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Graphical Abstract

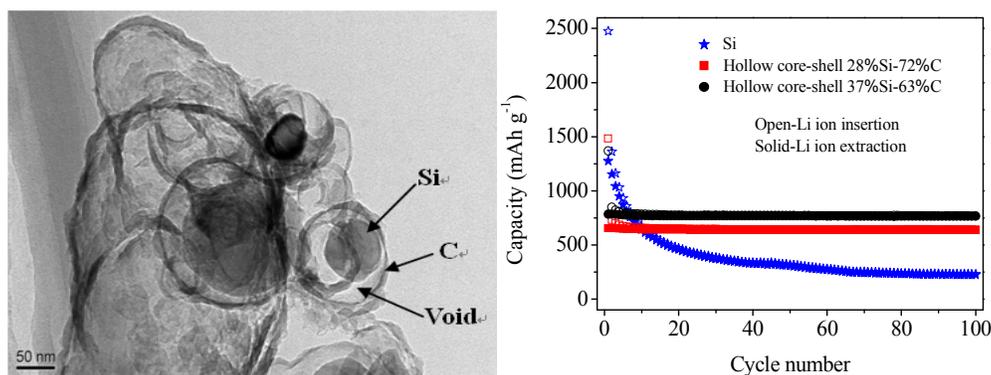
Hollow core-shell structured Si/C nanocomposites as high-performance anode materials for lithium-ion batteries

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Hollow core-shell structured Si/C nanocomposites were prepared to adapt for the large volume change during charge/discharge process. The Si nanoparticles are well encapsulated in a carbon matrix with internal void space between Si core and carbon shell. The hollow core-shell structured Si/C nanocomposites demonstrate a high specific capacity and excellent cycling stability, with capacity decay as small as 0.02% per cycle. The enhanced electrochemical performance can be attributed to the fact that the internal void space can accommodate the volume expansion of Si during lithiation, thus preserving the structural integrity of electrode materials, and carbon shell can increase the electronic conductivity of electrode.

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PAPER

Hollow core-shell structured Si/C nanocomposites as high-performance anode materials for lithium-ion batteries

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Hollow core-shell structured Si/C nanocomposites were prepared to adapt for the large volume change during charge/discharge process. The Si nanoparticles were coated with a SiO₂ layer and then carbon layer followed by etching the interface SiO₂ layer with HF to obtain the hollow core-shell structured Si/C nanocomposites. The Si nanoparticles are well encapsulated in a carbon matrix with internal void space between Si core and carbon shell. The hollow core-shell structured Si/C nanocomposites demonstrate a high specific capacity and excellent cycling stability, with capacity decay as small as 0.02% per cycle. The enhanced electrochemical performance can be attributed to the fact that the internal void space can accommodate the volume expansion of Si during lithiation, thus preserving the structural integrity of electrode materials, and carbon shell can increase the electronic conductivity of electrode.

Introduction

Lithium ion batteries with high energy density and long cycle life are generally employed in portable electronic devices and recently electric vehicles. Various efforts have been made to improve their energy and power densities, prolong cycle life. Among various anode materials, silicon has been extensively investigated due to its highest theoretical capacity (4200 mAh g⁻¹) and low charge-discharge potentials (<0.5 V vs. Li/Li⁺).^{1,2} However, the significant volume changes (>300%) of Si during lithium ions insertion and extraction cause cracking and crumbling of electrode materials and fast capacity loss.^{3,4} In addition, the practical application is limited by the intrinsic low electric conductivity of Si. To overcome these barriers, nanostructured silicon such as silicon nanowires,⁵ silicon nanotubes,⁶ silicon nanoparticles,^{7,8} silicon nanoarrays⁹ and silicon nanonests¹⁰ have been used to enhance the electrochemical performance through accommodating the volume strain and shortening the Li diffusion path lengths. In addition, hollow or porous structure can effectively buffer the volume strain of Si-based materials during the charge-discharge process, thus preventing the crumbling of active materials and the breaking of the conduction network. Porous Si-based electrode materials such as three-dimensional (3D) porous Si@C composite,¹¹ 3D macroporous Si@Ag composites¹² and porous Si@C nanorods¹³ have been prepared to improve the cycle performance. Recently, hollow Si nanospheres¹⁴ and hollow Si/C nanocomposites¹⁵ have been studied to enhance the performance as anode for lithium ion batteries. The pre-existing hollow structure can provide space for volume expansion of Si, thus preserving the structural integrity of electrode materials and preventing the capacity from fading.

Furthermore, many efforts have focused on reducing huge volume changes using the core-shell structured Si/C^{16,17}

nanocomposites to enhance the cycling stability. The carbon core or shell experiences less structural stress or damage during lithium ions insertion/extraction process and can act as a mechanical support for strain release. And the carbon core or shell can provide an efficient electron conducting pathway, improve the electronic conductivity and stabilize the solid electrolyte interphase layer (SEI) of Si anode. In addition, the core-shell structure can combine the advantages of both Si and carbon and display the core-shell synergistic effects.

Taking advantages offered by both hollow nanostructure and core-shell structure, we herein report hollow core-shell structured Si/C nanocomposites with internal void space synthesized for enhanced discharged capacity as anodes for lithium ion batteries. The advantage of this structures lies in the presence of the internal void space to accommodate the large volumetric expansion of silicon during lithiation, thus preserving the structural integrity of the electrodes.

Experimental

Fabrication of hollow core-shell structured Si/C nanocomposites

The silicon nanoparticles (~100 nm, 99.99%) were purchased from Hefei Kaier Nanometer Energy&Technology Co., LTD. The hollow core-shell structured Si/C nanocomposites with internal void space were synthesized by three steps. Firstly, 100 mg Si nanoparticles were uniformly dispersed into a 240 mL deionized water and ethanol (1:1 by volume) solution. Then, 30 mL ammonia water (30 wt%) was added into this solution. To form a layer of SiO₂ coating on the surface of Si nanoparticles, 8 g tetraethyl orthosilicate was dropwise dropped into the above solution under vigorous stirring. Secondly, the Si@SiO₂ nanocomposites were calcined at 950 °C for 3 h and 7 h under

nitrogen atmosphere at a flow rate of 200 standard cubic centimeters per minute. A carbon layer was coated by chemical vapor deposition using the toluene as carbon source. Finally, the obtained Si@SiO₂/C composites were etched with 30% HF solution for 12 h to remove the SiO₂ layer. The resulted solid was washed with water and dried in a vacuum oven.

Structural and electrochemical characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku/mac 250 diffractometer using Cu K α radiation. The morphology was carried out on a JEM-200CX high-resolution transmission electron microscope (HR-TEM) and a JSM-6330 field emission scanning electron microscopy (FE-SEM). Raman spectra were recorded using a 514.5 nm Ar-Ion laser on HR800. Thermogravimetric analysis (TGA) was carried out in air from 25 °C to 1000 °C by using a Perkin-Elmer 2400II analyzer.

The as-prepared hollow core-shell structured Si/C nanocomposites were used as the electrode materials for rechargeable lithium ion batteries. The working electrodes were prepared by mixing the active materials (hollow core-shell structured Si/C nanocomposites or Si nanoparticles) with Super P, and polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP) with the weight ratios of 8:1:1 to form a slurry, which was then pasted on a copper foil and dried under vacuum at 120 °C. The coin cells were cycled from 0.01-1.5 V versus Li⁺/Li using lithium foil as the counter electrode. The electrolyte was 1M LiPF₆ in a mixture of ethylene carbonate (EC) / dimethyl carbonate (DMC) / ethylmethyl carbonate (EMC) in a 1:1:1 volume ratio. A microporous membrane (Celgard 2400) was used as the separator. The cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen below 1 ppm. Galvanostatic charge-discharge tests were carried out using a LAND battery tester from 0.01 to 1.5 V at a current density of 100 mA g⁻¹. Specific capacity values were calculated based on the weight of active materials.

To further understand the improved electrochemical performance of hollow core-shell structured Si/C nanocomposites, the morphology of electrode materials after 20 cycles was observed. The electrode for characterizing morphology was prepared by coating active materials and PVDF in a weight ratio of 9:1 on copper foil. The counter electrode, separator, electrolyte and electrochemical testing parameters are the same as the above experiments. The cycled electrode materials were immersed in NMP to remove the binder PVDF. The resulting solid was filtered and dried in a vacuum oven. The morphology of hollow core-shell Si/C nanocomposite after 20 cycles was obtained in the discharged state.

Results and discussion

Bare Si nanoparticles undergo large volumetric expansion during lithiation process, and cause the pulverization of the electrode materials, thus resulting in rapid capacity decay (Figure 1a). Although the conventional core-shell morphology provides a protective coating, cracking of the shell may occur upon volume expansion of Si during lithiation (Figure 1b).¹⁸⁻²⁰ The hollow core-shell morphology provides internal void space to accommodate the volume expansion of Si during lithiation,

resulting in a structural integrity of electrode materials (Figure 1c).^{21,22} In comparison with bare Si and core-shell structured Si/C nanocomposites, the advantage of hollow core-shell structures lies in the presence of the internal void space to accommodate the large volumetric expansion of silicon during lithiation, thus preserving the structural integrity of the electrodes.

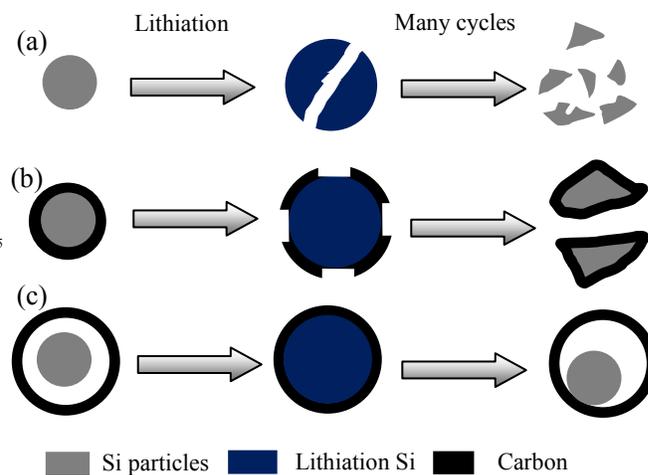


Figure 1 Schematic diagram of the lithiation process in various Si-based electrodes. (a) bare Si nanoparticles, (b) core-shell structured Si/C nanocomposites, (c) hollow core-shell structured Si/C nanocomposites.

Figure 2a illustrates the schematic diagram of the fabrication procedure and the morphology of hollow core-shell structured Si/C nanocomposites with internal void space. Si@SiO₂/C nanocomposite was obtained by coating SiO₂ layer on the surface of Si particles followed by coating a carbon layer using chemical vapor deposition method. Subsequently, the interface SiO₂ layer was removed with HF solution etching to achieve hollow core-shell structured Si/C nanocomposites. From the TGA curves (Supporting Information Figure S1), the carbon contents of hollow core-shell structured Si/C nanocomposites heated at 950 °C for 3 h and 7 h are 63 wt% and 72 wt%, and the corresponding silicon weight contents are 37 wt% and 28 wt%, respectively. According to the different carbon and silicon contents, the hollow core-shell structured Si/C nanocomposites heated for 3 h and 7 h are abbreviated as hollow core-shell 37%Si-63%C and hollow core-shell 28%Si-72%C.

TEM image of hollow core-shell 37%Si-63%C nanocomposite indicates that Si nanoparticles are well encapsulated in carbon shell, and the internal void space between Si core and carbon shell is also observed (Figure 2b). The hollow core-shell structured nanocomposite has a Si particle ~100 nm with voids ranging from tens of nanometers between Si core and carbon shell. The void space in the structure mainly depends on the thickness of SiO₂ layer. In addition to the voids between Si cores and carbon shells, a porous structure of carbon also exists in the composite. The HR-TEM image in Figure 2c further proves that the crystalline Si is encapsulated in carbon layer and the void structure exists between Si and carbon. Si cores have point contact to the carbon shells instead of being suspended in the

centers. The contact of silicon core and carbon shell is beneficial to transport of electrons and lithium ions in the electrode materials. The marked d-spacing of 0.31 nm corresponds well with that of (111) plane of Si.

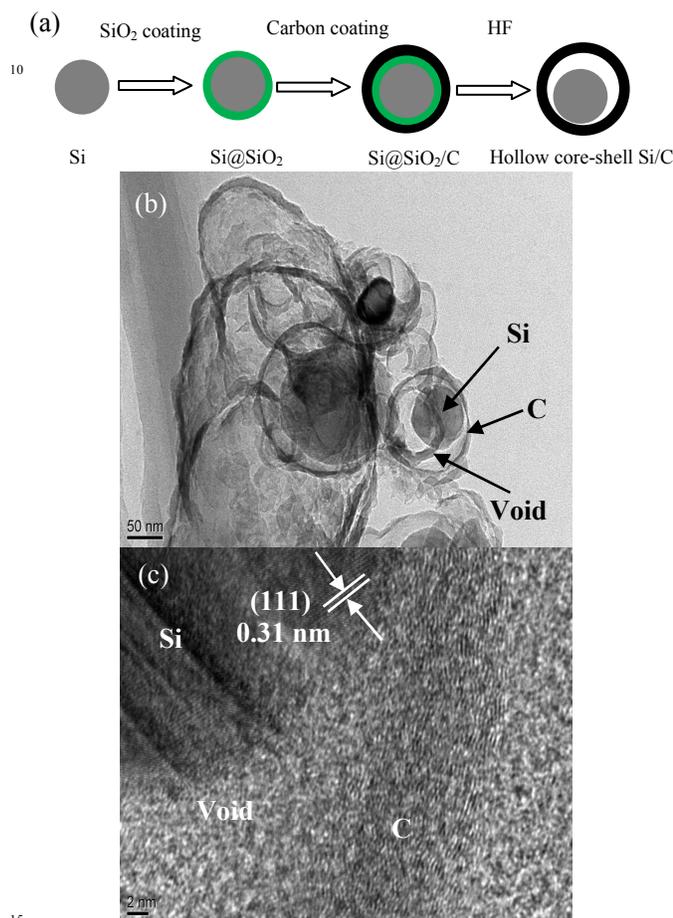


Figure 2. (a) A schematic diagram of the fabrication of hollow core-shell structured Si/C nanocomposites; (b) TEM image and (c) HR-TEM image of hollow core-shell 37%Si-63%C nanocomposite.

Figure 3 presents XRD patterns and Raman spectra of hollow core-shell structured Si/C nanocomposites and Si nanoparticles. For the hollow core-shell structured Si/C nanocomposites, the appearance of a broad diffraction peak at $2\theta=26.5^\circ$ for the graphite, indicating that the carbon shell is partly graphitization. The diffraction peaks of the hollow core-shell structured Si/C nanocomposites appear at 28.4° , 47.3° and 56.1° can be as the (111), (220) and (311) planes of Si crystallites (JCPDF NO. 27-1402), respectively, suggesting the presence of both carbon and Si nanoparticles. An obvious difference can be observed in the Raman spectra between Si nanocomposites and hollow core-shell structured Si/C nanocomposites (Figure 2b). In the case of hollow core-shell structured Si/C nanocomposites, the peak at about 515 cm^{-1} is in agreement with the spectrum of Si nanoparticles, while the peaks at 1355 cm^{-1} and 1585 cm^{-1} correspond to the D band and G band of carbon, respectively.²³ The intensity ratio of the D band and the G band is 0.95 and 0.98 for hollow core-shell 28%Si-72%C and hollow core-shell 37%Si-63%C, respectively, indicating the presence of the graphitization carbon in

the nanocomposites,²⁴ which is consistent with the above XRD results.

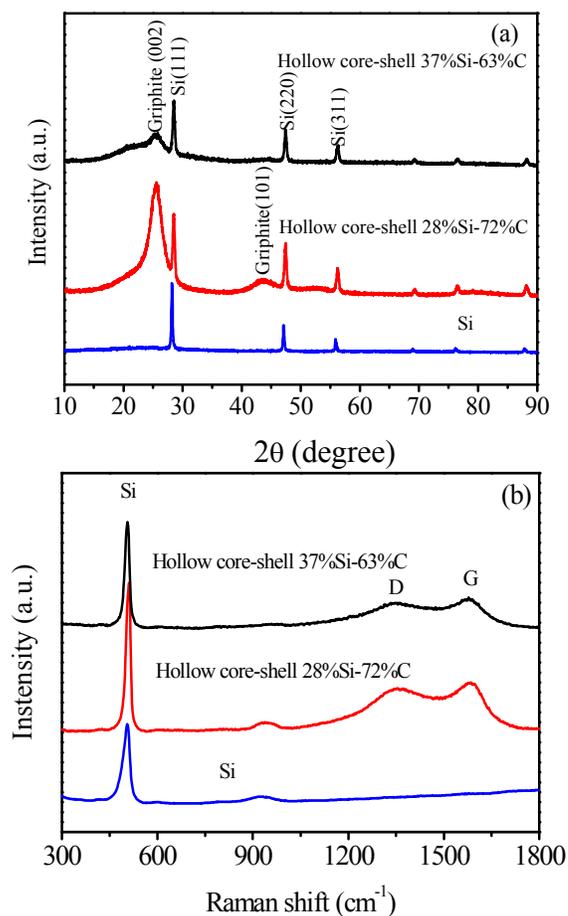


Figure 3. (a) X-ray diffraction patterns and (b) Raman spectra for hollow core-shell structured Si/C nanocomposites.

The first discharge (lithium insertion)-charge (lithium extraction) curves of the hollow core-shell structured Si/C nanocomposites and Si nanoparticles at a rate of 100 mA g^{-1} are presented in Figure 4a. The hollow core-shell structured Si/C nanocomposites exhibit excellent stable cycling performance over 100 charge/discharge cycles at a rate of 100 mA g^{-1} as displayed in Figure 4b. The high initial discharge capacity of 1370 mAh g^{-1} for hollow core-shell 37%Si-63%C nanocomposite is approaching its theoretical capacity of 1788 mAh g^{-1} (the theoretical capacity of nanocomposite is based on the theoretical capacities of 372 mAh g^{-1} for carbon and 4200 mAh g^{-1} for Si), suggesting that the Si nanoparticles in the nanocomposite exhibit extremely high discharge capacity. After an initial charge capacity of 783 mAh g^{-1} , the hollow core-shell 37%Si-63%C nanocomposite achieves capacity retention of 98% at the end of 100 cycles, which corresponds to a very small capacity decay of 0.02% per cycle. It has relatively higher reversible capacity than hollow core-shell 28%Si-72%C nanocomposite because of the existence of less carbon in the hollow core-shell 37%Si-63%C

nanocomposite considering that the capacity of carbon is much lower than that of silicon. The huge initial irreversible capacity is due to the formation of SEI layer and the decomposition of electrolyte.^{25,26} In comparison, the hollow core-shell structured Si/C nanocomposites demonstrate higher capacity and better cycling stability than bare Si nanoparticles (Figure 4b). The low initial discharge capacity of about 2500 mAh g⁻¹ for bare Si electrode may be due to the agglomeration and low electronic and ionic conductivities of Si nanoparticles.

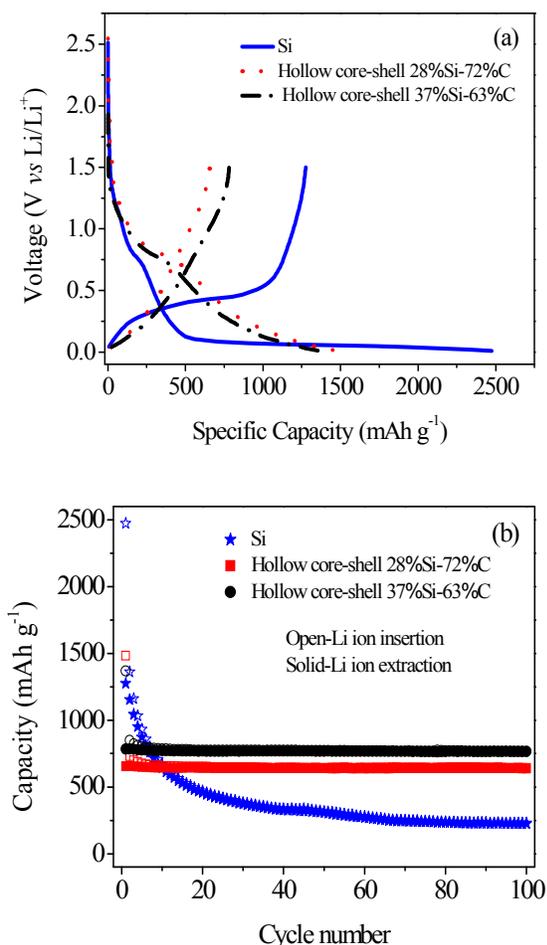


Figure 4. (a) The first charge-discharge curves of the hollow core-shell structured Si/C nanocomposites and Si nanoparticles at a rate of 100 mA g⁻¹; (b) cycling stabilities of hollow core-shell structured Si/C nanocomposites and Si nanoparticles at a rate of 100 mA g⁻¹.

There are two important characteristics of such a hollow core-shell design that imparts the Si/C nanocomposites with stable cycling performance. First, sufficient void space is present to allow for volume expansion of Si. In order to quantify the interlayer SiO₂ content in the nanocomposite, TGA of Si@SiO₂/C nanocomposite was carried out in air atmosphere from 50 to 1000 °C (Supporting Information Figure S2). It can be estimated that the weight content of carbon in the nanocomposites are about 63 wt% and 30 wt% for the hollow core-shell 37%Si-63%C nanocomposites and the corresponding

Si@SiO₂/C nanocomposites, respectively. In the case of Si@SiO₂/C nanocomposite, the total weight contents of Si and SiO₂ are about 70 wt%. The carbon content is supposed to be invariant during the HF etching process, the weight ratio of the interface SiO₂ layer to Si nanoparticles is about 3 from Eq. (1).

$$\frac{W_{SiO_2}}{W_{Si}} = \frac{\frac{W_{Si} + W_{SiO_2}}{W_C} - \frac{W_{Si}}{W_C}}{\frac{W_{Si}}{W_C}} = \frac{70 - 37}{30 - 63} = 2.97 \quad (1)$$

Where W_{SiO_2} , W_{Si} and W_C are the weight contents in the nanocomposite, respectively. The volume of empty space in the hollow core-shell 37%Si-63%C nanocomposites is estimated to be more than 300% of Si nanoparticles because the density of the SiO₂ nanoparticles is less than that of Si nanoparticles. This volume of void space can be accommodated ~300% volume expansion of the Si present within the shell. Therefore there is sufficient void space for volume expansion without causing the shell crack and fracture. To characterize the morphology of hollow core-shell structured Si/C nanocomposites after many cycles, the morphology of hollow core-shell 37%Si-63%C nanocomposites before and after 20 cycles were observed (Figure 5). Compared with the pristine morphology, there is no obvious change for hollow core-shell 37%Si-63%C nanocomposite after 20 cycles and the particles are still intact without cracking, suggesting that the existing empty volume is allow to accommodate the volume expansion of Si without causing the carbon shell crack and fracture. Moreover, the intact carbon shell is effective in increasing the electrical conductivity.

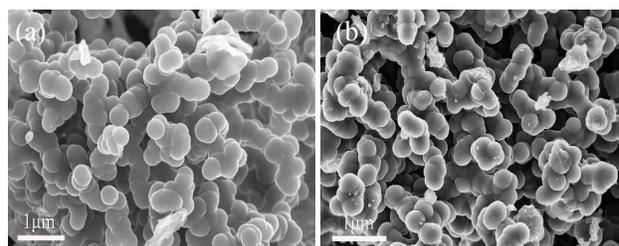


Figure 5. FE-SEM images of hollow core-shell 37%Si-63%C nanocomposite: (a) before and (b) after 20 cycles.

Conclusion

In summary, the hollow core-shell structured Si/C nanocomposites exhibit a high specific capacity and capacity retention owing to the presence of internal void space to accommodate the volume expansion of Si during lithiation, resulting in an intact shell to provide the integrity of Si-based electrode materials. The enhanced electrochemical performance can be attributed to the fact that the void structure between carbon shell and Si core can efficiently suppress the volume effect of the Si particles and carbon in composites can increase the electronic conductivity of electrode. This structural design can be applied to other undergoing large volumetric expansion electrode materials, and provides a wide insight for the fabrication of other high-capacity

lithium-storage materials with a huge volume variation and poor electronic conductivity.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: TGA curves of hollow core-shell structured Si/C nanocomposites, and Si@SiO₂/C nanocomposite.
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65