优异的锂离子电池负极材料发展具有重要的意义.