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博士論文題目 Study on Structure Control and Electrochemical Investigation of  
Si-based Composite Materials for Energy Storage Device  
(シリコン基複合材料を用いた材料の構造制御及び蓄電デバイスへの応用に関する研究)

## 1. Introduction

In the past decades, lithium-ion batteries (LIBs) have been getting great deal attention as an energy storage device for their high energy density and long cycle life as well as environmental friendliness. Because of the ever-increasing quantity of portable electronic devices and electric vehicles, the global market of LIBs is considered that will rapidly grow and reach around 38 billion dollars by 2020. Hence, it is still worth developing LIBs for the flourish energy-storage market. Nevertheless, the theoretical energy density of LIBs with graphite as the anode is being approached. The demands of LIBs with higher energy and power density, larger capacity, as well as a long lifespan and safer is attracting more and more attention. Many efforts have been invested to explore new LIBs systems, such as lithium-silicon (Li-Si), lithium-sulfur (Li-S), and all-solid-state batteries that are free of dendrite-forming lithium metal anodes.

Silicon-based materials, as the foundation of modern industrialization, are widely used in various fields. In addition, as the second highest content element in the crust of earth and especially high potential capacity. In recent years, it is being considered as a promising alternative to substitute the traditional low-capacity graphite anode in LIBs because of its high theoretical capacity.

However, it has also been reported that pure Si anodes face one thorny issue. As all known, the alloying reaction between Li-ion and Si is main reason to contribute the superhigh specific capacity. But it subsequently causes large volume expansion, resulting in the pulverization of electrode structure and unstable solid electrolyte interphase (SEI) growth during charge-discharge cycles. Subsequently, it leads to severe capacity fading and shortens the cycle life of Si anodes, which hinders its practical application.

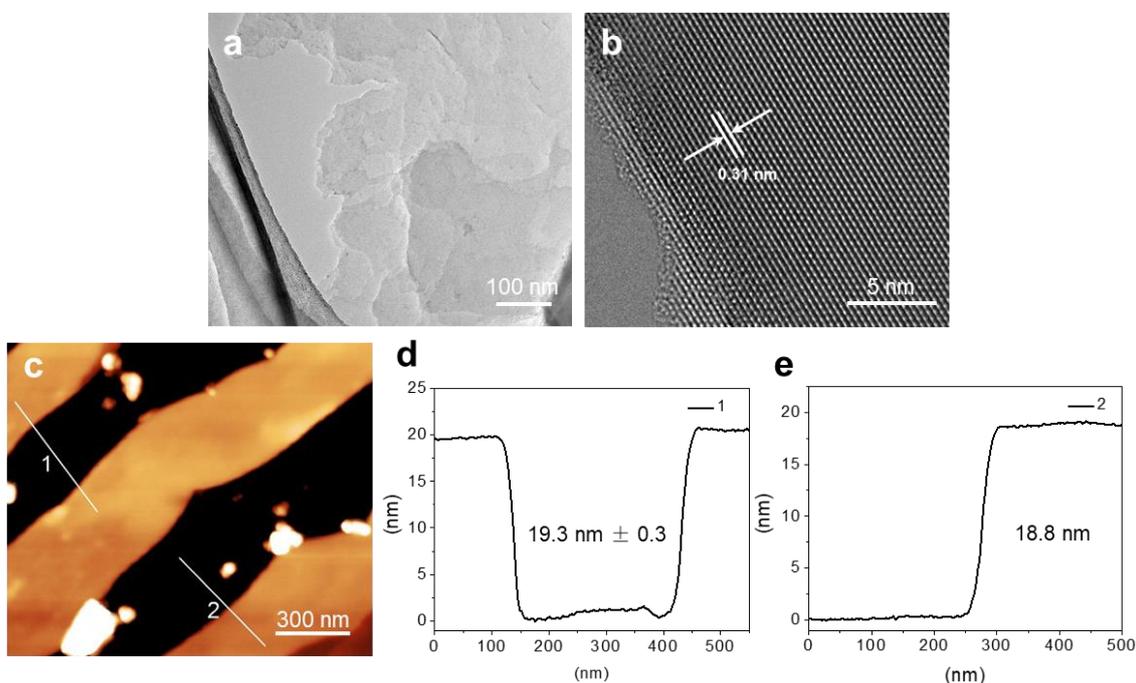
To date, many strategies have been investigated to tackle above issues, such as element or nanoparticle-doping (boron, silver). morphology-control (nanowires, nanotubes). structure-engineering (hollow/porous structure) and surface-coating (metal oxides, carbon-based materials). Although some remarkable improvements have been achieved, these investments still do not fulfill all the demand for Si anodes. So, it is worth seeking other facile and efficient methods for constructing high-performance Si-based anode. In this research, different improved strategies of Si anode are implemented to enhance its electrochemical performance.

## **2. The Investigation of Two-dimensional Silicon-based Materials as Anode for Lithium-Ion Batteries**

So far, there have been many methods reported to enhance the performance of Si anode by constructing diverse structures. Such as, Shi et al. reported a method for synthesizing vertical graphene encapsulation of silicon-based microparticles via a chemical vapor deposition (CVD) process. Yoon et al. prepared nanocubic silicon anode by high temperature magnesiothermic reduction reaction. Choi et al. demonstrated that highly elastic binders could maintain contact with the electrode material to achieve high electrochemical performance. Nevertheless, the defects of are obvious by utilizing these approaches in constructing Si anode structure. Firstly, the cost is high with consumption of precious metals, meanwhile the process is complex make many strategies not practical. Secondly, the target structure needs to be processed multiple times, such as creating abundant mesopores on the surface of the silicon material and covering the bulk silicon with a high

elastic conductive polymer. Next, the Li ion diffusion is relatively sluggish in bulk silicon. Therefore, constructing a feasible and reasonable Si anode structure is still a challenge to receive the benefits of the Si anode.

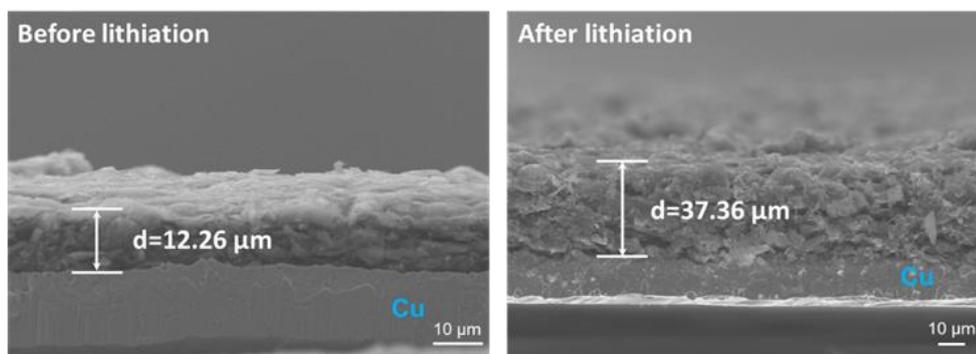
Two-dimensional materials are fascinating in many aspects. Many two-dimensional materials and their derivatives have been recently adopted to great success in various purposes due to their unique structure. Herein, we report a unique layered Si material (LSM) as an anode material for LIBs. This LSM can be easily fabricated through a one-step topological reaction with relatively low cost, while maintaining the structural integrity of silicon electrode simultaneously. Structurally, the LSM not only possesses a two-dimensional structure consisting of a hexatomic corrugated Si structure but  $\text{Si}_6$  rings are also interconnected and terminated with functional groups. Especially, one of its most important characteristics is that the two-dimensional structure can naturally generate more space without modification but stack by themselves, which can accommodate the expansion stress. Thus, this LSM can be a competitive anode candidate for LIBs.



**Figure 1.** Morphology and microstructure of LSM. (a) TEM image at low magnification, (b) TEM image at high magnification, (c) AFM image, (d, e) the thickness of LSM.

Transmission electron microscopy (TEM) measurements were employed to observe the two-dimensional structure and the results are shown in Figure 1. These images demonstrate that as-product LSM has a flat and smooth surface at several hundred nanometers. High-resolution TEM further displays a clear lattice image of Si atoms in Figure 1b. In addition, atomic force microscopy (AFM) was further conducted to test the thickness of layers in LSM dispersed on a Si wafer. It shows that this sample displays some ultrathin nanosheets with a thickness of about 19 nm, which can be observed that the width ranges from hundreds of nanometers to several micrometers.

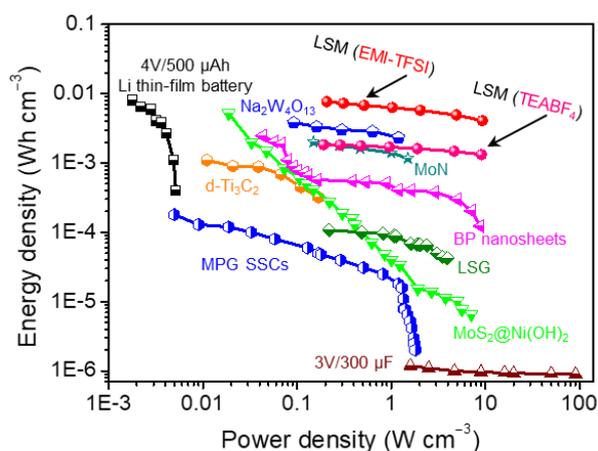
When employed as a LIB anode, this LSM showed much higher specific capacities with prolonged cycling stability than that of bulk silicon electrode. As we know, large volume expansion is the main issue due to the alloying reaction of Li and Si. In the present study, the SEM results of pure LSM before and after lithiation are shown in Figure 2. It can be seen in Figure 2 that the volume change is about 205% after lithiation comparing with original electrode, which demonstrates that LSM exhibits similar properties with common naked Si materials but has smaller volume expansion benefiting from its two-dimensional structure.



**Figure 2.** SEM images of the LSM (a) before lithiation, (b) after lithiation.

As the electrode materials of supercapacitor, the excellent electrochemical performance of the LSM electrode could be ascribed to the following: first, the utilization of advisable ionic liquid electrolyte provides a favorable and broad OVR. Then, good electrical conductivity, an intrinsic feature of Si-based materials, is beneficial for electron transport kinetics. Subsequently, two-dimensional structure of LSM offers more contact area and adequate active site for ion

intercalation and de-intercalation. At last, the existence of functional groups in the Si skeleton further promotes the formation of large interlayer spacing and abundant pore size to accelerate ion transmission and diffusion. Altogether, these results affirm the potential application of LSM as an excellent electrode material of supercapacitor.



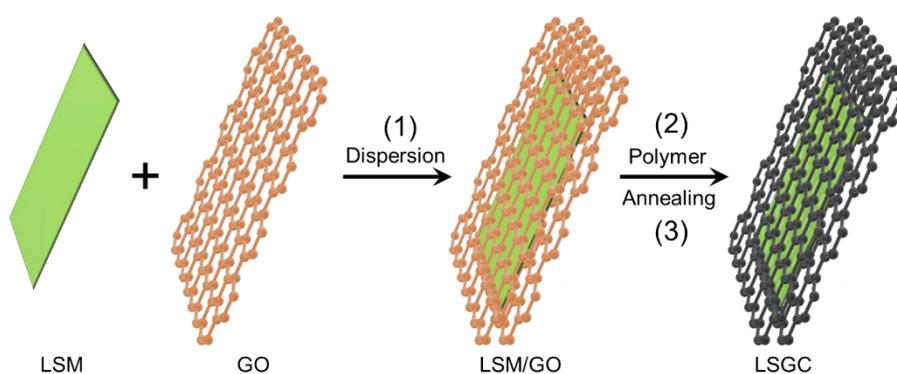
**Figure 3.** Ragone plot of the LSM device, and the comparison of reported device on other two-dimensional materials.

### 3. Self-assembly Layered Silicon-based Materials/Carbon Composite for Highly Stable Lithium-Ion Batteries

In previous work, we successfully synthesized the layered Si-based materials by a facile topology reaction. Although the layered Si-based materials have improved electrochemical performance compared to the naked Si materials, its rate capability and cycling stability still need to further enhance to satisfy the practical application. Carbon-based materials have been certified as an efficiently protective shell in solving some disadvantages of Si-based materials due to their good conductivity and great mechanical flexibility. Moreover, they can accommodate the volumetric fluctuation well and maintain the intact electrode structure during the continuously expanding and dwindling process.

In this work, a novel high-pressure driven dispersion and subsequently self-packing method was employed to construct layered SiO<sub>x</sub>-based material /carbon composite structure and further

address these defects of  $\text{SiO}_x$ -based materials. Owe to electrostatic interactions between PEI and LSM/GO, the formation of gel-like LSM/GO/PEI is instant and observed evidently instead of being dispersed. Scanning electron microscopy (SEM) was measured to intuitively observe the microstructure in various synthesis steps. After the mixing procedure of LSM and GO, it is clearly show that LSG was only covered with a very thin GO layer, suggesting the relatively weak chemical interaction between them. Comparison of the SEM results of the addition of PEI, a compressed and substantial composite structure attributing to the electrostatic interactions.



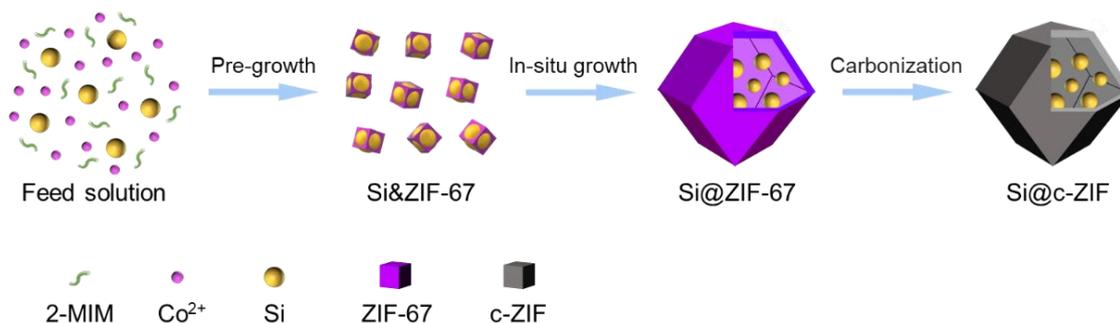
**Figure 4.** Schematic illustration of the preparation of LSGC.

The coated-carbon shell not only provides a protective layer to form a stable solid electrolyte interface membrane but improves the electrochemical conductivity and activity. Meanwhile, the release effect of volume change can be inhibited by carbon shell with good mechanical flexibility. This designed composite electrode has a compact and robust interfacial structure, which also greatly increase tap density of the electrode. As an anode material, it could show a high reversible capacity and excellent rate capability. The continued cycling stability is also illustrious even after rate performance test, which presents a high-level capacity retention.

#### **4. In-situ Construction MOFs-derived Carbon Shell for Improved Lithium-Ion Storage Properties of Silicon Anode**

Metal-organic-frameworks (MOFs) with excellent physics-chemical properties and functional

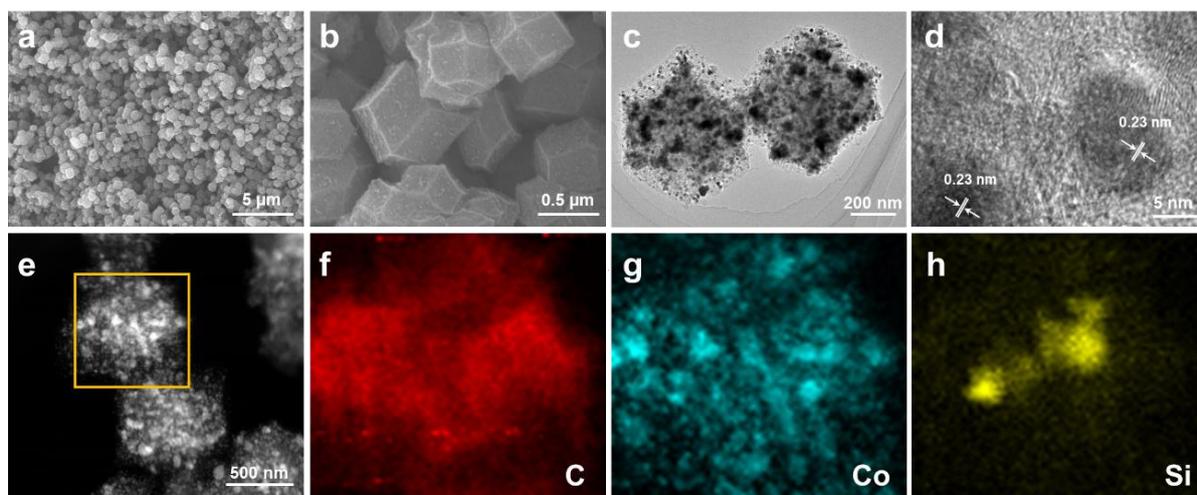
diversity could be designed by tuning various structures with uniform pores, which have been already investigated in many fields. Many different types of materials like metal nanoparticles and nanoclusters, graphene quantum dots, drug molecular have also been encapsulated into MOFs for studying. Therefore, we also adopt an in-situ encapsulation method to enhance Li storage performance of the Si-based anode through growing the zeolitic imidazolate framework (ZIF) layer on the surface of Si particles as shown in Figure 5. Comparison of common approaches, in-situ construction formed closely interfacial interaction and avoided unfavorable exposure to improve the electrochemical properties of electrodes.



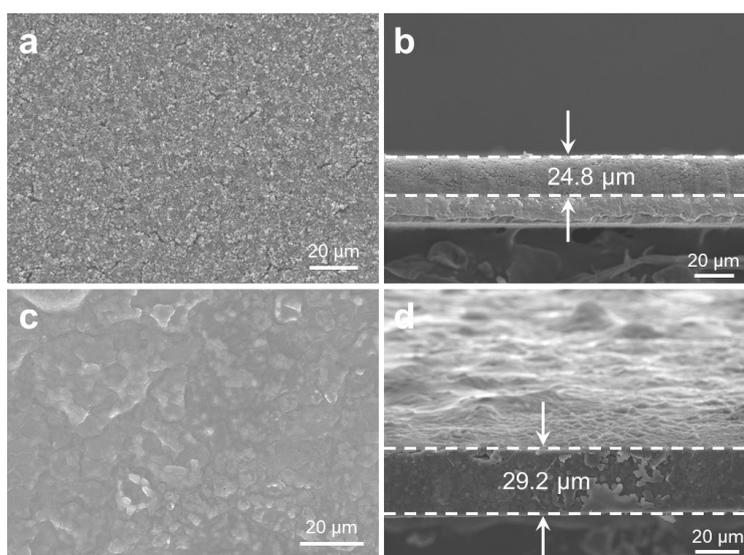
**Figure 5.** Schematic illustration of the synthesis of Si@c-ZIF.

Scanning electron microscopy (SEM) results confirm that these Si nanoparticles can be encapsulated very well in Figure 6a and 6b. As shown, Si@c-ZIF has a well-defined uniform polyhedral structure that is similar to that of ZIF-67 polyhedrons, which confirms the structure was robust and integrally inherited in the transformation process from ZIF-67 to MOF-derived carbon (c-ZIF). Transmission electron microscopic (TEM) was also used to investigate the internal layout of Si@c-ZIF. It proves a homogeneous distribution of Si nanoparticles and a dense composite structure in the MOF-derived carbon shell without excessive exposure of Si nanoparticles. Meanwhile, the high-resolution TEM image of the Si@c-ZIF further confirmed that the composite has a compact carbon shell, and Co nanoparticles were also detected and covered by carbon shell. By viewing the elemental mapping patterns of Si@c-ZIF in Figure 6e-6h, the various elements of carbon, cobalt, and silicon can be clearly observed. Carbon and cobalt were homogeneously

scattered, while Si element lies in the middle of the composite.



**Figure 6.** (a, b) SEM images and (c, d) TEM images of Si@c-ZIF at different magnification; (e) HRTEM image of Si@c-ZIF; and (f-h) elements mapping images of the carbon, cobalt, and silicon.

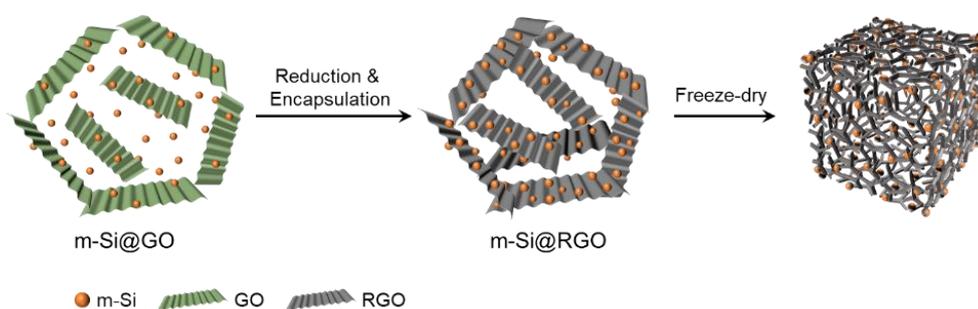


**Figure 7.** SEM results of Si@c-ZIF composite electrode. Surface images (a) before and (c) after 400 cycles; cross-sectional images (b) before and (d) after cycles.

To better understand the structural stability of this composite electrode, the top-view and cross-sectional SEM images of the Si@c-ZIF electrode were investigated before and after cycling and the results were shown in Figure 7. Figure 7a and 7c deliver the comparison of surface microstructure, which obviously demonstrates that serious cracking and pulverization are not

observed after cycling. Meanwhile, cross-sectional SEM results prove that the Si@c-ZIF electrode indeed inhibitive volume expansion, whose thickness variation is only 4.4  $\mu\text{m}$  corresponding to 17.7% increase in the volume compared to the original morphology. Therefore, the Si@c-ZIF nanocomposite structure maintains its original structure well and relieves the adverse impact of volume variation during the long-term cycles.

## 5. Green Strategy for Preparation of Honeycomb-like Silicon Composite with Enhanced Lithium Storage Properties



**Figure 8.** Schematic illustration of the preparation of m-Si@G.

Herein, a honeycomb-like Si-based composite was also prepared to address these issues via a facile and green reduction approach at room temperature. The pre-anchored Si nanoparticles could be packaged and interconnected through three-dimensional graphene network to further enhance electrochemical properties of active materials. As an electrode, this composite shows good rate capabilities and cycling stability. The continued cycling measurement delivers a  $-0.049\%$  capacity decay rate per cycle within 600 cycles. The direct comparison further exhibits the obviously improved performance between as-designed Si-based composite and naked Si, suggesting a potential application of this convenient strategy for other high-performance electrode materials.

## 6. Conclusion

We adopted different approaches to improving the electrochemical properties of Si-based

anodes in this research. Benefiting from the rational strategies of structural regulation and the surface-coating with the aid of electrostatic interactions and in-situ growth, the comprehensive electrochemical performance of as-prepared Si-based composites have somewhat improved, as while its large volume expansion could be relieved compared to pure Si anode. Presently, nanoscale structures have confirmed that it can address most challenges. Nevertheless, the mass loading of nanomaterial limits its energy output. To solve this, the investigation involving increased mass loading of Si-based materials will be carried out.