Pomegranate-like Porous Carbon Coated $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2$ Submicrospheres as Superior Lithium Ion Battery Anode

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Abstract

The Cu-Sn alloy compounds have low volume expansion but suffer from poor cycling performance as anode materials for lithium ion batteries (LIBs). In order to improve the electrochemical performance, the pomegranate-like porous carbon coated $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2$ submicrospheres assembled by nanoparticles (abbreviated as pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres) were facilely prepared by in situ polymerization of dopamine (DA) on the surface of $\text{CuSn}(\text{OH})_6$ submicrospheres, followed by carbonization and reduction in H_2/Ar atmosphere. Based on the advantages of nanometer-sized particle, porous structure and amorphous carbon coated, the as-prepared pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres behaved excellent cycling and rate performance as anode materials for LIBs. At the current density of 200 mA g^{-1} , the electrode materials could keep a capacity of 604 mAh g^{-1} after 150 cycles. Importantly, pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2$ submicrospheres could maintain the initial structure after 150 cycles. Relied on the excellent electrochemical performance, the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres were expected to become a promising anode material for LIBs.

Keywords: pomegranate-like; $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres; porous structure; anode materials; lithium ion batteries (LIBs).

1. Introduction

As anode materials for lithium ion batteries (LIBs), Sn-based materials (Sn, Cu_6Sn_5 , SnO_2 , etc.) [1-3] have aroused wide attentions of researchers due to their high specific capacity, abundant content and non-toxicity [4-6]. However, pure Sn suffer from fast capacity fading owing to 260 % volume expansion when it is transformed to $\text{Li}_{4.4}\text{Sn}$ after lithiation ($\text{Li} + \text{Sn} \rightarrow \text{Li}_{4.4}\text{Sn}$) [7]. Consequently, intermetallic compounds M-Sn [8] (M does not react with Li^+ , such as Cu-Sn, Ni-Sn, Fe-Sn alloy etc.) [9-11] have been studied a lot for their small volume expansion. Especially, Cu-Sn intermetallic compounds has left a deep impression to researchers for its high theoretical specific capacity. For example, Cu_6Sn_5 own a theoretical specific capacity of 605 mAh g^{-1} , which is higher than that of graphite (372 mAh g^{-1}) [12, 13]. Unfortunately, in the previous work, the Cu-Sn alloys only delivered a low capacity of $\sim 100 \text{ mAh g}^{-1}$ after 20 cycles at 50 mA g^{-1} [14]. Therefore, there is a large space for improving the performance of Cu-Sn alloys.

Up to date, various measures were taken to improve the electrochemical performance of Cu-Sn alloys for LIBs. For example, preparing nano-sized particle was employed to enhance the electrochemical performance for nano-size could shorten the transmission distance of electron and Li ions as well as provide a fast transport speed for Li ions [15]. Wang et al. prepared nano-sized Cu_6Sn_5 samples which delivered reversible capacities of 370 mAh g^{-1} after 20 cycles at 0.2 mA cm^{-2} [16]. Moreover, porous structure was designed to enhance the electrochemical performance. This is due to that pores could effectively buffer the volume change

during the discharge-charge process [17, 18]. Xue et al. synthesized three-dimensional porous Cu-Sn alloy foam which showed a reversible capacity of about 404 mA h g^{-1} up to 100 cycles at 100 mA g^{-1} [19]. In addition, carbon coating was adopted to improve the electrochemical performance because it could restrain the volume expansion as well as enhance the electrical conductivity [20-25]. Cui et al. reported the synthesis of carbon coated Cu_6Sn_5 nanoparticles as high performance anode materials for LIBs and it could keep 437 mAh g^{-1} after 50 cycles at 100 mA g^{-1} [26]. Liu et al. also reported that carbon-coated Cu-Sn alloy delivered a capacity of 460 mAh g^{-1} after 40 cycles at 50 mA g^{-1} [14]. Introducing pure Sn is also expected to improve the capacity of Cu-Sn alloy. For example, some of researchers have prepared the multiphase Cu-Sn alloys thin film with Sn to improving the capacity [27, 28, 29]. However, it suffered inferior cycling performance for the micrometer-sized particle and imporous structure, which were not beneficial to the transmission of Li ion and the relief of volume expansion. Although many works have been devoted to improve the electrochemical performance of Cu-Sn, most of them only adopted one or two of above strategies. For example, Kang et al. obtained the $\text{Cu}_6\text{Sn}_5@\text{void}@\text{C}$ composites with carbon layer and yolk-shell structure, while the particle size of Cu_6Sn_5 reached to 500 nm [30]. In the present work, multi-strategies were applied to improve the electrochemical performance of Cu-Sn alloy.

Herein, we have designed and prepared the pomegranate-like porous carbon coated $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2$ submicrospheres assembled by nanoparticles (abbreviated as pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres). In the preparation process,

the dopamine (DA) was directly in situ polymerized on the surface of CuSn(OH)_6 precursor and used as carbon source. Then the CuSn(OH)_6 was reduced and polydopamine (PDA) was carbonized in H_2/Ar atmosphere. In this design, the obtained porous structure could not only adjust the volume changes but also provide more channels for Li ion transportation. Furthermore, carbon layer could restrain the volume expansion and enhance the electrical conductivity. In addition, the small nanoparticle could shorten the transmission distance of Li ions. Owing to these superiorities of carbon modified, porous structure and nano-sized particles, the as-synthesized pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres exhibited excellent cycle and rate performance.

2. Experimental

2.1 Preparation

Preparation of the CuSn(OH)_6 submicrospheres [31]. 2 mL of ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$) was dropped into 32 mL of copper(II) chloride dehydrate ($\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, 0.05 mol L^{-1}) and a dark blue solution was obtained. Then 32 mL of potassium stannate ($\text{K}_2\text{SnO}_3\cdot 3\text{H}_2\text{O}$, 0.05 mol L^{-1}) was added into the aforementioned solution with drop by drop under stirring. The mixed solution was further stirred for 15 minutes. Finally, the obtained precipitation was collected with centrifugation, washed by deionized water and dried at 70 °C for 12 hours in the vacuum oven.

Preparation of the pomegranate-like porous $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres. 200 mg of CuSn(OH)_6 microspheres were dispersed in 80 mL of Tris-HCl solution (pH = 8.5). Then 200 mg of dopamine hydrochloride (DA) was added into

aforementioned solution and stirred for 4 hours. After that, the precipitation (denoted as $\text{CuSn}(\text{OH})_6\text{@PDA}$) was collected by centrifugation, washed with deionized water and dried at 70 °C for 12 hours in the vacuum oven. The obtained product was annealed at 500 °C for 5 hours with a heating rate of 3 °C min⁻¹ under H_2/Ar (1:9, V/V) atmosphere to prepare the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres. The synthetic scheme of the $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres could be described as shown in Fig. 1.

Preparation of the pure Cu_6Sn_5 [32]. 500 mg of sodium citrate dehydrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3\cdot 2\text{H}_2\text{O}$), 112 mg of Tin (II) chloride dehydrate ($\text{SnCl}_2\cdot 2\text{H}_2\text{O}$) and 102 mg of copper (II) chloride dehydrate ($\text{CuCl}_2\cdot 2\text{H}_2\text{O}$) were dissolved in 50 mL of deionized water in order. Then the solution was dropwise added in 50 mL of sodium borohydride aqueous (NaBH_4) solution which contained 473 mg of NaBH_4 under vigorous stirring. After 1 h, the black precipitation was collected by centrifugation, washed with deionized water and dried at 70 °C for 12 hours in the vacuum oven.

2.2 Characterization

The X-ray diffraction (XRD, BRUCKER D8, Germany) was employed to characterize the crystalline structures from 20° to 80° at a scan speed of 6° min⁻¹. Renishaw Raman microscopy (Renishaw Invia Raman spectrometer, Renishaw, UK) and the X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, USA) was used to analyze the materials. The scanning electron microscopy (SEM, S-4800, Hitachi, Japan) was applied to observe the surface morphologies. The transmission electron microscope (TEM, Tecnai G2 F20 S-TWIN, USA) was employed to investigate the microstructures. Automatic surface area and porosity

analyser (ASAP 2460, Micromeritics, USA) was carried on measuring the specific surface area and pore size. Thermal gravimetric analyzer (TG, METTLER TG/DSC 1 SF/1382, Switzerland) was used to measure the carbon content.

2.3 Electrochemical measurements

The CR2032 coin cells, used to perform the electrochemical properties of the as-prepared samples, were assembled in the argon-filled glove box. The working electrode of the cell was constructed by pressing the mixture, which was made up of active materials 70 *wt. %*, super P 20 *wt. %*, sodium carboxy methyl cellulose (CMC) 10 *wt. %*, on the copper current collectors (diameter = 1.6 cm). And the loading of the active materials was about 1 mg cm⁻². Lithium plate played the role of the counter electrode, and Celgard 2300 acted as separator. Furthermore, electrolyte was prepared by dissolving 1 mol·L⁻¹ LiPF₆ in ethylene carbonate/diethyl carbonate (EC : DEC =1:1, V / V). The battery tester (Land CT2001A, China) was used to measure the galvanostatic cycling of the half coin cell from 0.005 to 2 V. The electrochemical workstation (CHI660D, Chenhua, China) was employed to measure the cyclic voltammetry (CV) curves from 0.005 to 2 V with a sweep speed of 0.5 mV s⁻¹, and test the electrochemical impedance spectroscopy (EIS) plots from 0.1 Hz to 10000 Hz.

3. Results and discussion

The crystalline structures of as-prepared samples was studied by the X-ray diffraction (XRD) and the related pattern was presented in Fig. 2. Curve a was the XRD patter of the pomegranate-like porous Cu_xSn_y/Sn/SnO₂/C submicrospheres. The

peaks appeared at $2\theta = 30.1^\circ, 35.1^\circ, 41.2^\circ, 43.3^\circ, 53.4^\circ, 60.0^\circ, 62.6^\circ, 70.8^\circ$ and 79.0° were accorded with the crystal faces (22-1), (40-2), (42-1), (42-2), (24-1), (62-3), (44-2), (351) and (35-4) of Cu_6Sn_5 (JCPDS No. 45-1488) respectively. The peaks (addressed as Δ) were corresponded to Sn (JCPDS No. 01-0926), which were matched with the crystal faces (101), (211) and (400) in order. The rest of those small peaks were attributed to Cu_3Sn (JCPDS No. 03-1010, $2\theta = 37.8^\circ, 57.5^\circ, 67.8^\circ$) and SnO_2 (JCPDS No. 01-0625, $2\theta=26.2^\circ, 51.6^\circ$) due to the uncompleted reduction. However, we cannot find any peaks of carbon in the curve a, suggesting that the carbonized polydopamine is amorphous [33]. Curve b was the XRD patten of the pure Cu_6Sn_5 , the four peaks were accorded with the crystal faces (22-1), (42-2), (44-2) and (060) of Cu_6Sn_5 (JCPDS No. 45-1488) in order.

Raman spectroscopy was employed to investigate the structural properties of carbonaceous materials and the Raman spectra of as synthesized sample was shown in Fig. 3a. It was easy to find a broad peak at around 1358 cm^{-1} and a sharp peak at around 1590 cm^{-1} . The two peaks were accorded with the D and G band of carbon which were attributed to disordered sp^3 carbon and graphitic crystallites or sp^2 bonded carbons respectively [34,35]. In order to further investigate the content of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres, thermal gravimetric analyzer (TG) measure and XPS spectra were employed. Fig. 3b showed the TG curve of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres. The weight loss of the sample (0.5%) from 20°C to 170°C was due to the sublimation of the water. And the weight of the sample firstly increased about 1.8% from 220°C to 276°C was ascribed to the

oxidation of metallic tin [36,37]. Then, the weight was decreased from 276 °C to 417 °C and increased from 417 °C to 800 °C. The phenomenon can be attributed to the oxidation of amorphous carbon, Cu₆Sn₅ and Cu₃Sn [26, 38]. The final product owned a weight content of 93%, and it was made up of CuO and SnO₂. Fig. 3c and 3d depicted the XPS spectra of the pomegranate-like Cu_xSn_y/Sn/SnO₂/C submicrospheres. The Cu 2p peaks (Fig. 3c) revealed two kinds of the Cu in Cu₆Sn₅ (933.1eV and 952.7eV) and Cu₃Sn (954.6eV and 935.2eV) [39]. And the Cu in Cu₆Sn₅ and Cu₃Sn was calculated to be 71% and 29% of the total Cu. In Fig. 3d, the peaks at 486.9eV and 495.3 eV were caused by the Sn⁴⁺, other two peaks (482.1 eV and 493.5 eV) were attributed to the Sn⁰ [40]. The data of the XPS showed that the atomic ration of Cu to Sn was 4:5 in the pomegranate-like Cu_xSn_y/Sn/SnO₂/C submicrospheres. Based on the above TG and XPS data, the weight contents of Cu₆Sn₅, Sn, SnO₂, Cu₃Sn and carbon in the pomegranate-like Cu_xSn_y/Sn/SnO₂/C submicrospheres were calculated to be 40.4%, 6.6%, 22.6%, 10.2% and 19.7%, respectively.

The scanning electron microscopy (SEM) images of the as-prepared samples were exhibited in Fig. 4. Fig. 4a demonstrated that the size of the CuSn(OH)₆ submicrospheres ranged from 500 nm to 1 μm. Compared with the CuSn(OH)₆ submicrospheres, the CuSn(OH)₆@PDA submicrospheres (Fig. 4b) were coated by a layer of floccules, which maybe attributed to the formation of polydopamine. After annealing, the pomegranate-like porous carbon coated Cu_xSn_y/Sn/SnO₂ submicrospheres were obtained. The size of submicrospheres did not change but some nanoparticles with a diameter of 50~100 nm were formed on the surface of spheres

(Fig. 4c) which was owed to the reduction of $\text{CuSn}(\text{OH})_6$. The chemical reaction could be described as follows:

Fig. 4d showed the SEM image of pure Cu_6Sn_5 with a particle size of about 50 nm. To further study the composition of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres, the composites were characterized through the elemental mapping. As shown in Fig. 5b-e, the green, blue, yellow and violet dot represented the uniform distribution of C, Cu, Sn and O element, respectively.

The microstructure of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres was further measured by transmission electron microscope (TEM). Fig. 6a illustrated that the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres owned porous structure due to reduction of the precursors and amounts of small particles which were coated with carbon layer (about 3 nm) (see Fig. 6b, 6c). High resolution transmission electron microscopy (HRTEM) of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres was displayed in Fig. 6c. The crystalline interplanar spacing in the image was calculated to be 0.297 nm, which matched with the (22-1) plane of Cu_6Sn_5 (JCPDS No. 45-1488). As depicted in Fig. 6d, the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres possessed a specific surface area of $57.5 \text{ m}^2 \text{ g}^{-1}$

and an average pore diameter of 7.4 nm. The higher specific surface area could increase the contact area and the porous structure could buffer the volume expansion.

Fig. 7a showed the galvanostatic voltage profiles of the 1st, 2nd, and 5th cycle for the $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres at a current density of 200 mA g^{-1} . The discharge and charge capacity of the 1st cycle were 1178 and 827 mAh g^{-1} , respectively. The initial coulombic efficiency was calculated to be 70.2%, and the lost lithium storage was due to the Li ions consumption in the solid electrolyte interface film [41]. The 2nd, and 5th cycle exhibited discharge capacity of 797 and 793 mAh g^{-1} , respectively. It could be observed that these capacities were all higher than the theoretical capacity of Cu_6Sn_5 (605 mAh g^{-1}), which was owing to the existence of Sn (994 mAh g^{-1}) and SnO_2 (1494 mAh g^{-1}). The differential capacity plots (DCPs) of the 1st, 2nd, and 5th cycle were presented to explain the anode behaviors during the cycling procedure (Fig. 7b). In the first discharge plot, the DCP peak located at 1.0 V (inset in Fig. 7b) was caused by the lithiation of SnO_2 to form Li_2O and Sn. The DCP peaks occurred at 0.65 V and 0.33 V were due to the alloying of Sn and lithiation of Cu_6Sn_5 [38]. Another DCP peak at $\sim 0.1 \text{ V}$ was caused by lithiation of Cu_3Sn [29, 42]. The peaks in subsequent discharge plots had a slight shift which could be attributed to the fact that the minor structural rearrangement of the active material [43]. In charge plots, the peaks appeared at 0.5V, 0.62V and 0.79 V were due to the delithiation of Li-Sn and Li-Sn-Cu phases [28, 29]. The reaction between Sn and Li_2O led to the generation of broad peak at 1.11 V (inset in Fig. 7b) [38, 44]. Those discharging and discharging peaks appeared in the 2nd and 5th cycle indicating the reversible of the

peaks. Furthermore, the CV curves of the 1st, 2nd and 5th cycle for pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres were also measured and presented in Fig. 7c. The tendency and peak position in the CV curves were accorded with that of the DCPs.

The cycling performance of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres and pure Cu_6Sn_5 nanoparticles were conducted at the current density of 200 mA g^{-1} (Fig. 7d). The first discharge capacity of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres (1178 mAh g^{-1}) was higher than that of pure Cu_6Sn_5 nanoparticles (743 mAh g^{-1}), it can be attributed to the introducing of pure Sn and SnO_2 . In addition, compared with the rapid attenuation of capacity for pure Cu_6Sn_5 nanoparticles, the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrosphere exhibited excellent cycling performance and its capacity could keep at 604 mAh g^{-1} after 150 cycles. Furthermore, the electrochemical performance of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres prepared in this work was superior than other Cu-Sn alloy anode materials reported previously (see Tab. 1).

Fig. 7e displayed the rate performance of pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrosphere and pure Cu_6Sn_5 at the current density of 100, 200, 500, 1000 and 100 mA g^{-1} . It can be found that the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrosphere showed stable discharge capacities of 800, 670, 570, 430 and 860 mAh g^{-1} respectively, which were all higher than that of pure Cu_6Sn_5 (500, 370, 220, 130 and 370 mAh g^{-1}). The superior rate performance of pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrosphere could be owed to the porous structure and carbon layer. The EIS plots of pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres and

pure Cu_6Sn_5 nanoparticle were showed in Fig. 7f. Both of the two spectra were consist of two parts. The depressed semicircle was caused by the charge-transfer impedance (R_{ct}) at high-to-medium frequencies and the slope was as a result of ion diffusion inside the electrode at the low frequencies. It was easy to calculate that the R_{ct} of pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres was $150\ \Omega$ which was lower than that of pure Cu_6Sn_5 . The improvement of the electric conductivity was due to the carbon layer, and it could enhance the electrochemical performance of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres.

To further verify the reason of the excellent cycling and rate performance, the morphology of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrosphere after cycling was characterized. Fig. 8a displayed the low-resolution SEM image of the electrode surface after 150 cycles, and many spheres can be observed. The larger diameter of the spheres may be caused by the fact that the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres were coated by solid electrolyte. In addition, a submicrosphere structure (Fig. 8b) could also be obtained after ultrasound washing and drying from the electrode, which was similar to the pristine $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrosphere. The result indicated that the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrosphere had a relatively stable structure, which was attributed to the fact that amorphous carbon layer coated and porous structure can buffer the volume expansion. Therefore, the electrode had an excellent cycling and rate performance.

4. Conclusion

In summary, the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres

assembled with nanoparticles (50~100 nm) were successfully prepared through polymerization and calcination. The coated amorphous carbon layer on the nanoparticles restrained the volume expansion and enhanced the electroconductivity. Furthermore, the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres with porous structure (average pore diameter of 7.4 nm) could further buffer the volume expansion and facilitate the transportation of Li ions. Therefore, the obtained pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres behaved superior cycling performance and excellent rate performance compared with the pure Cu_6Sn_5 nanoparticle. The results showed that the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ kept a reversible capacity of 604 mAh g^{-1} up to 150 cycles at the current density of 200 mA g^{-1} . Importantly, the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2$ submicrospheres could maintain the initial structure after 150 cycles. The design and preparation of pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres provided a valuable guidance for improving the electrochemical performance of M-Sn alloy as anode material for LIBs.

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Fig. 1 The synthetic scheme of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres.

Fig. 2 XRD patterns of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres (a) and pure Cu_6Sn_5 nanoparticles (b).

Fig. 3 Raman spectra (a), TG curve (b) and XPS spectra (Cu 2p (c), Sn 3d (d)) of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres.

Fig. 4 The SEM pictures of the $\text{CuSn}(\text{OH})_6$ (a), $\text{CuSn}(\text{OH})_6/\text{PDA}$ (b) and pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres (c). The SEM picture of pure Cu_6Sn_5 nanoparticles (d).

Fig. 5 SEM image (a) and element mapping images (b-e) of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres.

Fig. 6 TEM images (a, b) and HRTEM image (c) of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres. The nitrogen adsorption-desorption isotherms and pore size distribution isotherm (inset) of pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres (d).

Fig. 7 The galvanostatic voltage profiles (a), differential capacity plots (b), cyclic voltammogram curves (c) of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres. The capacity-cycle plots (d), rate performance (e) and electrochemical impedance spectra (f) of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres and pure Cu_6Sn_5 .

Fig. 8 The SEM images of the electrode surface (a) and pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrosphere (b) after 150 cycles at 200 mA g^{-1} .

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Tab. 1 Summary for the performance of the pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres and other Cu-Sn alloys anode materials reported previously.

Samples	Current density	Discharge capacity / mAh g^{-1}	Reference
Carbon-coated Cu-Sn alloy	$50/\text{mA g}^{-1}$	460 (40 th cycle)	14
Porous Sn-Cu alloy	100 mA g^{-1}	404 (100 th cycle)	19
Carbon-coated Cu_6Sn_5	100 mA g^{-1}	405 (50 th cycle)	26
Sn/ Cu_6Sn_5 thin film	$100\text{ }\mu\text{A cm}^{-2}$	350 (50 th cycle)	28
Sn-Cu thin film	$100\text{ }\mu\text{A cm}^{-2}$	340 (30 th cycle)	29
$\text{Cu}_6\text{Sn}_5@\text{void}@\text{C}$	300 mA g^{-1}	241 (30 th cycle)	30
Cu_3Sn	100 mA g^{-1}	~350 (30 th cycle)	42
$\text{Cu}_6\text{Sn}_5/\text{Sn}$	100 mA g^{-1}	457.8 (20 th cycle)	45
PCNNWs- $\text{Cu}_6\text{Sn}_5@\text{C}$	1000 mA g^{-1}	366.4 (200 th cycle)	46
Sn rich Cu_6Sn_5	200 mA g^{-1}	445 (50 th cycle)	47
Cu-Sn thin film	50 mA g^{-1}	300 (100 th cycle)	48
C-coated Cu_6Sn_5	300 mA g^{-1}	315 (20 th cycle)	49
Core/shell Cu_6Sn_5	100 mA g^{-1}	420 (50 th cycle)	50
Pomegranate-like $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2/\text{C}$ submicrospheres	200 mA g^{-1}	604 (150th cycle)	This work

Pomegranate-like Porous Carbon Coated $\text{Cu}_x\text{Sn}_y/\text{Sn}/\text{SnO}_2$ Submicrospheres as Superior Lithium Ion Battery Anode

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