



Article A Hollow Silicon Nanosphere/Carbon Nanotube Composite as an Anode Material for Lithium-Ion Batteries

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Abstract: Silicon possesses a high theoretical specific capacity and is a promising high-performance anode material for lithium-ion batteries (LIBs). However, it shows a poor cycling performance because of volume expansion. A hollow structure can improve Si cycling performance, and the template method is one of the most common methods for hollow micro/nanosphere preparation. A polystyrene (PS) microsphere has the advantages of having a uniform and controllable particle size, easy modification, and high stability, thus being an ideal template for preparing hollow structure material. Herein, PS microspheres are used as templates to obtain hollow silica spheres, and then obtain hollow silicon spheres with an inner pore diameter of ~50 nm by a magnesium thermal reduction method. Lithium-ion battery anode material is obtained using carbon nanotubes supporting hollow silicon spheres (Si-CNTs). Si-CNTs exhibit excellent cycling performance (1188 mAh g⁻¹ after 200 cycles) and excellent rate capability (484 mAh g⁻¹ at 1 A g⁻¹). Hollow porous Si-CNTs show great potential, providing a promising idea for solving the volume expansion problem of Si.

Keywords: polystyrene microspheres; nano hollow silicon; lithium-ion batteries; carbon nanotubes

1. Introduction

In recent decades, nanomaterials have been used in a wide range of research fields, such as energy storage materials [1,2], electrocatalysts [3–5], and sensors [6–8]. The design and synthesis of hollow nanomaterials are two of the hotspots in material science research, which is very attractive in the field of material science applications [9–15]. Various types of hollow nanomaterials have a wide range of applications in the fields of lithium-ion batteries (LIBs) [16], supercapacitors [17], and catalysts [18]. Silicon is an attractive material for use as an anode in energy storage devices as its theoretical capacity (4200 mAh g⁻¹) is ~10 times higher than that of the carbon materials (graphite: 372 mAh g⁻¹) currently available on the market for LIBs. The main challenges associated with silicon anodes are drastic volume change (about 300%) during cycling, side reactions with the electrolyte, and low volume capacity upon material size reduction. The issues lead to structural degradation and instability of the solid electrolyte interphase (SEI) [19–22].

Particle cracking and electrical contact loss have long been considered the main reasons for the capacity decline of silicon-based anodes. Pioneering work has shown that reducing the feature size to the nanoscale allows materials to withstand large (de)lithiation stresses without fracture [23–25]. However, the cycle life of nano silicon is still limited due to the unstable SEI on the surface. At the operating potential of the anode ($0.5 V vs. Li^+/Li$), the organic electrolyte decomposes and forms a thin SEI layer. As the silicon expands and contracts, the SEI layer deforms and cracks. The formation of new SEI on the newly exposed silicon surface leads to poor coulombic efficiency of the battery, and the accumulated SEI will eventually prevent the transport of lithium ions. Due to this mechanism, the capacity decreases as the SEI increases, even though most active materials remain electrically connected. In order to control the formation of SEI, electrolyte barriers and internal void spaces



Citation: Tang, H.; Xu, Y.; Liu, L.; Zhao, D.; Zhang, Z.; Wu, Y.; Zhang, Y.; Liu, X.; Wang, Z. A Hollow Silicon Nanosphere/Carbon Nanotube Composite as an Anode Material for Lithium-Ion Batteries. *Coatings* **2022**, *12*, 1515. https://doi.org/ 10.3390/coatings12101515

Academic Editor: Je Moon Yun

Received: 6 September 2022 Accepted: 6 October 2022 Published: 10 October 2022

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need to be designed in the structure. Various literature has demonstrated such designs, including Si/C structures [26].

Herein, emulsion polymerization was used to synthesize 50 nm polystyrene microspheres with controlled particle size. Using the prepared 50 nm polystyrene microspheres as templates, hollow silicon spheres with the same inner diameter were obtained. Then, we prepared carbon nanotubes supporting hollow nano-silicon microspheres (Si-CNTs) with polystyrene microspheres as templates, resulting in a high capacity and stable structure, alleviating the problem of silicon volume expansion, which can provide a solution to the poor silicon cycling performance. The Si-CNT composite exhibits higher stability (the capacity reached 1188 mAh g⁻¹ after 200 cycles) and superior rate capability (484 mAh g⁻¹ at 1 A g⁻¹, and the capacity of Si-CNTs recovered to 797 mAh g⁻¹ after current densities of 0.05 A g⁻¹) than pure Si material (665 mAh g⁻¹ after 147 cycles). Si-CNT composite exhibits excellent mass specific capacity, superior rate capability, and stable cycling performance, contributed by the hollow silicon sphere structure and the confinement of CNTs on Si volume changes.

2. Materials and Methods

2.1. Materials

All reagents were directly used after purchase except styrene which needed to be further processed. The styrene was filtered through a 16 mm inner diameter column with alkaline alumina to remove the polymerization agent so that the polymerization reaction could proceed normally. Styrene (St); methyl methacrylate (MMA); analytical grade alumina and ethanol; hydrofluoric acid, which is a guaranteed reagent; magnesium powder, with a purity of >99.0%; sodium chloride, with a purity of >99.5%; and tetraethyl orthosilicate (TEOS), with a purity of 28.4% were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) 2,2'-azobis (2-methylpropionamidine) dihydrochloride (AIBA/V50), 2,2'-azobis (2-methylpropionitrile) (AIBN), cetyltrimethylammonium bromide (CTAB), and sodium carboxymethylcellulose (CMC) were analytical grade and were provided by Aladdin Reagent (Shanghai) Co., Ltd. (Shanghai, China) The ammonia concentration was 27%, and the hydrochloric acid concentration was 37.5%; both were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China) The purity of the lithium sheet was 98%, the purity of the copper foil was >99.7%, and the purity of the polyacrylic acid (PAA) was 4%. The electrolyte (lithium battery electrolyte with 5% FEC) and acetylene black were purchased from Guangdong Canrd New Energy Technology Co., Ltd. (Shanghai, China) The purity of the CNTs was more than 97%, the diameter was 3-15 nanometers, and the length was $15-30 \mu m$, and all were purchased from Shenzheng Suiheng Technology Co., Ltd. (Shanghai, China)

2.2. Preparation of the PS Microsphere

First, 2.5 g of cationic emulsifier hexadecyltrimethylammonium bromide (CTAB, purity: A.R.) was fully dissolved in 110 g of deionized water. Then, 50 g of monomer styrene was added and heated up, 0.2 g of initiator 2,2'-azobis [2-methylpropionamidine] dihydrochloride (AIBA) was dissolved in 20 g of pure water, and when the temperature reached 80 °C, the initiator treatment was carried out. The initiator residual was rinsed with water before the polymerization reaction started. The reaction was completed after 8 h, followed by post treatments. Centrifugation was carried out to remove excess emulsifier, solvent, etc., and the as-collected material was finally dried, collected, and stored for future use.

2.3. Preparation of Hollow Si and Hollow Si/CNT Composite

Polystyrene microspheres at a size of 50 nm were used as a template, and tetraethyl orthosilicate was used as a silicon source. A nanocomposite material with a core-shell structure was prepared, and then a hollow nano-silicon material was prepared by calcination. Subsequently, 0.6 g of CTAB and 39.5 g of ethanol were added into a round-bottomed

flask, stirred until the CTAB was completely dissolved, and then 1 g of ammonia water was added and continued to stir. The CTAB guided the PS microspheres to combine with the tetraethyl orthosilicate (TEOS). Ammonia water was added to adjust the pH of the solution, and ethanol was used to prevent excessive hydrolysis. Furthermore, 2 g of polystyrene emulsion was dissolved in 100 g of deionized water, stirred, transferred to a round-bottom flask, and stirred for 30 min. Next, 1 mL of TEOS was slowly added dropwise into the flask. As with the silicon source, the TEOS wrapped a layer of SiO2 outside of the PS microspheres. After the dropwise addition of the TEOS was completed, the temperature was kept unchanged for 12 h.

Mg powder was used to reduce hollow SiO₂ to nano hollow Si without changing the material morphology. The Mg powder and hollow SiO₂ were mixed at a mass ratio of 1:1 with 10 times the mass of Mg powder NaCl, fully ground in a glove box with a mortar for 15 to 20 min, and placed into a tube furnace filled with argon for 15 min. The temperature was raised to 650 °C at 2 °C/min and kept for 4 h, and then the temperature was naturally cooled. After cooling to room temperature, the product was taken out, slowly added to 40 mL of 1 M HCl solution, and then stirred uniformly at room temperature for 4 to 6 h. The material was then centrifuged, washed twice with water and once with ethanol, and then put into a plastic beaker. Subsequently, 20 mL of 4% hydrofluoric acid (HF) was added and stirred at room temperature for 10–15 min. The material was centrifuged, washed twice with water, once with ethanol, and vacuum-dried at 60 °C for 12 h to obtain the Si-CNTs.

2.4. Material Characterizations

X-ray diffraction (XRD, Rigaku MiniFlexll, Tokyo, Japan) patterns were collected at the angle range from 10° to 80° with Cu K α radiation (λ = 1.5408 Å). X-ray photoelectron spectra (XPS, Thermo Scientific K-Alpha, Waltham, MA, United States) measurements were performed using an Al K α X-ray source. Thermal gravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851, Zurich, Switzerland) was conducted by a thermal analyzer in N₂/O₂ flow at a heating rate of 10 °C min⁻¹. The morphology and surface details were analyzed by scanning electron microscopy (SEM, JEOL JSM-7800F Field Emission, Tokyo, Japan) and transmission electron microscopy (TEM, JEOL JEM, 1011, Tokyo, Japan).

2.5. Preparation of Electrodes

The as-prepared hollow nano-Si and CNTs were mixed as follows: the hollow nanosilicon material and the carrier material CNT were put into a beaker in a ratio of 6:4, 40 mL of ethanol was added, the temperature was controlled at 50 °C, heated and stirred with a magnetic stirrer until dry. The prepared composite material acetylene black and waterbased binder polyacrylic acid (PAA) were mixed in a ratio of 8:1:1. In order to ensure the stability of the system during the stirring process, a PAA solution with a mass fraction of 0.5% should be prepared in advance, ground by hand for 15 to 20 min to make it uniform, stable and suitable; then coated on a 12 mm diameter round copper foil at 60 °C and dried in a vacuum oven for 12 h.

2.6. Electrochemical Measurements

Electrochemical tests were carried out on the Chi660E electrochemical workstation (Shanghai, Chenhua Co., Shanghai, China) and CT3001A (Wuhan LAND Electronic Co., Wuhan, China). The electrochemical performance was tested by a button-type half-cell; the electrolyte used was 1M LiPF₆ (EC: DMC = 1:1Vol%, 5% FEC), which was purchased from Guangdong Canrd New Energy Technology Co.; and the lithium sheet was used as the cathode. All tests such as the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), charge-discharge tests, rate performance, and cycling performance were performed at room temperature (~25 °C).

3. Results and Discussion

The preparation process of the Si-CNT electrodes is shown in Figure S1. Our prepared samples were firstly studied using an SEM. The samples were sprayed with 6 nm of gold to enhance the electron conductivity and observe the nanoscale polystyrene microspheres. As shown in Figure 1a, the particle size of the polystyrene microspheres was ~50 nm. The microspheres were further characterized by TEM in Figure 1b, which shows that the polystyrene microspheres are uniform, and the particle size is in agreement with the SEM. XRD was used to test the crystal structure of the microspheres. Figure 1c shows that the microspheres have a broad characteristic diffraction peak at $2\theta = 20^{\circ}$, which is consistent with polystyrene. The chemical bonds of the nanospheres were further analyzed by infrared spectroscopy, as shown in Figure 1d, in which the peaks at 3061.5 cm^{-1} and 3024.7 cm^{-1} correspond to the stretching vibration absorption peak of the unsaturated C–H bond on the benzene ring [27,28]. The two peaks at 2849.5 cm⁻¹ and 2921.7 cm⁻¹ are the stretching vibration absorption peaks of the C-H bond on -CH₂- [29,30], and the three characteristic peaks at 1603.3 cm⁻¹, 1494.3 cm⁻¹, and 1450.1 cm⁻¹ are due to the substitution on the benzene ring [31,32]. The peaks prove that it has a benzene ring structure, and the absorption peaks at 755.5 cm^{-1} and 698.8 cm^{-1} are the characteristic absorption peaks caused by the vibration of the monosubstituted C-H bond on the benzene ring. The measured infrared spectrum analysis pattern conforms the characteristic peaks of polystyrene. Therefore, it is evident that the synthesized material is polystyrene. The particle size of the polystyrene microspheres can be intuitively obtained through the electron microscope image. As shown in Figure 1e, the particle size of the polystyrene microspheres was ~55.2 nm, in agreement with the microscopy results.



Figure 1. (a) SEM images of polystyrene microspheres. (b) TEM images of polystyrene microspheres. (c) X-ray diffraction (XRD) patterns of polystyrene microspheres. (d) FT-IR spectrum of polystyrene microspheres. (e) Particle size analysis chart of polystyrene microspheres.

Polystyrene microspheres were used as the template, and tetraethyl orthosilicate was used as the silicon source. The nanocomposite with a core-shell structure was prepared, and then a hollow nano-silicon was prepared by calcination. Figure S2 shows the thermogravimetric curves (TGA) of PS and SiO₂@PS under an air atmosphere. When the temperature was 550 °C, the PS reacted completely in the air and no solid remained. Therefore, this composite was calcined at 550 °C for 4 h to completely remove the PS in the SiO₂@PS. The slow heating rate is beneficial to the structural stability of SiO₂@PS. The temperature was increased to 300 °C at 2 °C/min, kept for 2 h, and then continued to increase to 550 °C at 2 °C/min and kept for 4 h. The PS template was completely removed to obtain a hollow SiO₂. Figure S3 is the XRD pattern of hollow SiO₂. It can be seen that there is a broad diffraction peak at $2\theta = 25^{\circ}$, which is consistent with the characteristic diffraction peak of SiO₂ [33]. Figure 2a is the TEM image of the SiO₂@PS before calcination; the core-shell

structure of the SiO₂@PS can be seen, with clear boundaries; the inner core is the template PS, and the outer shell is SiO₂. Figure 2b is the TEM image of the SiO₂@PS after calcination. It can be seen that the template PS has been removed, the hollow sphere is SiO₂, and the thickness of the hollow spherical shell is about 8 nm. The hollow SiO₂ is reduced by the Mg powder, and nano hollow Si spheres are obtained. The advantage of Mg reduction is to reduce a series of substances without changing the morphology. Figure S4 is the crystal structure model of Si. As shown in Figure 2e, the XRD of the hollow Si obtained by magnesium reduction shows the following characteristic peaks: the peaks located at $2\theta = 28.38^{\circ}$, 47.28°, 56.08°, 69.12°, 76.32°, and 88.04° correspond to (111), (220), (311), (400), (331), and (422) facets of cubic Si [34]. It can be seen from the XRD pattern that the hollow silicon spheres have been successfully prepared by the magnesium thermal reduction method, and they have a high degree of crystallinity. The Raman spectrum of the hollow Si spheres in Figure 2f shows a strong characteristic peak of Si at 518.72 cm⁻¹, which further proves that the hollow silicon spheres were successfully prepared [35].



Figure 2. (a) TEM images of the SiO2@PS before calcination (a,b) after calcination. (c) Low-magnification SEM image of the hollow Si-CNTs. (d) High magnification SEM image of the hollow Si-CNTs. (e) X-ray diffraction (XRD) patterns of Si, CNTs, and Si-CNTs. (f) Raman spectroscopy of Si, CNTs, and Si-CNTs.

Nanoscale PS (solid white spheres) was prepared by emulsion polymerization. A layer of SiO₂ (green part) was coated on the PS microspheres with TEOS as the precursor, calcined at a high temperature to form hollow SiO_2 , and the hollow SiO_2 was reduced by the magnesium reduction method. The hollow Si (yellow shell) was prepared, and finally, the nanoscale hollow Si obtained by magnesium reduction was mixed with the carrier CNTs to obtain Si-CNTs. The morphology of the as-prepared Si-CNT composites was observed using an SEM. Figure 2c is a low-magnification SEM image of Si-CNTs, and Figure 2d is a high magnification SEM image of Si-CNTs. It can be seen from the figure that CNTs are disorderly stacked three-dimensional structures, and hollow silicon spheres are uniformly inserted into the CNTs. The nanotube-like structure can be observed from the SEM image of single CNTs (Figure S5). Si thereby alleviates the expansion and contraction of the Si material during charging and discharging, and finally enables the hollow Si material to exert its capacity higher and improve the cycle performance. The crystal types and molecular structures of the composites were analyzed by XRD and Raman spectroscopy, respectively. As shown in Figure 2e, the prepared hollow Si spheres showed standard diffraction peaks, and the diffraction peaks had a good correspondence with Si (ICDD-27-1402). The diffraction peaks of CNTs are consistent with the former report and reflection of graphite (ICDD-41-1487) [36]. For CNTs, the XRD curve shows only two broad diffraction peaks, where the broad peak at $2\theta = 25.46^{\circ}$ corresponds to the (002) crystal plane of CNTs, and the weak diffraction peak at $2\theta = 43.06^{\circ}$ corresponds to the (100) crystal plane of

CNTs, indicating that CNTs have poor crystallinity [37,38]. The XRD diffraction peaks of hollow Si correspond to the (111), (220), (311), (400), (331), and (422) crystal planes of silicon. The XRD curve of the composite Si-CNTs shows the diffraction peaks of CNTs and Si. In order to further confirm the distribution of the two in the Si-CNT composite, we performed Raman spectroscopy. As shown in Figure 2f, CNTs exhibit two typical diffraction peaks at 1345.7 cm⁻¹ and 1602.2 cm⁻¹, corresponding to the D peak and G peak of carbon, respectively [39–43]. Si showed a strong diffraction peaks of both Si and CNTs, indicating that we successfully prepared Si-CNT composites [44].

To evaluate the electrochemical properties of the as-synthesized hollow Si-CNT composites, we assembled a coin-type half-cell. Figure S6 shows the CV curves of the hollow Si electrode for the first three cycles at a scan rate of 0.1 mV/s. The tested voltages range from 0.01 V to 3.0 V, and each peak corresponds to a single electrochemical reaction with lithium ions. Due to the formation of the SEI film on the anode surface, for the first cycle, it can be seen that a small peak appears at about 1.00 V, corresponding to the formation of a thin SEI layer of the SEI film on the anode surface [45-50]. However, this peak disappeared in the subsequent cycles, indicating that an SEI film with excellent stability of nano hollow Si spheres has been formed. In addition, the first cycle discharge curve shows the appearance of two weak cathodic reduction peaks located near 0.33 V and 0.47 V, and the peak intensity at 0.33 V and 0.47 V becomes more and more intense in the last two cycles of the first three cycles. The larger it is indicating that the nanoscale hollow Si spheres gradually stabilize as electrodes and the reaction intensify. In the next two turns of the discharge curve, a distinct cathodic reduction peak was observed at 0.18 V, possibly corresponding to the formation of a Li_xSi phase. The weak peak at 0.18 V during lithiation is mainly due to Li insertion [51,52]. Figure 3a shows the CV curves of the hollow Si electrode at different scan rates. As the scan rate increases, the current intensity shows a trend of increasing gradually. The positions of the redox peaks tend to be consistent at different scan rates, and the shapes of the cyclic voltammetry curves remain consistent, indicating that the material has excellent stability and reversibility.

Figure S7 shows the CV curves of the first three cycles of the Si-CNT electrode at a scan rate of 0.1 mV/s. It can be observed that the CV curves of the last two cycles are more overlapped than those of the pure Si material, indicating that the Si-CNT material has a higher degree of overlap. Compared with pure hollow nano-Si spheres, stability and reversibility of electrochemical reactions during battery charge and discharge have improved. The peaks at 0.33 V and 0.47 V are increasingly strong, and obvious lithiation and delithiation peaks are observed, especially the peak intensity at 0.47 V increases more obviously, indicating that the redox reaction of the Si-CNT material electrode is sufficient. The Si-CNT material is more stable than pure hollow Si. Figure 3b shows the cycling CV curves of Si-CNT electrodes at different scan rates. The recorded curves show that the anodic and cathodic currents are lower than before, which is possibly due to the capture of charge carriers by the CNTs themselves during the electrochemical process. The amplitude and intensity of these peaks increase with the scan rate, indicating a progressive activation of the Si substrate. Figure 3c,d are the voltage-capacity curves of the hollow Si and Si-CNTs at the current density of 200 mA g^{-1} for the 2, 20, 50, 60, 80, and 100 cycles. The SEI film is formed to consume more Li⁺ in the first cycle, and the coulomb efficiency is low in the first cycle, and in the next cycle, the coulomb efficiency is close to 100%. After 50 cycles, the capacity of the Si-CNT material is 696 mAh g^{-1} , pure Si's capacity is 627 mAh g^{-1} , and the Si-CNT material exhibits excellent cycle performance. The voltage-capacity curves of the 60th, 80th, and 100th cycles have a high degree of coincidence, indicating that the electrode material has high reversibility. The capacity of the Si-CNT material increases with the increase in the number of cycles since the silicon is encapsulated by carbon nanotubes and gradually activated with the progress of the reaction. The improved cycling performance of Si-CNTs is mainly due to silicon, because after lithiation, the volume expansion of Si nanoparticles may lead to the pulverization of Si particles, thereby losing

the electrical connection with the conductive agent. The CNTs facilitated the deposition of hollow Si nanoparticles, alleviating the volume expansion. Second, the CNTs enhanced the conductivity of the active material particles [53–58], which is consistent with the CV measurements described above. Therefore, Si-CNT electrodes have increased cycling stability compared with hollow Si electrodes.



Figure 3. (a) CV curve of 50 nm Si at different scanning speeds. (b) CV curve of 50 nm Si-CNTs at different scanning speeds. (c) Charge and discharge curves of 50 nm Si electrode at different cycling number. (d) Charge and discharge curves of 50 nm Si-CNT electrodes at different cycling numbers.

Figure 4a is a schematic of the Si-CNT structure. The CNTs are tubular and intertwined with hollow nano-Si spheres, which provide a certain expansion space for the hollow Si spheres during charging and discharging. This limits the expansion space to a certain range and is the purpose of controlling the excessive expansion of the Si material. We further studied the electrochemical impedance in Figure 4b. The curve consists of two parts: the high-frequency part is a semicircle, which represents the electron transport resistance, and the low-frequency part is a diagonal line, which represents the ion diffusion resistance. According to the fitting calculation, the R_{ct} values of the hollow Si and Si-CNTs are 149.2 Ω and 80.3 Ω , respectively, indicating that Si-CNT material has a higher electron transport ability than pure Si material. In addition, the structural integrity of Si-CNTs also ensures the stability of electron transport and ion transport channels. Figure 4c shows the rate maps of Si-CNTs, Si, and CNTs, and the three electrode materials were subjected to charge-discharge cycles at current densities of 0.05, 0.1, 0.2, 0.5, and 1.0 A g^{-1} . CNTs contributed a lower capacity, and the average discharge capacities of the hollow Si materials at different current densities of 0.05, 0.1, 0.2, 0.5, and 1.0 A g^{-1} were 938, 712, 600, 494, and 407 mAh g^{-1} , respectively. The average discharge capacities of Si-CNT composites at different current densities of 0.05, 0.1, 0.2, 0.5, and 1.0 Å g^{-1} were 1203, 958, 769, 607, and 484 mAh g^{-1} , which were significantly higher than the Pure Si material. After the high-current charging and discharging, the material electrode was continuously cycled at the current density of 0.5, 0.2, 0.1, and 0.05 A g^{-1} , and the pure Si material was cycled at the current density of 0.05 A g^{-1} . The capacity recovered to 514 mAh g⁻¹, while that of the Si-CNTs recovered to 797 mAh g^{-1} , further demonstrating the cycling stability and reversibility of the Si-CNT material. Figure 4d shows the cycle performance of the electrodes of the three materials at a current density of 0.2 A g⁻¹. The coulombic efficiency of Si-CNTs/Si/CNTs is shown

in Figure S8. After the initial few cycles, the coulombic efficiencies of the three electrodes are close to 100%, but both Si and Si-CNT electrodes have a large capacity decay, which is due to the formation of the SEI film in the initial stage of battery cycling, which consumes capacity. When the number of cycles is 45 cycles, the capacity of the Si-CNT material slowly stabilizes due to the particularity of the material structure, while the capacity of the pure Si material is still attenuating. When the number of cycles is 94, the capacity of the pure Si electrode remains at 505 mAh g^{-1} , while the capacity of the Si-CNT material is 830 mAh g^{-1} ; the capacity curve shows an upward trend, which is attributed to the gradual activation of silicon wrapped by carbon nanotubes, increasing specific capacity. The results demonstrate the increased structural stability of the Si-CNT material. Finally, we compared the cycle performance of the solid silicon spheres by keeping the battery test conditions unchanged and replacing the anode with solid nano-silicon spheres; the cycle performance is shown in Figure S9. The initial specific capacity of the solid silicon spheres is 1240.7 mAh g^{-1} . After 80 cycles, only 302.1 mAh g^{-1} is obtained, and the retention rate is 24.35%, which shows that the hollow structure is beneficial to alleviating the volume expansion of silicon during the process of delithiation and intercalation. After compounding the CNTs, the specific capacity and stability of the electrode were further improved. The cycle performance comparison between our work and some of the currently published work can be found in Table S1, which is superior to the cycling performance of other solid silicon composite anodes.



Figure 4. (a) Hollow Si-CNT material structure model and EIS curve. (b) Rate performance. (c) Cycle performance at 0.2 A g^{-1} . (d) Si-CNT electrode.

4. Conclusions

In conclusion, nano-polystyrene microspheres are used as a template to synthesize hollow silica, and then magnesium thermal reduction is used to obtain hollow silicon. Subsequently, carbon nanotubes are used as carriers to support the hollow silicon as a negative electrode material for LIBs. The hollow structure can reduce silicon spheres' volume change during the lithium deintercalation process. After compounding with carbon nanotubes, the bent carbon nanotubes encapsulate the hollow silicon spheres, further constraining its problematic volume change. Electrochemical tests show that the Si-CNT composites show improved stability (the capacity can reach 1188 mAh g^{-1} after 200 cycles)

and rate performance (484 mAh g^{-1} at 1A g^{-1} and the capacity of the Si-CNTs recovered to 797 mAh g^{-1} after current densities of 0.05, 1.0, and 0.05 A g^{-1}). All the above-mentioned advantages make hollow silicon composite carbon nanotubes attractive as lithium-ion battery anodes. In addition, the polystyrene microsphere template method introduced here has the advantages of large-scale mass production and low cost. Combined with industrial production techniques, Si-CNTs can be obtained with high efficiency and low cost, and these above-mentioned advantages of the material illustrate the great potential and easily attained practical applications.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/coatings12101515/s1, Figure S1: Synthesis method of Si-CNTs composite material.; Figure S2: Thermogravimetric curves of PS and SiO2@PS in an air atmosphere.; Figure S3:XRD patterns of hollow SiO₂.; Figure S4: A model of the silicon crystal structure.; Figure S5: SEM image of CNTs.; Figure S6: CV of the 50 nm hollow Si for the first three cycles at a scan rate of 0.1 mV/s.; Figure S7: CV curves of the first three cycles of the Si-CNTs at a scan rate of 0.1mV/s.; Figure S8: Columbic efficiency of these electrodes at 0.2A g⁻¹.; Figure S9: Cycling performance for solid nano-silicon spheres.; Table S1: Comparison of cycle performance of different silicon-based anodes. References [59–62] are cited in the Supplementary Materials.

Author Contributions: Writing—original draft preparation, H.T.; writing—review and editing, Y.X.; methodology, L.L.; investigation, formal analysis, D.Z.; data curation, visualization, Z.Z.; validation, resources, and Y.W.; upervision, Y.Z.; conceptualization, project administration, and funding acquisition, X.L. and Z.W. All authors have read and agreed to the published version of the manuscript.

Funding: National Key Research and Development Project (2018YFE0124800).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data that support the findings of this study are included within the article.

Acknowledgments: The authors acknowledge support from the National Key Research and Development Project (2018YFE0124800).

Conflicts of Interest: The authors declare no conflict of interest.

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