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Si@C nanosponges application for lithium ions batteries synthesized by templated magnesiothermic route



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ABSTRACT

Carbon coated silicon nanosponges (Si@C NSs) used for anode in lithium ion batteries have been synthesized at a large scale via a templated magnesiothermic route, in which cheap ZnO nanoclusters and non-toxic glucose were employed to serve as sacrificial template and carbon source, respectively. The microstructure of Si@C NSs and its electrochemical performance in lithium ion batteries were investigated in detail. A reversible capacity with little fading after 500 cycles was obtained and the possible reasons for such superiority were discussed. The present results indicate potential application of the as-obtained Si@C NSs in lithium ion batteries.

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1. Introduction

Silicon based composite electrodes for lithium ion batteries have aroused wide interest because of their potential to be the high-capacity alternatives to the commonly used graphitic carbon anodes [1]. However, the alloying process of Si with Li during cycle accompanies with large volume change, which easily results in unstable solid electrolyte interphase (SEI) and rapid pulverization of Si-based anodes [2]. As a consequence, hollow nanostructure of Si is highlighted because of its ability to accommodate large strains without pulverization [3]. Among many routes for the synthesis of hollow nanostructures of silicon, template-based methods exhibit various advantages [4,5]. Chemical vapor deposition (CVD) process was widely employed to synthesize silicon hollow structures through templating against ZnO rod or anode aluminum oxide (AAO) [6–8]. However, the silicon sources (like SiH₄, SiH₂Cl₂) used in CVD are expensive, poisonous and dangerous [9]. In addition, it is always a great challenge to synthesize silicon hollow structures at a large scale by CVD process. Therefore, there has been a strong desire to find a facile, less-expensive and non-toxic high-yielding method for the synthesis of silicon hollow nanostructures in order to meet the urgent requirement in Li-ion batteries. Distinguished from silicon, hollow silica nanostructure can be synthesized at a large scale by solution method under mild condition using abundant and nontoxic raw materials [10]. Recently, a cheaper way, i.e. magnesiothermic reduction method, was developed to

transform silica into silicon easily [11], which has been successfully applied to fabricate multitudinous silicon nanostructures at large scales. On the other hand, it has been reported that carbon coating could be an admirable way to improve the cycling performance of nanostructured electrode materials [3,12].

Herein, hollow interconnected Si@C nanosponges (Si@C NSs) that are capable of accommodating large strain with less pulverization were synthesized at a large scale by a templated magnesiothermic route, in which ZnO nanoclusters and glucose are employed as sacrificial template and carbon source, respectively. The microstructure and application performance of the prepared Si@C NSs as an anode material in Li-ion batteries were investigated in detail.

2. Experimental

The templated magnesiothermic synthetic route for Si@C NSs was illustrated schematically in Fig. 1. Typically, 10 g commercial ZnO nanoclusters (AR, SCRC) template were dispersed in the mixture of ethanol, deionized water and concentrated ammonia solution (volume ratio=150 mL:100 mL:15 mL) under stirring at 30 °C. Then a mixture of tetraethoxysilane (TEOS) and ethanol (volume ratio=20 mL:20 mL) was added drop by drop in the solution to form SiO₂ shell on ZnO template. After 2 h continuing stirring, the resulting ZnO@SiO₂ was collected by vacuum filtration and then soaked in excessive amounts of diluted HCl solution to remove the ZnO core to form hollow SiO₂ nanosponges (SiO₂ NSs). The obtained hollow SiO₂ NSs were stirred in silane coupler solution (V_{silane coupler}:V_{ethanol}=2 mL:100 mL) overnight, then filtrated

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Synthetic steps of Si@C NSs

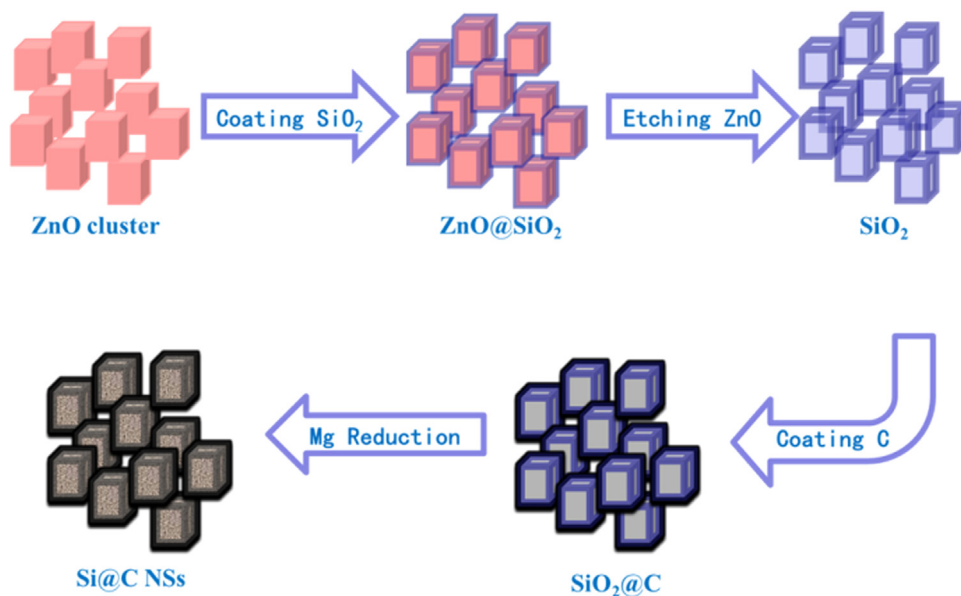


Fig. 1. Schematic illustration of the synthetic route for Si@C NSs.

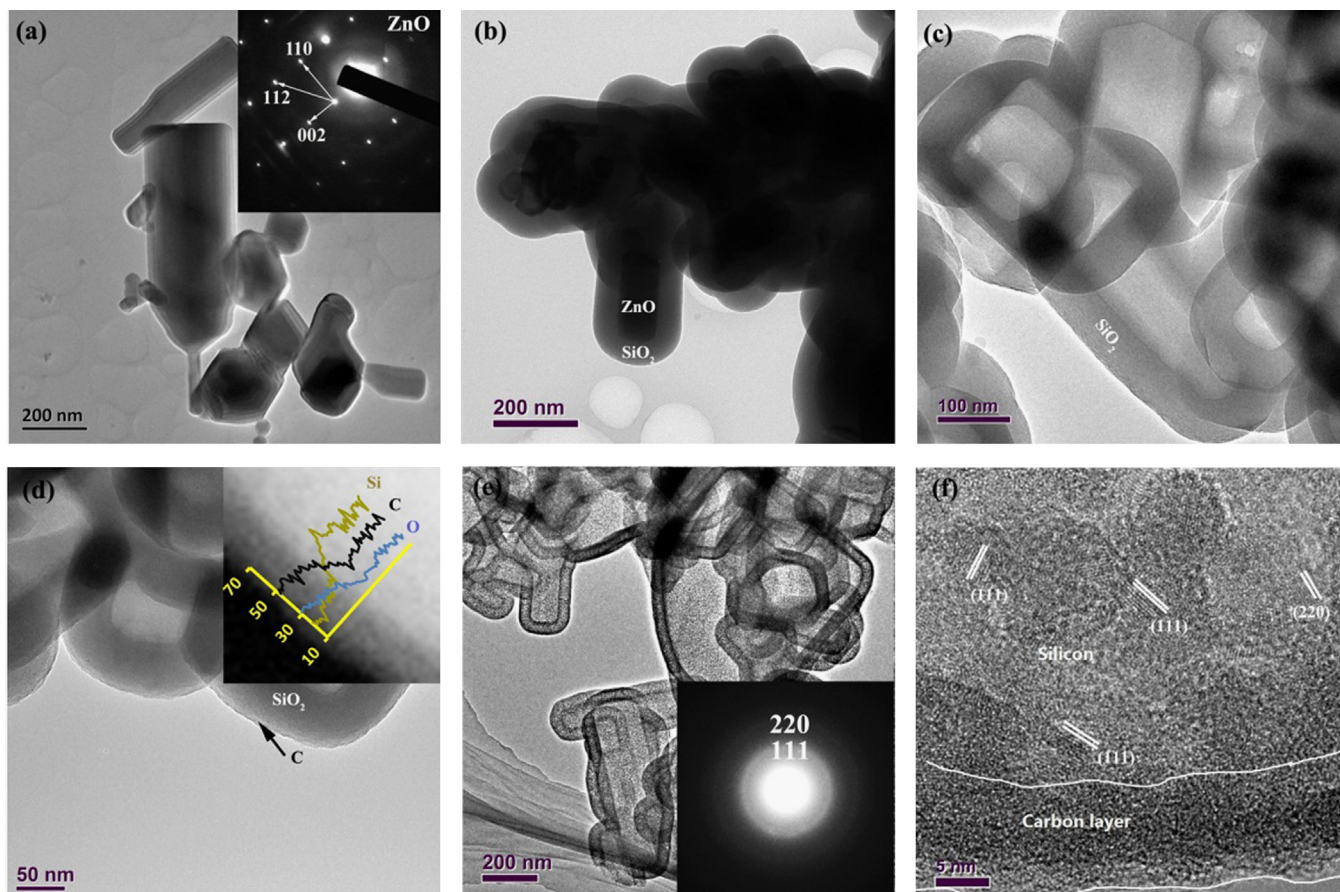


Fig. 2. TEM images of (a) ZnO, (b) ZnO@SiO₂, (c) SiO₂, (d) SiO₂@C, (e) Si@C and (f) HRTEM image of Si@C. The inset of (d) is High Angle Annular Dark Field (HAADF) image of SiO₂@C and its EDS elemental line-scan. The inset of (e) is the selected area electron diffraction pattern of Si@C NSs.

and mixed with glucose solution (0.5 M, 10 mL per gram SiO₂ NSs), and finally hydrothermally reacted under 180 °C for 5 h to fabricate carbonaceous layer. The resulting black product (mostly SiO₂@C) was

vacuum filtrated and dried under 80 °C for more than 4 h. Finally, the SiO₂@C NSs were magnesiothermally reduced at 650 °C for 2 h under argon gas protection to form Si@C NSs. Si nanospheres (Si

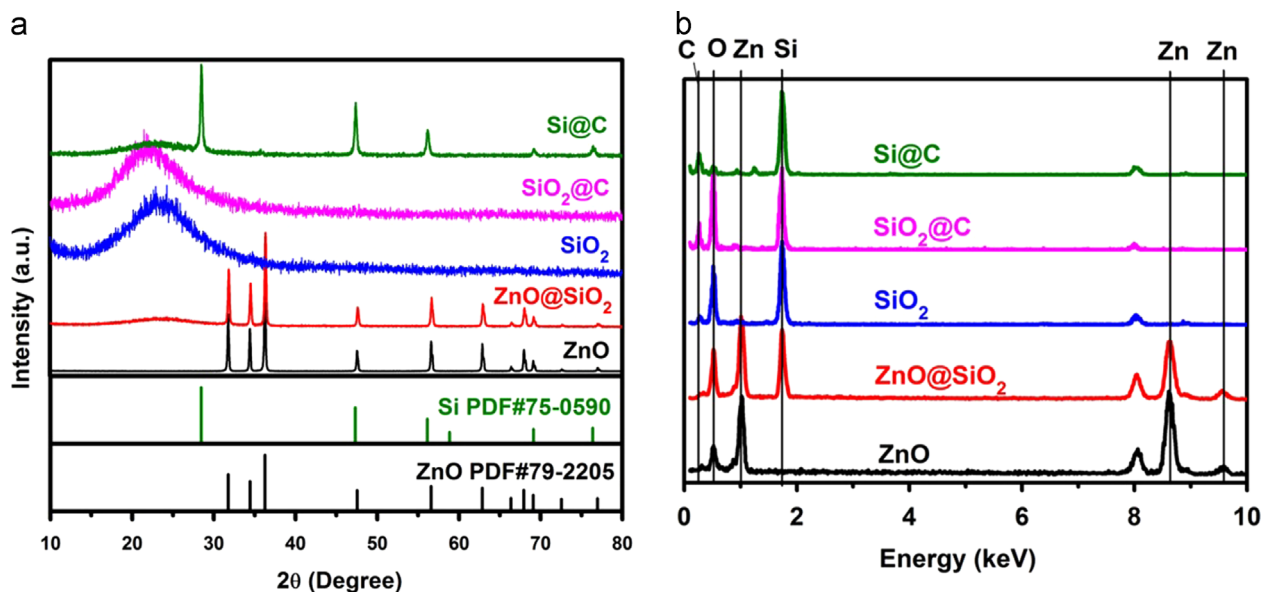


Fig. 3. (a) XRD and (b) EDS results of products from each synthetic step.

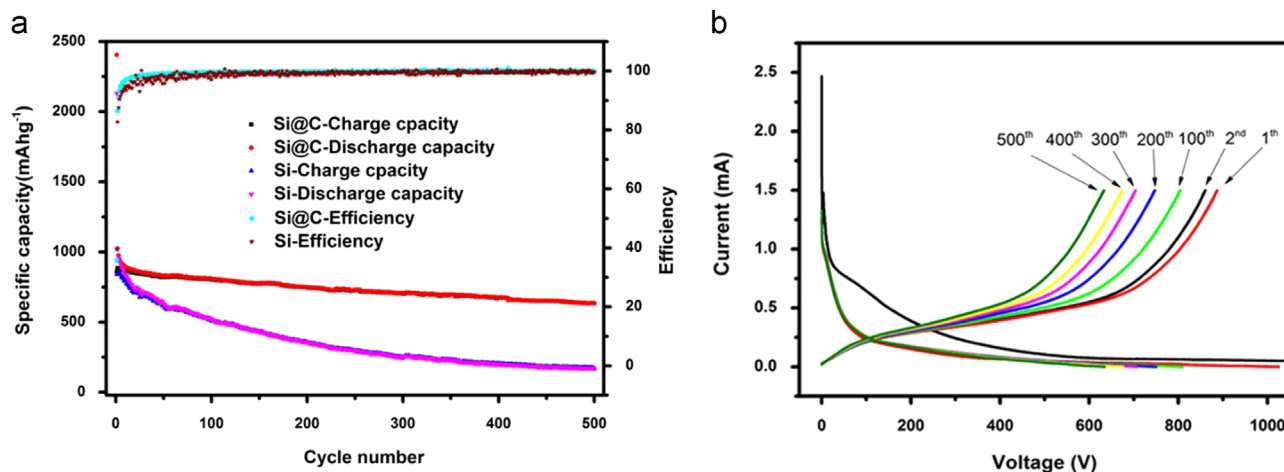


Fig. 4. (a) Electrochemical cycling results for Si NSs and Si@C NSs electrode. (b) Voltage profiles plotted for the 1st, 2nd, 100th, 200th, 300th, 400th and 500th cycles for Si@C NSs electrode.

NSs) as a reference material were also synthesized by the same method without using glucose to form carbon coating.

The phase structures of products obtained at each synthetic step were characterized using powder X-Ray Diffractometer (XRD Ultima IV). Microstructures of the samples were examined using TEM (JEM-2100F) equipped with Oxford energy dispersive spectroscopy (EDS) system. The electrodes were prepared by a mixture of Si@C NSs active material, acetylene black and polyvinylidene fluoride binder (weight ratio = 7:2:1), which were then dispersed in *N*-methyl-2-pyrrolidone (NMP). The resulting slurry was cast on a Cu foil using a 120 μm gap opening blade and then dried in vacuum at 80 °C to remove the NMP. After compressing at 10 MPa pressure, the cells were assembled in an argon-filled glovebox with Li foil as counter electrode. The electrolyte used was 1 M LiPF₆ in a 50:50 weight ratio ethylene carbonate (EC): dimethyl carbonate (DMC) solvent. Electrochemical investigations were conducted using a CT 2001 battery tester.

3. Results and discussion

TEM (Fig. 2), XRD (Fig. 3(a)) as well as EDS (Fig. 3(b)) characterization of the product at each synthetic step confirms the validity of the designed process. XRD patterns clearly show the transformation processes from ZnO to ZnO@SiO₂, SiO₂ and finally Si (Fig. 3(a)). The ZnO template consists of multiple ZnO nanorods with the mean diameter of 50–200 nm and length about hundreds of nanometers (Fig. 2(a)). After being treated with tetraethoxysilane (TEOS), silica shells were coated on ZnO templates (Fig. 2(b)). It is worth to note that the ZnO@SiO₂ particles are interconnected by the SiO₂ shells with a thickness of 50 nm. Hollow SiO₂ with nanosponge-like morphology can be obtained by removing the ZnO template (Fig. 2(c), Fig. 3). A thin carbonaceous layer was then coated on these SiO₂ nanospheres by crosslinking and polymerization from glucose (see Fig. 2(d), and the inset for EDS line-scan analysis which gives a molar ratio of Si:C:O ≈ 55%:30%:15%). The SiO₂@C NSs are finally transformed to crystallized Si@C NSs (see

Fig. 2(e)) by magnesiothermic reduction process in which the carbonaceous layer can be further reduced to carbon layer [13]. XRD (Fig. 3(a), electron diffraction (inset in Fig. 2(e)) and high-resolution transmission electron microscopy (HRTEM) (Fig. 2(f)) clearly visualize high crystallinity of polycrystalline Si@C NSs. The obtained Si@C NSs exhibit the same sponge-like morphology as SiO₂@C NSs, except that every cell wall in the sponge is constructed by aggregated Si nanoparticles in the size of several nanometers.

Electrochemical cycling performance of Si@C NSs electrodes examined at 200 mA g⁻¹ indicates that Si@C NSs exhibit superiority in term of specific capacity and cycling stability by comparison with that of Si nanosponges without carbon coating (Si NSs). The first discharge and charge capacities for Si@C NSs electrode were 2408 and 860 mA h g⁻¹, respectively, suggesting an initial coulombic efficiency of 35.7% (Fig. 4(a)). However, the discharge capacity dropped dramatically (~1025 mA h g⁻¹) at the second cycle owing to the formation of SEI. Fig. 4(b) shows the typical charge–discharge curves of Si@C NSs measured between 0 and 1.5 V. In the initial discharge (alloying reaction between Si and Li), two main plateau at 0.8 V and 0.3 V appeared. The former is associated with electrolyte decomposition and concomitant SEI formation on the electrode surface. The latter at 0.3 V is indicative of the alloying reaction between crystalline Si and Li [14]. An increase in charge capacities has been observed at the second cycle, which could be due to the activation of more Si atoms reacting with Li [15]. In the following cycles, the Si@C NSs electrode displayed a very small decrease of capacity, i.e. about 6% decreasing per hundred cycles while the Si NSs electrode exhibits a rapid decrease. The excellent stability could be ascribed to the hollow structure of Si@C NSs, which provides enough space for alleviating the effect of volume change during cycling while the interconnected structure of Si@C NSs further prevents pulverization of electrode materials. Moreover, the carbon layer could help to form relatively stable SEI layers [16]. Though a high-yield and facile synthetic route for Si@C NSs electrode is achieved in the present study, it should be noted that the as-prepared Si@C NSs showed a much lower initial coulombic efficiency (~35%) than commercial graphite (90%). The main reason could be the presence of residual O (see XRD and EDS results in Fig. 3) in both silicon and carbon layer. More efforts should be made to lower the O content to improve the initial coulombic efficiency while still keep the good cycling stability.

4. Conclusion

In summary, low-cost and easy to scale-up method is demonstrated for the synthesis of Si@C NSs with nontoxic ZnO nanoclusters

as sacrificial templates and glucose as carbon source based on magnesiothermic reduction kinetics. The as-prepared Si@C NSs exhibit sponge-like morphology with size of ~100 nm in internal diameter and 50 nm in wall thickness. Electrochemical performance of Si@C NSs served as anode material in Li-ion batteries shows a reversible capacity of 617 mA h g⁻¹ with little fading after 500 cycles. The hollow interconnected structure and the skeleton carbon coating must be responsible for the superiorities of Si@C NSs, which could effectively prevent structural fracture during alloying–dealloying processes. The as-prepared Si@C NSs could be a potential candidate for high-performance anode material in advanced Li-ion batteries.

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