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ARTICLE TYPE

Facile synthesis of yolk-shell structured Si-C nanocomposites as anode for lithium-ion battery

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Yolk-shell structured Si-C nancomposites are easily synthesized by using a new method based on alkaline etching technology, and exhibit high specific capacity, good cycling stability and rate performance as anode for lithium-ion
10 **battery.**

The development of lithium-ion batteries (LIBs) with high energy density, high power density, long life and low cost is of great importance for applications such as electrical vehicles, portable electronic devices and renewable energy storage.[1,2] To meet these 15 requirements, the electrode materials of LIBs must have high specific capacity and good cycle life. Silicon (Si) is considered to be one of the most promising anode materials for next-generation LIBs because of its natural abundance, low discharge potential, and most importantly its high theoretical specific capacity (4200 20 mAh g^{-1}), which is ten times higher than that of traditional graphite anodes (370 mAh g^{-1}).[1,2] However, the practical application of Si anodes has been mainly hindered by low intrinsic electrical conductivity of Si, and the enormous volume change during the lithiation/delithiation process.[1,2] The volume 25 change can cause bulk Si to be pulverized and lose electrical contact with the conductive additive or current collector, and will also lead to instability of the solid electrolyte interphase (SEI) resulting in continuous consumption of the electrolyte for reformation of SEI layers, both of which thus lead to a fast 30 capacity fading in the LIBs.[2] In order to solve these issues, considerable efforts have been made, such as the development of Si materials composed of nanostructures,[3,4] porous structures,[5,6] or nanocomposites,[7,8] the addition of electrolyte additives[9] and the use of novel binders.[10]

35 Among these efforts, Si-C nanocomposites with yolk-shell (or named hollow core-shell) structure have been considered as one type of promising materials for applications in LIBs. For example, Si-C nanocomposites in which Si nanoparticles (SiNPs) are encapsulated into hollow carbon materials, such as Si-hollow 40 carbon nanotubes[11] and Si-hollow carbon spheres,[12] can not only increase electrical conductivity of nanocomposites, but also provide built-in buffer voids for SiNPs to expand freely without damaging the carbon layer. However, the Si-hollow carbon materials require a sophisticated binder-free fabrication process. 45 In comparison, direct synthesis of Si-C nanocomposites with the yolk-shell structure shows good electrochemical performance for LIBs, and is suitable for scalable fabrication.[13-15] Liu et al. prepared the Si-C yolk-shell structured nanocomposites using a conventional industrial coating procedure (a gas-phase carbon 50 coating method).[13]Using the gas-phase carbon coating method, however, it is very difficult to obtain the conformal and homogeneous carbon coating in the Si-C composites. Uncoated (bare) Si surface can be found in their experiments. Cui et al.[14] and Wang et al.[15] reported a solution growth method to 55 synthesize the Si-C yolk-shell structured nanocomposites. In their approaches, SiNPs were first coated with SiO_2 sacrificial layer by using the sol-gel process, and then conformably coated with a polydopamine (PODA) layer followed by carbonization to form a nitrogen-doped carbon coating, and finally treated by 60 hydrofluoric acid (HF) to remove the SiO_2 sacrificial layer. With their approaches, SiNPs were completely sealed inside conformal, thin and self-supporting carbon shell. However, the sol-gel processing for the coating SiO_2 layer onto SiNPs demands precise control reaction conditions, such as pH and concentration of 65 reagents.

Herein, we reported a novel method to synthesize the yolk-shell structured Si-C nanocomposites based on the reaction listed as follows:

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2 \uparrow (1)$$
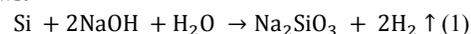
70 A carbon shell was first coated onto the commercialSiNPs followed by selective NaOH alkaline etching of Si to obtain the yolk-shell structured Si-C nanocomposites. In comparison with the synthesized methods preciously, our method is more economic and scalable. In general, the more smaller is the 75 diameter of the SiNPs, the more better electrochemical performance of LIBs is.[1,2] However, the preparation of the smaller size SiNPs is normally used by some complicated processes such as laser irradiation and chemical vapor deposition (CVD).[16]These processes require special and expensive 80 equipments, which will increase the production cost. In our method, it is easily to control the diameter of the SiNPs and the void space between the SiNPs and the carbon shell by using the NaOH etching time, do not need any special equipments. Then, some economic Si particles with bigger diameters can be used, 85 which will reduce the production cost as well. In addition, the reaction rate of the equation (1) is normally too slow at room temperature, however, the rate will be too fast at high temperature (60-90 °C). In our experiments, it only took several minutes to obtain the yolk-shell structured Si-C (Si@Void@C) 90 nanocomposites. In addition, NaOH aqueous solution used in our experiments is more safety compared with HF aqueous solution used in the method reported by Cui et al.[14] and Wang et al..[15] The

whole fabrication is scalable, and the powder-like Si@Void@C product is fully compatible with current slurry coating technology (Fig. S1).
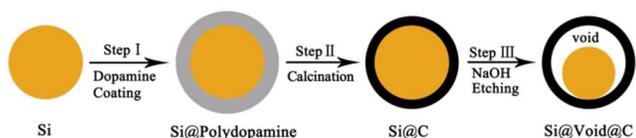
Fig. 1 Schematic illustration of the synthesis process of Si-C nanocomposites with yolk-shell structure.

The Si@Void@Cnanocomposites were prepared through a three-step method shown in Fig. 1. First, the PODA layer was spontaneously coated onto the surface of the commercial Si nanoparticles (an average diameter about 100 nm, see Fig. S2) through the self-polymerization of dopamine in Tris-buffer (pH 8.5) aqueous solution in the presence of oxygen at room temperature. The PODA layer was confirmed by Fourier transform infrared spectroscopy (FT-IR) measurements (see Fig. S3). Subsequently, the PODA layer was converted into carbon layer by calcinations in argon atmosphere at 800 $^\circ$C. Through such process, core-shell Si@Cnanocomposites with inner Si nanoparticle and an outer carbon shell with about 5-8 nm were obtained (Fig. 2b). Then, the Si@Cnanocomposites were put into 0.5M NaOH aqueous solution, and etched for 10 minutes at 60 $^\circ$C. After this treatment, the Si@Void@Cnanocomposites were obtained after centrifugation and washing several times with de-ionized water (Fig. 2c and 2d).
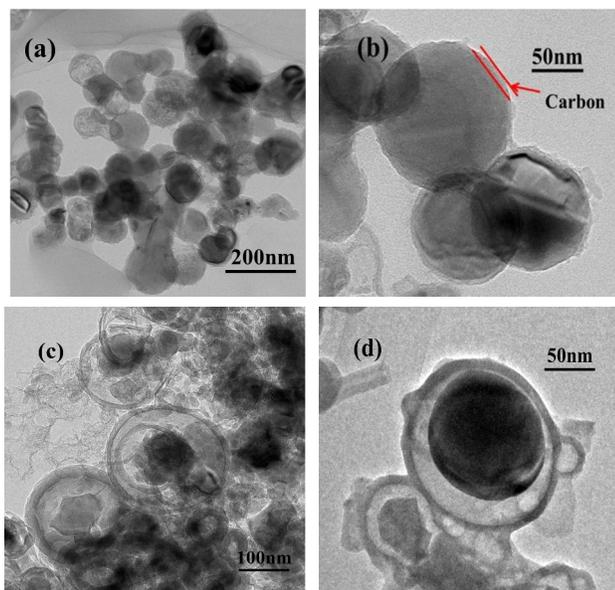
Fig. 2 TEM images of Si@C (a, b) and Si@Void@C (c ,d) nanocomposites.

The void space between carbon shell and SiNPs core depends on factors such as SiNPs size, NaOH etching time and temperature. Assuming a 300-400 volume change after full lithiation, the void space in the Si@Void@C nanocomposites should be >30 nm to accommodatethe volume change without rupturing the shell (see Fig 2d). From Fig. 2, it can be found that the carbon shell did not change after the NaOH etching. In addition, the average diameter of the Si@Void@C was about 100 nm (see Fig. 2c), which is similar to that of the bare SiNPs. The

Si content of our Si@Void@C is about 75 wt% confirmed by
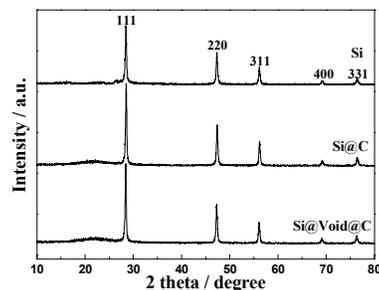
TGA measurement (see Fig S4).

Fig. 3 X-ray diffraction patterns of Si, Si@C and Si@Void@Cnanocomposites.

Fig. 3 shows the X-ray diffraction (XRD) patterns of the SiNPs, Si@C and Si@Void@Cnanocomposites. It can be found that five diffraction peaks at 28°, 47°, 56°, 69° and 76° appear in all the samples, which can be indexed to the cubic diamond phase of crystalline Si (JCPDS card no. 27-1402).[17]A very board peak between 20° and 25° can be found in the patterns of Si@C and Si@Void@Cnanocomposites, which is attributed to the
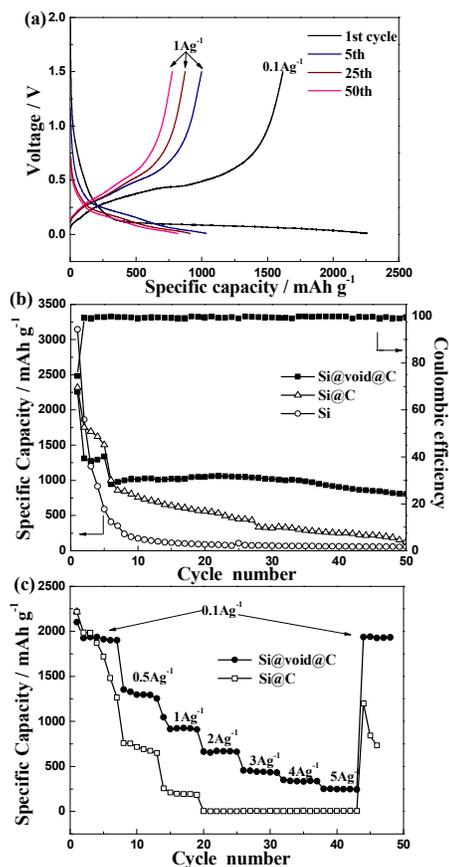
amorphous carbon (carbon shell).

Fig. 4 Electrochemical performance of electrodes. (a) Discharge-charge profiles of the Si@Void@C nanocomposites for first, 5th, 25th and 50th cycles. (b) Cycling stability of the Si, Si@C and Si@Void@C nanocomposites. All electrodes were cycled at 0.1 A g^{-1} for the first cycle, 0.5 A g^{-1} for 4 cycles and 1 A g^{-1} for the later cycles. (c) Rate performance of the Si@C and Si@Void@Cnanocomposites.

The electrochemical performance of the Si@Void@C nanocomposites were shown in Fig. 4. The specific capacity values reported are calculated on the basis of the total weight of the Si@Void@C nanocomposites, in which SiNPs comprise about 75 wt% of the mass determined by TGA measurement. Since the carbon shell is also lithiated, therefore, the specific capacity of the Si@Void@C nanocomposites was contributed by both the SiNPs and the carbon shell. Fig. 4a shows the discharge-charge profiles of the Si@Void@C nanocomposites after different cycles. A long discharge plateau below 0.2 V due to the Si crystalline structure was observed in the first discharge. The reversible capacity reaches 2258 mAh g^{-1} for the first cycle at 0.1 A g^{-1} and remains at 900-1000 mAh g^{-1} at 1 A g^{-1}.

The yolk-shell structured Si-C nanocomposites show good cycling stability and high rate performance. The cycling performance of the Si, Si@C and Si@Void@C electrodes were shown in Fig. 4b. The rate was 0.1 A g^{-1} for one cycle, then 0.5 A g^{-1} for 4 cycles, and 1 A g^{-1} for the later cycles. Due to the presence of carbon shell, the initial specific capacities of both Si@C (2318 mAh g^{-1}) and Si@Void@C (2258 mAh g^{-1}) nanocomposites were lower than that of the SiNPs (3144 mAh g^{-1}) at a current density of 0.1 A g^{-1}. However, a rapid decay of the SiNPs was observed upon further cycling, which is due to the pulverization and disruption of the electrode's microstructure caused by silicon expansion/contraction repeatedly without appropriate buffer space during the Li^+ insertion/extraction process. The similar results have also been reported in the literature.[17,18] A rapid decay of the Si@C (SINPs directly coated with carbon without the void space in between) electrode was found in our experiments. It indicates that the carbon shell on the Si@C nanocomposite is not enough strength to limit the volume change (300-400%) of Si during the lithiation/delithiation process. Compared with both the Si and Si@C electrodes, the Si@Void@C electrode shows higher specific capacity and better cycling stability. From Fig. 4b, it shows that the Si@Void@C exhibits a high capacity of ~977 mAh g^{-1}(354 mAh g^{-1} for Si, 858 mAh g^{-1} for Si@C) after formation cycles (formation of SEI film). After 50 cycles, the specific capacity of the Si@Void@C is about 804 mAh g^{-1}, which corresponds to ~83% capacity retention. These behaviours are attributed to the emergence of a void space between the carbon shell and SiNPs core which was prepared by etched by NaOH alkaline aqueous solution. The void space cushions the huge volume expansion during Li^+ insertion thus preserving the integrity of the electrode framework as a result that can improve the cycling stability of the electrodes. The similar results are also reported in the literature.[13-15] After 50 cycles, the yolk-shell structured of Si@Void@C was still observed in our experiments (see Fig. S5). It indicates that the yolk-shell Si@Void@C nanocomposite has good stability of structure. The Si@Void@C nanocomposites show not only high specific capacity and good cycling stability, but also good rate capability (shown in Fig. 4c). It can be observed that the rate performance of the Si@Void@C nanocomposites was much better than that of the Si@C nanocomposites with the current density from 0.1 A g^{-1} to 5 A g^{-1}. The discharge capacity was ~2200 mAh g^{-1} for the first cycle at 0.1 A g^{-1} which faded gradually with increasing rate, then stabilized to about ~928 mAh g^{-1} at 1 Ag^{-1}, ~670 mAh g^{-1} at 2 A g^{-1}, ~350 mAh g^{-1} at 4 A g^{-1}, and ~250 mAh g^{-1} at 5 A g^{-1},

respectively. When the rate was reset to 0.1 A g^{-1} after more than 40 cycles, the capacity was about 1938 mAh g^{-1}. It should be noted that these values were obtained from the samples without any specific efforts such as the binder and electrolytes without any optimization. However, the rate performance of our Si-C nanocomposites is higher than that of results reported in the literature.[13,17,18]

In summary, we reported a new approach to synthesize the yolk-shell structured Si-C nanocomposites using NaOH etching technology. This approach shows more simple, low-cost and scalable. Due to the protective effect of the carbon shell and the void space, the Si@Void@Cnanocomposites show high specific capacity, good cycling stability and rate performance. It opens up a new route to develop Si-based anodes for LIBs. Further work on the selection of Si materials with different diameter size, optimization of the amount of carbon shell, the selection and optimization of the binders or electrolytes are still under investigation.

Notes and references

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