



Sn accommodation in tunable-void and porous graphene bumper for high-performance Li- and Na-ion storage



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ABSTRACT

Nanoscale microstructure designing is playing an important role in improving the performance of electrode materials of an electrochemical battery. The Sn based anode is among the very high-capacity but less-stable materials, and has been used mostly for anode of the Li-ion battery with unsatisfactory performance. In this work, we design a new type of 3D porous graphene and nano-Sn composite (Sn/Void@G) by simple one-step annealing of graphene oxide, polystyrene spheres and stannic chloride for both high performance Li- and Na-ion battery anodes. More importantly, the 3D porous graphene formed tunable micro-nano void as a highly efficient “bumper” to accommodate the large volume expansion of nano-Sn particles. As results, the discharge specific capacity of the Sn/Void@G, anode still remains 45.3% while the charge-discharge current is increased 50 times, and the capacity is more than 400 mAh g⁻¹ after 500 cycles at 5C rate. For Na storage, the integrated anodes deliver the Na storage capacity of 786.1 mAh/g at 0.1C rate and the capacity of more than 340 mAh/g after 800 cycles at 2C rate. The present result on Li and Na ion battery may pave the way to next generation high power and energy density batteries.

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1. Introduction

In the past decades, Lithium-ion batteries (LIBs) and Sodium-ion batteries (SIBs) [1–4], as electrical energy storages, have been widely used in portable electronic devices [5–8]. However, the increasing demand for their emerging applications in electric vehicles and large-scale energy storage requires us to enhance its energy and power density. As we know, electrode materials play a crucial role in the battery performance. Thus, higher specific

capacity and longer cycling life anodes, which are important factors for the battery performance, need to be developed while commercial graphite anode (theoretical capacity for LIBs: 372 mAh g⁻¹) is reaching the energy and power limitation. Because of their higher theoretical capacity, many metals have been intensively studied as anodic electrodes for the next-generation LIBs, such as Ge [9], Si [10], Sn [11]. Thanks to the advantages of a high theoretical specific capacity (993 mAh g⁻¹), low cost, abundance in nature, and environmental friendliness, Sn has been considered as one of the promising anode candidates [12,13]. However, the large volume change results in severe mechanical damage of Sn-based electrodes and subsequently leads to rapid capacity fading during the repetitive discharge/charge process [14,15].

In order to overcome the challenges thereof, two main effective methods have been reported in research. One approach is to reduce the particle size of Sn to the nanoscale to alleviate the large volume

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change [16–19]. However, nanosized Sn particles prefer aggregating during the cycling, resulting in rapid capacity fading [20]. Another way is to integrate Sn nanoparticles with a conductive carbon matrix [21], which can mitigate the mechanical stress and accommodate the volume variation. So far, various carbon matrices have been applied [22–33], such as mesoporous carbon [20], amorphous carbon [34], graphite [35], carbon nanotubes [36], and carbon nanofibers [37].

In this study, we reported a novel 3D porous reduced graphene and nano-Sn composite (Sn/Void@G) electrode through a facile template strategy involving a self-assembly process of graphene sheets (in nickel foam using stannic chloride, graphene oxide, polystyrene spheres as precursors), removal of polystyrene spheres (PS) template, thermal activation, and carbothermal reduced Sn⁴⁺ into Sn nanoparticles. The Sn/Void@G electrodes possess a hierarchically porous structure for being of the macro-porous architecture of Ni foam, and porous reduced graphene, which could effectively improve the mechanical strength and provide sufficient contact areas between the Sn/Void@G electrode and electrolyte. The prepared Sn/Void@G electrode exhibits a relatively good reversible specific capacity, an excellent rate capability, and durable cycling stability for both Li and Na ion batteries, because of their hierarchical three-dimensional architecture and expandable graphene interlayer distance. This unique micro-/nanostructures are beneficial to achieve high energy and power densities. For example, the Sn/Void@G as LIB anode exhibited the reversible specific capacity of 868.9 mA h g⁻¹ at 0.1C rate. Its discharge specific capacity still remained 45.3% when the charge-discharge current increased to 50 times higher and the first coulomb efficiency was 62.5% and then ~99.6% in the following cycles. Moreover, a sodium storage capacity of 786.1 mAh g⁻¹ was obtained when it was used as electrode for SIB at 0.1C rate. A specific capacity as high as 166 mAh g⁻¹ can be achieved at 20C, and no obvious capacity fading was observed after more than 800 cycles of continuous charge/discharge at 2C rate. Furthermore, the synthesized Sn/Void@G electrode avoids the addition of binder and conductive additives and thus could be more beneficial to a large-scale application.

2. Experimental details

2.1. Preparation of composite electrodes

Nickel foam (110PPI, 420 g/cm², thickness 1.4 mm) was first cut into electrode wafers with a diameter of 1.5 cm and then washed with ethanol several times. The pre-treated Ni foam wafers were immersed into *n*-methyl-2-pyrrolidone containing polyaniline (0.025 wt %) several hours. In a representative preparation process, 27.4 mg SnCl₄·2H₂O (Sinopharm Chemical Reagent Co., Ltd.) was first dissolved in 4 mL deionized (DI) water and then graphene oxide (1 mL, 9.3 g/mL) and polystyrene spheres (3 mL, 380 nm, 10.97 wt%) were added into the solution under magnetic stirring. The preparation of graphene oxide can be found in the Supporting information. The gray mixture was continuously sonicated and magnetically stirred to form a homogeneous suspension. The pre-treated Ni foam wafers were immersed in the precursor solution, and then dried in a dry oven at 60 °C. The dry samples embedded in the nickel foam wafers were calcinated in Ar at 200 °C for 1 h and then at 800 °C for 2 h, while the Sn⁴⁺ was converted to metallic Sn via a carbothermal reduction step [38]. Eventually, the final products, the Sn/Void@G electrode, were ready to directly serve as the anode of LIBs and SIBs.

2.2. Characterization

X-ray diffraction (XRD) analysis was performed with a Rigaku

RU-200BVH diffractometer employing a Cu-K α source. The diffraction patterns were collected at room temperature in the 2 θ ranges of 10–90°. Scanning electron microscopy (SEM) was conducted using a Hitachi S-4800 scanning electron microscope operating at 15 kV. Transmission electron microscopy (TEM) images were taken with a JEOL2010F at an acceleration voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5400 ESCA System Al at 1486.6 eV. Raman spectra were collected using a 532 nm laser in a WITec CRM 200 confocal.

2.3. Electrochemical measurements

The electrochemical properties of the Sn/Void@G electrodes were measured using two-electrode CR2032 (3 V) coin-type cells. The half cell assembled in an argon-filled glovebox (Vigor Glove Box from Suzhou, China) with water and oxygen contents of below 1.0 ppm. Lithium sheets were used as the counter electrode and reference electrode with a polypropylene (PP) film (Cellgard 2400) as the separator. The electrolyte was 1 M LiPF₆ in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 in volume), without any additives. The Sn/Void@G electrodes were directly used as the anode. The galvanostatic charge-discharge property of the batteries was examined using a channels battery analyzer (NEWARE CT3008, China) at a voltage window between 0.01 and 3.0 V (vs. Li⁺/Li). For sodium ion battery fabrication, metallic Na foil was used as the counter/reference electrode, glass fiber (Whatman) was used as the separator, and 1 M NaClO₄ in ethylene carbonate (EC)-diethyl carbonate (DEC) (1:1 in volume) was used as the electrolyte. The discharge-charge performance of the batteries was tested using a battery analyzer (Neware CT-3008) with the voltage cut-off between 0 and 3.0 V vs. Na/Na⁺. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were performed using a CHI660E electrochemical workstation. EIS was recorded with a frequency ranging from 100 kHz to 10 mHz and an AC signal of 5 mV in amplitude as the perturbation. The voltage range of the CV measurements was 0–3.0 V and the scanning rate was 0.5 mV s⁻¹. All the tests were performed and measured at room temperature.

3. Results and discussions

A schematic illustration of the general preparation process for the Sn/Void@G electrode is depicted in Fig. 1. The first step of the fabrication process is pre-treating nickel foam. Nickel foam is cut into electrode wafers and washed with ethanol several times, then immersed in *n*-methyl-2-pyrrolidone containing polyaniline several hours. The second step is to impregnate the pre-treated nickel foam wafers with the precursor solution containing GO, PS, and SnCl₄·2H₂O. The water in the precursor composite is removed from the surface of Ni foam with a dry oven. Finally, the Sn/Void@G electrodes are obtained by claiming the dried nickel foam wafers coating precursor composite in Ar atmosphere, where PS spheres are decomposed and leaving lots of sphere-like voids (Fig. 1). Furthermore, a precursor composite of dried GO was in situ reduced, and the tin ion is oxidized without any auxiliary reagents. As a result, Sn particles are embedded between graphene sheets on pore wall of 3D porous structure at the same time.

The morphology of Sn/Void@G-800 electrode (After impregnating with the precursor solution and annealing at 800 °C) is shown in Fig. 2a and Figs. S1a and a visible black carbon coating layer can be found on the whole nickel foam skeletons uniformly. The macroporous structure form can be obviously observed from high-magnification SEM images (Fig. 2b and Fig. S2b). The inner surface of macropores is rough and the pore walls are composed of graphene sheets with embedded Sn nanoparticles. Due to the

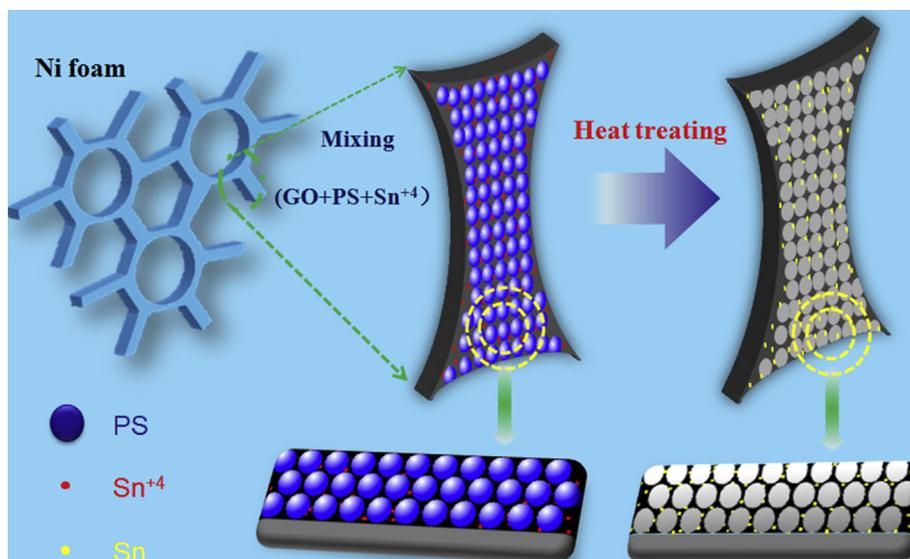


Fig. 1. Schematics illustration for the fabrication of the Sn/VOID@G electrodes.

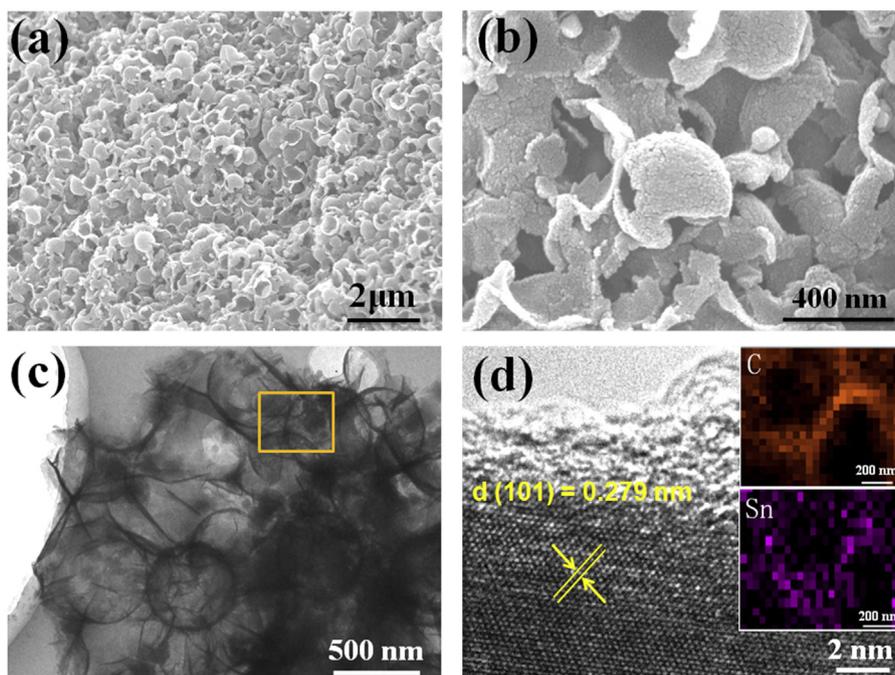


Fig. 2. (a–b) SEM images of the Sn/Void@G-800 sample; (c) TEM image of the Sn/Void @G-800 samples; (d) HRTEM images of the Sn/Void @G-800 sample; inset images for the elemental mapping images of C and Sn elements in the Sn/Void @G-800 sample.

existence of the graphene porous microstructure of on the Sn/Void@G-800 electrode, the hydrophobic performance of the Sn/Void@G-800 electrode is observably improved compared with the original nickel foam in Figs. S1b and c (the morphology of original nickel foam is shown in the low-magnification SEM image of Fig. S2a). Besides, Fig. 2c reveals that the average diameter of individual macropores is approximate 400 nm, which is in agreement with the size of PS precursor template. Obviously, the nano architecture enables the Sn/Void@G-800 electrode to possess high surface electrochemical reactivity, and the high hydrophobic macroporous structure is effective for the infiltration of the organic electrolyte [39]. In order to further proving the formation mechanism of the porous structure, the different annealing temperature

has been controlled. At 600 °C annealing, the 3D interconnected porous graphene frameworks with Sn particle (named Sn/Void@G-600) were also formed. This means that the formation of 3D interconnected porous structure is due to the pyrolysis of PS templates, so the size of nanospheres making up a 3D porous microsphere could be easily manipulated by controlling the PS sphere size. When the size of PS template is larger than 500 nm, obtained 3D porous structure of Sn/Void@G is more easily broken. However, when the size of PS template is less than 300 nm, the 3D structure gets more irregular (see Figs. S3 and S4). Some typical TEM and HRTEM images of the Sn/Void@G-800 sample further exhibited in Fig. 2c–d. It was further proved that the wrinkled graphene sheets form the 3D interconnected porous structures, and the Sn particles

with the average particle size less than 100 nm are homogeneously dispersed on surface of the graphene matrix (in Fig. 2c). Meanwhile, the HRTEM images reveal that the interplanar distances of 0.279 nm can be viewed as $d(101)$ of crystal Sn (see Fig. 2d). An elemental mapping of Sn/Void@G-800 sample by energy-dispersive X-ray spectroscopy (EDS) analysis is shown in inset images of Fig. 2d. It verifies that the Sn nanoparticles are embedded in the filmy graphene sheets.

The crystal structures and phases of various samples can be further investigated by XRD [40], Raman and XPS spectroscopy. The XRD patterns of Sn/Void@G-800, in good agreement with reported data (JCPDS no. 04-0673), shows three strong diffraction peaks at 30.6° , 32.0° and 44.9° , which are corresponding to (200), (101) and (211) crystal planes of Sn respectively (see Fig. 3a). For the Sn/Void@G-800 sample, the diffraction peak at $2\theta = 32.0^\circ$ is attributed to the (101) crystal plane of Sn nanoparticle, which agrees with lattice spacing 0.279 nm in the HRTEM of Fig. 2d, and no peaks of impurities were found, indicating the Sn^{4+} are completely converted to crystalline Sn nanoparticle. The Sn/Void@G-800 samples have been also characterized by Raman spectroscopy in Fig. 3b, and the spectrum exhibit two characteristic peaks of graphene, at 1337 and 1590 cm^{-1} , which are corresponding to the D and G bands. The peak at approximately 1590 cm^{-1} (G-band) is due to the in-plane vibrations of sp^2 -bonded carbon atoms. Moreover, a peak at approximately 1337 cm^{-1} (D-band) is due to the presence of vacancies, grain boundaries and amorphous carbon species [41]. Meanwhile, the Raman peaks at ~ 2700 of sample is second order D band for identifying second order vibrational mode. The intensity ratio (I_D/I_G) associates with the size and disorder degree of sp^2

domains [42]. From the intensity ratio of the data, the I_D is lower than I_G , revealing that higher temperature can decrease the disorder degree. The wide angle XPS of Sn/Void@G-800 shows that the peaks of C, Sn, Ni and O are predominant signals in the general survey spectrum (see Fig. S5). The peak of Ni is due to the presence of nickel foams. In the C 1s spectra of Sn/Void@G-800, four peaks centered at 284.6, 285.5, 287.6 and 289.0 eV appear, generally assigned to C-C, C-OH, C-O and C=O, respectively (see Fig. 3c) [43]. Additionally, the spin energy separation of Sn $3d_{5/2}$ and Sn $3d_{3/2}$ centered at the binding energies of 485.1 and 493.5 eV, respectively, which is in well agreement with reported data for Sn element (see Fig. 3d), indicating the Sn in the Sn/Void@G-800 composite [44–48].

The electrochemical storage Li performance of the Sn/Void@G as the anode of lithium ion battery (LIBs) was investigated. Fig. 4a shows the first five galvanostatic charge-discharge profiles of Sn/Void@G. The initial discharge/charge capacities of Sn/Void@G-800 are $1390.8\text{ mA h g}^{-1}$ and 868.9 mA h g^{-1} with initial coulombic efficiency of 62.5%. The Sn/Void@G-800 anode has a higher reversible capacities and initial coulombic efficiency than Sn/Void@G-600 anode (see Fig. S6). The cyclic voltammograms (CVs) of the Sn/Void@G-800 and Sn/Void@G-600 electrodes shown in Fig. 4b and Fig. S7 are in agreement with the voltage plateaus for charge/discharge curves. There is a broad anodic peak at about 1.2 V, which is related to the reversible lithium reaction with Sn nanoparticles [49]. Meanwhile, a broad anodic peak at about 1.15 V might be attributed to the irreversible reaction of the electrode to form the solid electrolyte interface (SEI) layer on the surface of the electrode. Besides, obvious oxidation and reduction peaks at 0.1–0.2 V were

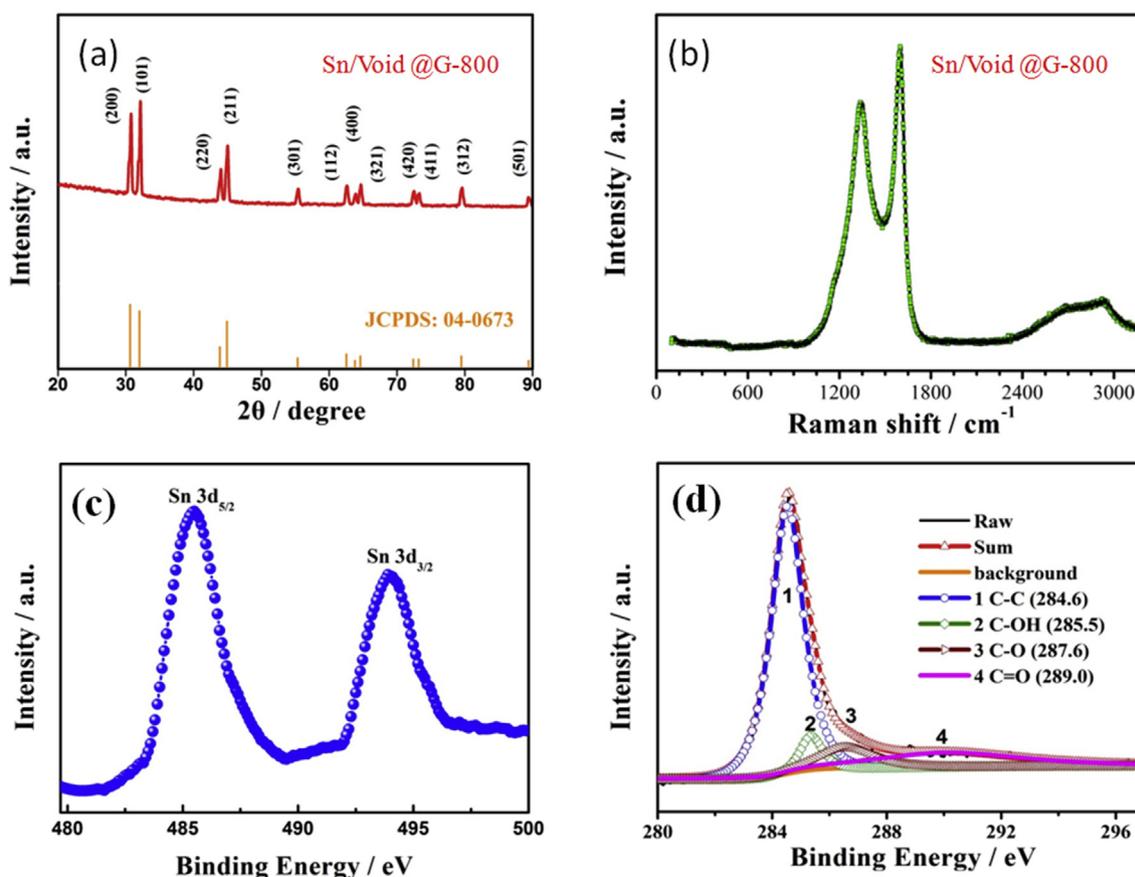


Fig. 3. (a) XRD pattern of Sn/Void@G-800 electrode materials; (b) Raman spectra of the Sn/Void@G-800 electrode materials; XPS spectrum of Sn/Void@G-800: (c, d) narrows scans of C1s and Sn3d, respectively.

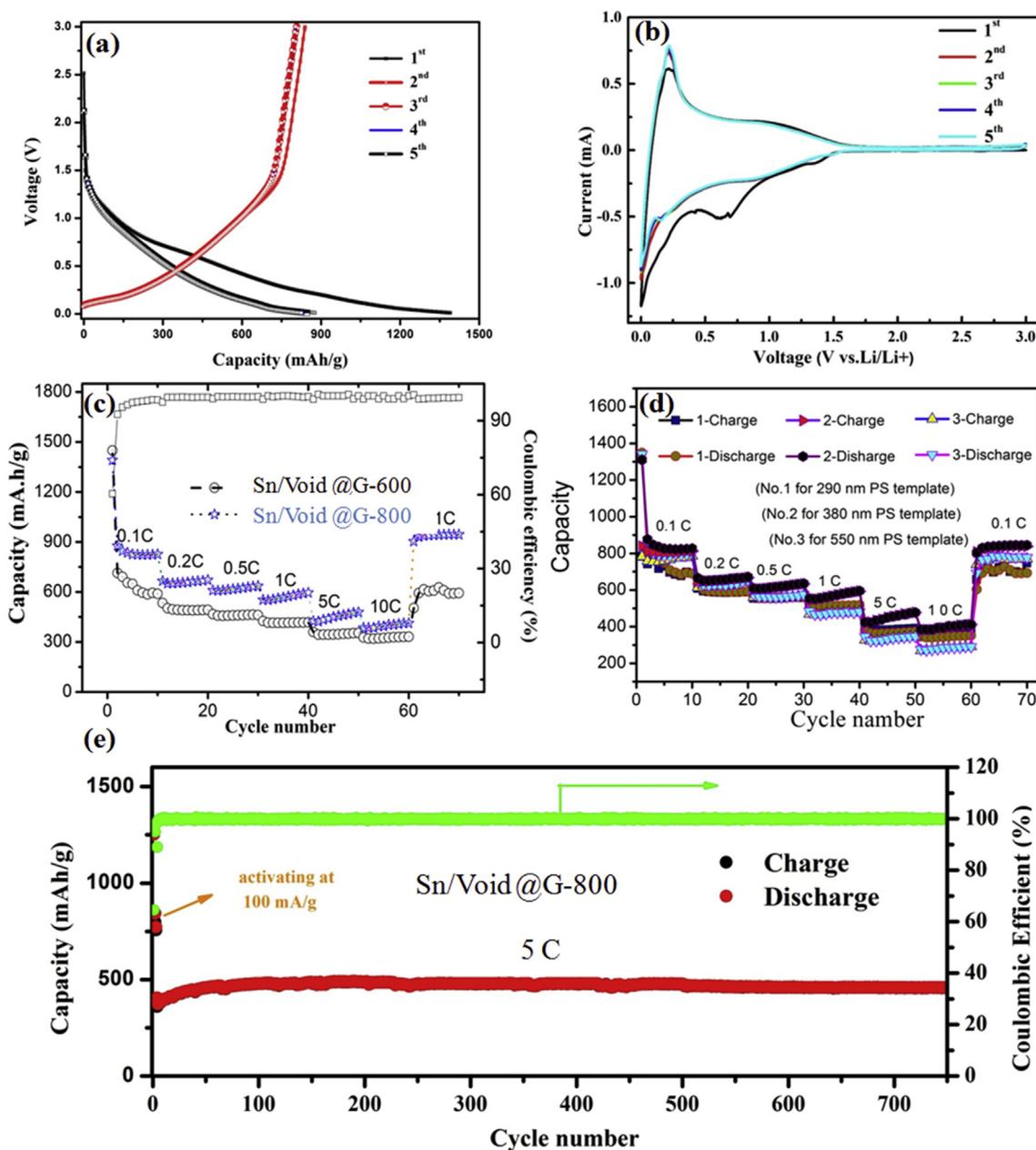


Fig. 4. (a) The first five cycle charge-discharge curves of the Sn/Void@G-800 an electrodes at 0.1C for LIBs; (b) CV curves of the Sn/Void@G-800 anode between 0.01 and 3.00 V (vs Li/Li⁺) at a scan rate of 0.1 mV s⁻¹; (c) The multi-rate testing of the Sn/Void@G-800 and Sn/Void@G-600 electrodes at the charge-discharge current of various C rate, respectively; (d) The rate performance of the Sn/Void@G-800 with different size void; (e) Cycling performance of the Sn/Void@G-800 and Sn/Void@G-800 anode of LIBs, at a current of 0.5C rate.

also observed, which are attributed to the insertion/extraction of Li into/from graphene [50]. In addition, the cathodic peaks at 0.3–0.7 V can be associated with multistep electrochemical reduction reactions of the Li_xSn alloy. Fig. 4c shows the multi-rate performance of Sn/Void@G-800 electrode at various current densities. The Sn/Void@G-800 electrode shows a reversible specific capacity of 868.9, 654.9, 616.3, 566.4, 450.1, 393.5 mA h g⁻¹ at 0.1, 0.2, 0.5, 1, 5 and 10C rates, respectively, which is better than that of the Sn/Void@G-600 electrode. When the C rate increases 100 times from 0.1 to 10C, the Sn/Void@G-800 anode shows high capacity retention ratio of 45.3%, revealing a good rate capacity. Besides, the electrochemical impedance spectra (EIS) studies further proved that the Sn/Void@G-800 electrode possesses the lower contact and charge-transfer resistances compared Sn/Void@G-600 electrode

(see Fig. S8). For comparative experiments on the different scales of PS particles (290, 380, 550 nm) template was performed, and the micro-nano void of Sn/Void@G-800 electrode was tuned. Fig. 4d show that the size of void on surface of the Sn/Void@G-800 anode has obvious effect on the capacity and rate performance of samples, the Sn/Void@G-800 with medium sized void (~400 nm) have the best capacity and magnification properties, however, the initial coulomb efficiency increases as increase of size of the void. The cycling performances of the Sn/Void@G-800 electrodes with medium sized void are shown in Fig. 4e. The electrodes were first discharged/charged for three and five cycles to activating at 0.1C rate for electrode activation, then C rate was up to 5C and maintained for 700 cycles, and the reversible specific capacity shows almost no decaying. The Sn/Void@G-800 electrode displays

excellent cycling performance could be attributed to three reasons: (1) graphene possess elastic properties, which ensure the contact with Sn nanoparticles and protect the Li ion transport pathways in the charge-discharge cycle [51]; (2) graphene possess a larger surface area and the Sn nanoparticles uniformly doped in graphene-based 3D architecture could largely alleviate the destructive changes from large volume changes in the intercalation and deintercalation process of Li ion [52,53]; (3) after a heat treatment at high temperature, the electrical conductivity of Sn/Void@G is increased considerably, attributed to the reduction of GO, carbonization of the carbonaceous polymer, which could significantly reduce the loss [54,55]. For comparison, other reported Sn-based electrodes research works are summarized in Table S1, revealing the Sn/Void@G-800 anode possesses an excellent cycling performance.

The storage Na performances of the Sn/Void@G-800 electrodes with medium sized void were studied. As shown in Fig. 5a, the Sn/Void@G-800 anode displays a capacity of 1153 and 751 mAh g⁻¹ in the first charge and discharge process with an initial coulombic efficiency of 65%. However, the Sn/Void@G-600 delivers initial coulombic efficiency of 35%, because low annealing temperature results in a low crystalline structure of graphene in Sn/Void@G-600 anode (see Fig. S9), which is proved by the TEM result. This BET result further proves that Sn/Void@G-800 have middle specific surface area (303.6 m²/g) and mesoporous structures with a few nanometers have been observed (see Fig. S10). It is obvious that Sn/Void@G-800 anode exhibits high capacities at various rate testing (751 mAh g⁻¹ vs 0.1C, 622 mAh g⁻¹ vs 0.2C, 566 mAh g⁻¹ vs 0.5C,

455 mAh g⁻¹ vs 1C, 348 mAh g⁻¹ vs 2C, 305 mAh g⁻¹ vs 5C, 248 mAh g⁻¹ vs 10C, 166 mAh g⁻¹ vs 20C, respectively). This indicates the Sn/Void@G-800 anode may possess good structural stability during the charge/discharge process, leading to a better electrochemical performance at different current densities. More interestingly, the Sn/Void@G-800 anode can charge and discharge under 10C rate within several-minute time and simultaneously remain a high capacity of 240 mAh g⁻¹. The Sn/Void@G-800 anode displays a capacity of 350 mAh g⁻¹ after 800 cycles, exhibiting excellent cycling stability (in Fig. 5d). The outstanding electrochemical storage Na performance of this new graphene-based composite electrode derives from its unique porous structure and tunable micro-nano void, which void as a highly efficient “bumper” to accommodate the large volume expansion of nano-Sn under charge and discharge process. The new type graphene based anode offers new opportunities for Na ion storage application of graphene composite in future.

4. Conclusions

In summary, the doped nano Sn 3D porous graphene structure were successfully fabricated by template method, and the tunable micro-nano void formed. The unique structure alleviates mechanical stress, accommodates volume variation, and ensures sufficient contact areas between the electrode and liquid electrolyte. With its use in an anode for LIBs, the discharge specific capacity still remains 45.3% of the as-prepared Sn/Void@G-800 electrode, when the C rate from 0.1C up to 5C. In addition, the Sn/Void@G-800 electrode

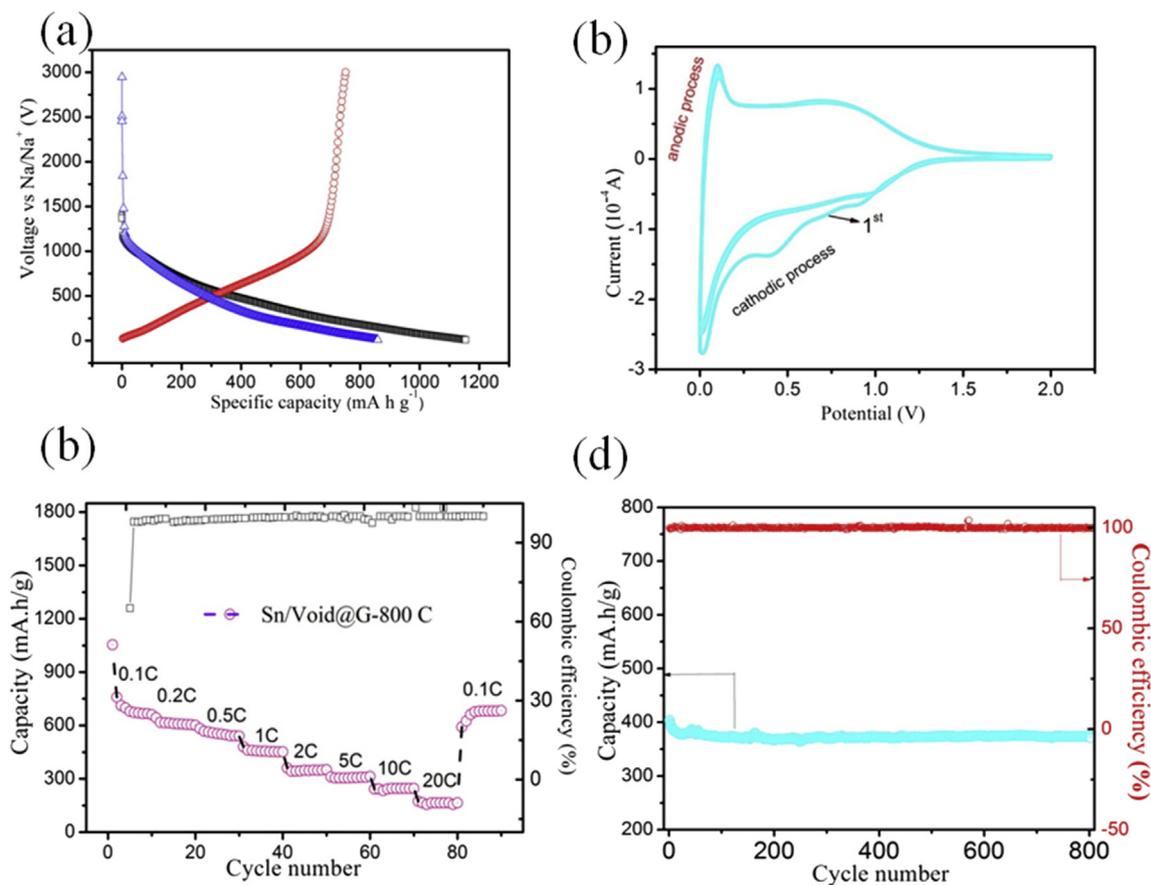


Fig. 5. (a) The first charge-discharge curves of the Sn/Void@G-800 electrodes at 1 A g⁻¹ for Na battery; (b) CV curves of the Sn/Void@G-800 anode between 0.01 and 3.00 V (vs Li/Li⁺) at a scan rate of 0.1 mV s⁻¹; (c) The multi-rate testing of the Sn/Void@G-800 electrodes at the charge-discharge current of various C rate, respectively; (d) Cycling performance of the Sn/Void@G-800 anode of Na battery at a current of 2C rate.

shows excellent cycling stability with the first coulomb efficiency is 62.5%. The Sn/Void@G-800 electrode is also suitable for using as the anode for Na ion batteries and delivers an ultrahigh rate capability of more than 166 mAh g⁻¹ at 20C and long-term cycling stability of 800 cycles at 2C. The outstanding electrochemical performance results from the uniform dispersion of Sn nanoparticles in the hierarchically porous graphene matrix with a buffered structure. The simplified synthesis approach and the well electrochemical performance of the Sn/Void@G electrode could be more beneficial to the large-scale application as the anode materials for an energy storage application.

Conflicts of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jallcom.2019.03.258>.

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