Synthesis of porous Si nanoparticles for high performances anode material in lithium-ion batteries

**Feng Yang**1,* E, Yulong Dai1, Dehuai Peng1 and Kai Huang2,*

1 School of Mechanical and Electronic Engineering, Jingdezhen Ceramic Institute, Jiangxi, 333403, People’s Republic of China
2 School of Physics and Optoelectronics, Xiangtan University, Hunan, 411105, People’s Republic of China
* Authors to whom any correspondence should be addressed.

E-mail: yangfeng@jci.edu.cn and huangk@xtu.edu.cn

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**Abstract**

As one of the most promising candidates for anode materials, Si-based electrodes can offer specific capacity an order of magnitude beyond that of conventional graphite. However, Si usually suffers from dramatic volume changes during cycling cause pulverization and capacity fade. The key to improving cycle life is to synthesize Si-based materials with suitable architectures and a rational design. Here, we developed an economical and efficient method to obtain porous Si nanoparticles from coal ash. The Si nanoparticles with several nanometers can significantly shorten ion/electron transportation paths and further avoid the cracking and pulverization induced by large volume changes, and the porous structure makes the penetration of electrolyte easier. After carbonization, the obtained porous Si nanoparticles@C exhibits excellent electrochemical performances, and the special capacity can stable at 750 mAh g\(^{-1}\) at 2.0 A g\(^{-1}\) after 200 cycles. When current density up to 6.0 A g\(^{-1}\), the reversible capacity is 565 mAh g\(^{-1}\). We believe this method will make it possible to facilitate the large-scale and low-cost production of porous Si nanoparticles, and contribute to the development of high-performance Si-based anode materials.

1. Introduction

Si anodes have been triggered significant research efforts in lithium-ion batteries (LIBs), because of its unparalleled theoretical specific capacity of 4200 mAh g\(^{-1}\) forming crystalline Li$_4$Si at room temperature, about an order of magnitude higher than that of commercial graphite anodes (\(~\sim 370\) mAh g\(^{-1}\))\cite{1–5}. Despite these appealing advantages, high-capacity Si anodes show dramatic volume expansion (> 300%) during Li insertion and extraction, leading to electrode failure, rapid capacity fading and poor rate capability\cite{1–7}. In recent efforts, enormous methods have been proposed to synthesize variety nanostructures, such as nanowires\cite{1,8}, nanotubes\cite{6,9–11}, nanoparticles\cite{4,12–19}, nanospheres\cite{20–22}, and nanosheets\cite{23–27} etc, which can effectively shorten the transmission path of lithium ions and electrons, accommodate volume expansion to improve Si anode electrochemical performances.

Among them, porous Si nanostructures have attracted great attention because of the sufficient free space to accommodate the large volume expansion and facilitate the penetration of electrolyte, thereby maintaining electrical integrity in the electrode and enhancing the cycling stability\cite{28,29}. Recently, various approaches have been developed to synthesize porous Si nanostructures, such as the top-down method (electro-chemical or metal-assisted etching)\cite{30,31}, and template-assisted method\cite{32–34}. However, there are some difficulties in large-scale synthesis of porous Si nanostructures in the near term, because of the present complex processes and elaborate design, expensive reaction precursor, and even prohibitively high synthesis techniques (such as chemical vapor deposition system). So, how to synthesize porous Si nanostructures with comparable cost and large-scale to graphite anodes is a critical challenge in practical application. Recently, an effective solution is to look for natural resources rich in silicon ingredients, just like the reported rice husks, un-recycled glass bottles,
2.2. The preparation of P-Si@C composites

Expected porous Si nanoparticles can be achieved. Contributing to the development of high-performance silicon-based lithium-ion batteries.

2.1. The synthesis of Si nanoparticles

As far as we know, coal ash is a by-product from coal combustion in a thermal power station, containing a variety of components, such as SiO2, Al2O3, Fe2O3, and CaO, etc. What’s more, the coal ash has natural microporous structures (up to 50% ~ 80%), and the mass percent of silica is as high as ~60%. It is easy to imagine if the non-silicon components (mainly metal oxides, such as Al2O3 and Fe2O3, etc.) can be removed, then a natural porous Si nanoparticle will be achieved under the assistance of magnesiothermic reduction. In addition, the coal ash is an abundant and sustainable material source with a supply that far exceeds the demand for LIBs anode raw materials. In this paper, we have successfully prepared porous Si nanoparticles (P-Si) from coal ash, through mechanical milling, purification, and magnesiothermic reduction. Without meticulous design process and oppressive synthesis conditions, we can easily get the P-Si with the average diameter only ∼ 10 nm. After carbonization, carbon not only can coat the surface of Si nanoparticles, but also can immerse into the porous structures to form an interconnected conductive channel. More importantly, the obtained P-Si and carbon composite (P-Si@C) presents excellent electrochemical performances. The special capacity can stable at about 750 mAh g\(^{-1}\) at 2.0 A g\(^{-1}\) after 200 cycles. When current density up to 6.0 A g\(^{-1}\), the reversible capacity is about 565 mAh g\(^{-1}\). We believe this strategy will facilitate the large-scale production of silicon nanostructures, and contribute to the development of high-performance silicon-based lithium-ion batteries.

2. Experimental

2.1. The synthesis of Si nanoparticles

All reagents are of analytical grade without any further purification. Commercial coal ash powder was purchased in Alibaba (¥2/kg). Magnesium powder (Mg, 100~200 mesh), hydrochloric acid, and hydrofluoric acid were supplied in Sinopharm (Sinopharm Chemical Reagent Co., Ltd, China). Resorcinol, cetyltrimethylammonium bromide (98%, CTAB), and formaldehyde (37% solution) were gained in Aladdin (Aladdin Biochemical Technology Co., Ltd, China). Firstly, 50 g of coal ash was calcined at 600°C for 2 h in ambient temperature to remove some organic impurities, then smashed by planetary ball milling for 24 h. Next, to remove the metal oxides, 10 g of coal ash was successively immersed in HCl (1 M) solution to stir for 24 h at 50°C. Then the obtained silica powder was washed by deionized water. Thirdly, the obtained silica powder was reduced by magnesiothermic reduction methods. Magnesium powder and silica particles with a weight ratio of 1:1 were added into a sealed metal container. Then, the container was heated at 650°C for 6 h in a tube furnace under Ar/H\(_2\) atmosphere. Finally, the resulting nut-brown powder was etched with 1M HCl and 10% HF acid, and the expected porous Si nanoparticles can be achieved.

2.2. The preparation of P-Si@C composites

The as-prepared Si nanoparticles (0.6 g) was well dispersed in deionized water (30 ml) with strong ultrasonic dispersion, an aqueous solution of CTAB (1 ml, 0.01 M) was dropped to vigorously stir for 30 min, and then mixed with resorcinol (0.05 g) and formaldehyde solution (0.07 ml). The composites were collected under magnetic stirring for 12 h, and heated at 600°C under Ar/H\(_2\) (98%/2%) atmosphere. Finally, the P-Si@C was finally obtained.

2.3. Material and electrode characterization

SEM (SEM, TESCAN, VEGA 3) was used to characterize the morphology of the obtained products. Transmission electron microscope (TEM, JEM-3000F, JEOL), micro-Raman spectroscope (WITec excited by \(\lambda = 633\) nm laser) and x-ray diffraction (XRD, D/MAX 2500) with Cu-Ka Radiation were employed to visualize internal crystalline structures. Thermal gravimetric analysis (TGA) (TG/DTA6300) was performed in an argon atmosphere to obtain the carbon content in composite.

For the electrode fabrication, slurries were prepared by dissolving 80 wt% P-SiNPs@C, 10 wt% Super P, and 10 wt% polyvinylidene fluorde in N-methyl-2-pyrrolidone (NMP) solution to form a homogeneous slurry. The resultant slurries were uniformly pasted on copper foils by using the doctor blade technique, vacuum dried at 120°C overnight, and punched into circular discs for 2025 coin-cell fabrication, in which Celgard 2400 and Li foil were used as separators and counter/reference electrodes. The electrolyte used was lithium hexafluorophosphate (1 M, LiPF\(_6\)), dissolved in 1/1/1 (volume rate) ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/diethyl carbonate (DMC). Particularly, the cells were assembled in an argon-filled glove box. Cyclic voltammetry (CV) curves were achieved with an electrochemistry system (CHI 660D, China). The
constant current charge and discharge measurements in a voltage range between 0.01 and 1.5 V (versus Li/Li⁺) were conducted using Neware Technology (NEWARE BTS-5V 5 mA, Neware Technology Co, Ltd, China).

3. Results and discussion

At present, we know that thousands of thermal power stations are spread all over the world to provide the necessary electrical energy for people’s lives, just like figure 1(a), and fossil fuel represented by coal dominates here. Coal ash is produced in large quantities every day, and piles up like mountains. It is conservative estimated that the coal ash from the thermal power generation will up to 650 million tons in 2020 on our earth. However, the coal ash is usually used in building materials, road engineering, backfilling, all of which have low value-added. How to effectively utilize coal ash to obtain high additional value products and reduce environmental pollution is a hot topic that many scientific researchers are interested in. Of course, the prerequisite is that we can effectively extract porous Si nanoparticles from coal ash. If it succeeds, which will fundamentally solve the practical application, and that will be a very promising market.

In this work, to obtain P-Si, we take full advantage of the waste coal ash from the thermal power station to extract the required silicon components. And the detailed experimental processes have been described in the experimental section. Briefly, the coal ash, a gray-black powder material in figure 1(d), was firstly calcined in air at 600 °C for 2 h to completely remove the impurities, as well as organic ingredients. Secondly, a mechanical ball milling has been employed to further reduce the size of the coal ash, which can increase the specific surface area resulting in improvement the electrochemical reaction rate. Next, the calcined and milled coal ash was treated by 1 M HCl solution to remove the undesired metallic oxides (such as Al₂O₃, Fe₂O₃, and CaO, etc.). After the above three steps, the original grayish black coal ash has been changed to grayish white, which can be clearly observed in figure 1(e). Finally, under magnesiothermic reduction, a brown P-Si powder as we expected can be achieved in figure 1(f).

In figure 2, SEM has been employed to observe the morphology evolution of coal ash powder under different steps. Figures 2(a)–(d) are the schematic representation of the morphology change, and the corresponding SEM images from figures 2(e) to (h). The commercially coal ash powders are about 1 ~ 5 um in diameter, a natural micron-sized and porous material. After calcination and ball milling processes, it can be clearly seen that the original spherical microparticles are destroyed into irregular small particles, exhibiting a fractured morphology with a narrow size distribution 0.2 ~ 2 um (see the figure 2(f)). Before and after acid treatment, the morphology and size have not significant change by comparing figures 2(f) and (g). It is conceivable that the removal of the metal oxide will form porous silica particles, just like the schematic of figure 2(c). Then, due to the pulverization effect of the magnesiothermic reduction process, the porous silica powder can be further cleaved and reduced to
form smaller Si nanoparticles, which can be observed from figures 2(g) and (h). Of course, to obtain pure Si component, the side reaction products containing magnesium, magnesium silicide, magnesium oxide were removed by HCl treatment, and the unreacted SiO₂ was etched out by HF solution. Comparing the commercial coal ash, the obtained Si nanostructures are more specific surface and high chemical activity.

Furthermore, to solve the poor conductivity of Si nanostructures, a common approach is to use the high-temperature carbonization of organic material to form a thin carbon layer on the surface of Si nanostructures. After carbonization in this work, the original brown Si powder changes to black, which can be distinctly observed from the inset of figure 3(a). The red curve in figure 3(a) is the Raman spectrum of the finally obtained P-Si@C powder. The sharp characteristic peak at ~519 cm⁻¹ is related to the Si-Si stretching mode. In addition, the emergence of D band (amorphous carbon) and G band (crystalline graphite) can also testify the presence of carbon in the prepared composite. To further confirm this result, we also employed the XRD to analyze the obtained Si nanostructures and coal ash, as shown in figure 3(b). The XRD pattern of the red curve can be readily indexed to a Si (JCPDS File Card No. 27-1402). The distinct diffraction peaks located at 28.4°, 47.3°, 56.7°, 69.1°, 76.3°, and 88.03° are assigned to the (111), (220), (311), (400), (331) and (422) lattice planes of Si, respectively. Through comparing the coal ash (black curve) and the P-Si powder (red curve) in figure 3(b), the typical diffraction peaks in coal ash almost disappear. However, there are still a few other elements (such as: Al, C, N, and F) with small amounts in the obtained P-Si nanostructures by means of the XPS analysis (supporting information figure S2 (available online at stacks.iop.org/MRX/8/025008/mmedia)).
Except for the Raman and XRD spectral analysis, we also use TEM to characterize the micro-structure of P-Si@C composite. Figure 4(a) is a TEM image with low magnification, we can see some particles are densely distributed in the composite. When we zoom in the red dotted area in figure 4(a), the Si nanoparticles show irregular morphology, with diameter about 5 ~ 10 nm, which are marked by white dotted circle in figure 4(b). What’s more, these Si nanoparticles connected to each other forming a porous structure, which has been also marked by ‘space’ in figure 4(b). Continue to magnify the red dotted area in figure 4(b), a very distinct interplanar spacing (0.31 nm) can be evidently observed from the HRTEM image in figure 4(c), corresponding to the (111) plane of the Si. So, we can know that the Si nanoparticles have good crystallinity, which also coincides with our Raman and XRD results. In addition, we can also see a layer of carbon coated with the Si nanoparticles in figure 4(c), identified with white dotted lines, and some carbon has been immersed in porous structures. Therefore, based on the above characterization, we ensure that this synthesis method is feasible and effective to achieve high quality and high yield of porous Si nanoparticles extracted from coal ash. And the average diameter of silicon nanoparticles is only several nanometers, which can facilitate the rapid transport of lithium ions and electrons in materials. Meanwhile, it is worthy to note that the nano Si nanoparticles are very expensive in the market. In addition, thermogravimetric analysis (TGA) has been employed to identify the mass content of Si in the composite, and the corresponding result shows in figure 4(d). From room temperature to 150 °C, the reduction (about ~2%) is attributed to the absorbed moisture. When the temperature increasing from 150 to 600 °C, the curve decreases dramatically, then keeps stable until the temperature reaching to 550 °C. And this part of mass reduction comes from the loss of carbon. Through analysis and calculation, the mass content of Si is about 76%.

To evaluate the electrochemical properties of P-Si@C powder, the two-electrode coin-type with metallic lithium as counter electrodes have been assembled, and the corresponding results are shown in figure 5. Cyclic voltammetry (CV) was firstly employed to evaluate insertion and extraction of Li ions in P-Si@C anode.
Figure 5(a) shows the initial CV curve at scan rate of 0.1 mV s\(^{-1}\) in the voltage range of 0.01–1.5 V. A distinct cathodic peak associated with the formation of the Li-Si alloy began at 0.20 V; and two anodic peaks appeared at about 0.3 V and 0.5 V, which are consistent with the reported delithiation process for the Si nanostructures at 0.3 \(\sim\) 0.6 V [36]. More importantly, the anodic peaks from carbon commonly observed at 0.2 V are almost invisible due to the limited capacity contribution from carbon. In figure 5(b), the initial discharging capacity of P-Si@C electrode is about 2600 mAh g\(^{-1}\) under the current density of 0.2 A g\(^{-1}\), and the obtained specific capacity is calculated based on the mass of P-Si. After 80 cycles, the capacity remains at 1050 mAh g\(^{-1}\), delivering 91.5% capacity retention compared with the second cycle capacity, which is superior to our previously reported Si@C nanofibers prepared by electrospinning [37].

In addition, to achieve high power densities for practical applications, the rate performance of LIBs is another critically important concern. Figure 5(d) shows the rate capability of P-Si@C electrodes. Excitingly, the composite anode delivers an outstanding rate performance, revealing a reversible capacity of 1200 mAh g\(^{-1}\) at a current density of 0.4 A g\(^{-1}\) in the first cycles, and a capacity of around 565 mAh g\(^{-1}\) at 6.0 A g\(^{-1}\). When the current density returns to 0.4 A g\(^{-1}\), after cycling under different high density, P-Si@C composite can still regain a reversible capacity of 1050 mAh g\(^{-1}\). Additionally, we also tested bare P-Si without carbon coating, which shows a poor rate performance in figure 4(c) (black curve). When current density up to 6.0 A g\(^{-1}\), the special capacity is basically disappearing only about 20 mAh g\(^{-1}\). At the same time, the galvanostatic charge-discharge curves of P-Si@C electrodes under different rate conditions are shown in figure 5(d), and all show typical charge and discharge curves. The cycling stability of P-Si@C anodes were further monitored with extended cycles (figure 5(e)). Importantly, the composite electrode can retain 750 mAh g\(^{-1}\), 81.5% for the initial capacity, after 200 cycles at 2.0 A g\(^{-1}\) current density. The excellent electrochemical cycle stability is superior to that of the Si@GRO nanosheets synthesized from commercial sand, which capacity declines by 37% after 50 cycles [25]. In addition, the rate performance of P-Si@C is also better than that of the previously reported blinder-free Si nanoparticles@carbon nanofibers prepared by electrospinning [37].

However, the bare P-Si electrode without carbon coating only presents 10.5% after 150 cycles at 0.2 A g\(^{-1}\). Combining the electrochemical performances of pure porous Si in figure 5(c), it has also been proved that carbon coating plays an important role in improving the electrochemical cyclic stability of the porous Si nanomaterials.

Furthermore, these results can be further confirmed by electrochemical impedance spectroscopy (EIS) measurements in figure 6. The semicircle in high-frequency region is ascribed to the charge transfer resistance at
electrolyte interface, and the straight line in low-frequency range is referred to as the Warburg impedance corresponding to Li-ion diffusion in cathode. Generally, a semicircle with smaller diameter in high-frequency region indicates low charge-transfer resistance. Obviously, the P-Si@C anode shows two semicircles with the lower charge transfer resistance ($R_T$, $R_i$) and Warburg impedance ($W_i$). All confirms that the electronic conductivity of P-Si@C is increased comparing to bare P-Si, and it also well reflected in the electrochemical cycling studies. To summarize the above results, we believe that the excellent electrochemical performances of P-Si@C mainly is attributed to the small Si nanoparticles with an average diameter about $5 \sim 10$ nm resulting in ultra-short lithium-ion insertion and delithiation path. Secondly, the porous nanostructure can accommodate the expansion of volume, and the infiltration of electrolyte. Another, the carbon embedded in the porous silicon provides an interconnected conductive channel, meanwhile, the carbon can hinder the mutual agglomeration of the Si nanoparticles during the cycle.
4. Conclusions

Here, we have successfully developed a low-cost and large-scale method to prepare porous Si nanoparticles from coal ash through simple mechanical ball milling, chemical purification, and magnesiothermic reduction. The obtained Si nanoparticles have an average diameter of $5 \sim 10$ nm, which will be more conducive to the rapid transport of lithium ions and electrons in materials. Through carbonization, the obtained P-Si@C composites present excellent electrochemical performances. The discharging capacity is 1050 mAh g$^{-1}$ at 0.2 A g$^{-1}$ after 80 cycles, and the special capacity can stable at 750 mAh g$^{-1}$ at 2.0 A g$^{-1}$ after 200 cycles. When current density up to 6.0 A g$^{-1}$, the reversible capacity is 565 mAh g$^{-1}$. We believe this approach can fundamentally solve the problem of large-scale preparation of porous Si nanoparticles, with comparable cost and large-scale to graphite anodes, which will contribute to the development of high-performance silicon-based lithium-ion batteries.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Feng Yang https://orcid.org/0000-0001-8847-3918  
Kai Huang https://orcid.org/0000-0002-0250-6553

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