Original Article

3D Si@Cu-Ni nano-pillars array composite as carbon/binder free anode for lithium ion battery

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In this work, Cu-Ni nano-pillars array (CNPs) with controlled morphology and compositions was synthesized via electro-deposition method as 3D current collector. Si@CNPs electrode was then prepared by magnetic sputtering with Si film thickness of 200 nm and used as the carbon/binder free anode for lithium ion battery. The coulombic efficiency of Si@CNPs anode was 98 %–99 % after 2 cycles. The discharge capacity of Si@CNPs anode reached to 1766.5 mAh g−1 and the high capacity retention was 91.6 % after 60 cycles. Furthermore, the reversible capacity of Si@CNPs anode can still remain above 1090 mAh g−1 at 2 C due to the improved diffusion rate of charge at the solid-liquid two phase interface and the collection efficiency of electrons in current collector, which was higher than that of 2D copper foil supported Si anode (Si@CF).

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1 Introduction

lithium ion battery (LIB) electrode Si based powder material has certain advantages in commercial application [1–5]. However, some auxiliary materials need to be introduced such as the conductive agent and binder in order to obtain the improved electrochemical properties [6–10]. These additives are inert to Li+ insertion and extraction and reduce the total specific capacity and energy density of electrode. On the other hand, Si powder is easier to loss electrical contact with the current collector due to its volume effect, leading to the capacity decline in cycling [11–13].

In order to solve the volume effect of Si powder materials, researchers have turned their attention from powder materials to development of 2D Si-based films materials. High quality and uniform 2D Si films have been facile prepared by evaporation [14], magnetron sputtering [15] and CVD methods [16] without introducing impurities relative to traditional preparation process such as hydrothermal method [17] and solvothermal method [18]. Furthermore, as-prepared Si films can act as conductive agents and binder free electrodes, and the high energy deposition process directly promotes the tight bonding of Si films to the current collector. During the charge and discharge process, the surface stress generated from the volume expansion can be effectively dispersed and alleviated

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by adhering current collector with active films which suppress the cracking and peeling of Si films [19].

Cracks may occur due to the lateral compressive stress generated by the planar Si electrode. Via the repeated stress generation and releases, the plane material will have more obvious pulverization and spalling. The detached powder active materials remain in the electrolyte and further seriously affect the migration of electrons and ions [20–24]. Various studies have shown that the negative effects can be alleviated on a 2D planar substrate through reducing film thickness and alloying [23–25]. For 2D electrodes, there is an unavoidable problem that the inability to effectively release the lateral stress generated during the process of deintercalating lithium. Therefore, 3D current collectors with different morphologies are respectively constructed by physical and chemical methods [26–30], and the cycling performance of Si-based electrodes can be effectively improved by 3D construction [31].

In this paper, a binder free method was applied to synthesis Si@Cu-Ni nano-pillars array (Si@CNPs) composite electrode. CNPs was deposited on copper foil via electrodeposition technology at optimal conditions as 3D current collector. Furthermore, the formation mechanism of 3D CNPs current collector was proposed. The active Si film was then deposited on CNPs 3D by magnetic sputtering with the tunable thickness as the carbon/binder free and 3D structure anode for LIB. As a comparison, Si film deposited on 2D copper foil (Si@CF) was also prepared via magnetic sputtering technology. The crystal characteristics, morphological features and electrochemical performance of the two electrodes were analyzed in detail.

2. Experimental section

2.1. Synthesis of Cu-Ni nano-pillars array current collector

Three-electrode system was applied to synthesis CNPs. The copper foil with a thickness of 30 µm acted as the work electrode. An inert graphite and a saturated calomel electrode (SCE) was acted as the counter electrode and reference electrode, respectively. The concentrations of NiSO₄, CuSO₄ and H₂BO₃ in plating solution were 0.75–1.5 M, 0.025 M and 0.5 M, respectively, and H₂BO₃ acted as the pH buffer solution. 3D CNPs current collector was prepared by constant potential plating in the experiment and the electro-deposition voltage was set at -0.85 V (see Fig. s1,s2 in Electronic Supplementary Information (ESI)).

2.2. Synthesis of Si@CNPs and Si@CF electrodes

Si film were deposited on the surfaces of two current collectors (3D CNPs and 2D CF) by using RF magnetron sputter. Firstly, the sputtering chamber was subjected to two-stage vacuum pretreatment to achieve the desired degree of vacuum, and then the working gas was introduced to adjust the working pressure to 1 Pa. Before the plating process. The pre-splashing was performed for about 10 min to remove impurities such as oxides on the surface of Si target and the power was adjusted to 50 W during the pre-sputtering process. The formal Si plating time was controlled at 15, 30, 60 and 90 min, respectively.

After the end of the sputtering, the composite were taken out and quickly placed in the sample bag to prevent oxidation. The weight of electrode before and after sputtering Si film were measured by using analytical Balances (METTLER AB135-S) and the loading of Si film at different deposition times can be calculated (Si film loading specific mass is about 0.146 mg/cm² corresponding to the sputtering of 60 min).

2.3. Structural characterization

The crystal characteristics and morphological features of Si@CNPs and Si@CF were characterized by the following techniques. Scanning electron microscopy (SEM, Hitachi S-4800). The crystal phase composition of the products was investigated by X-ray diffraction (XRD, Rigaku D/Max-2400) with Cu Ka radiation and atomic information in the crystals was also collected by an energy dispersive X-ray spectrometer (EDS) attached to SEM.

2.4. Electrochemical measurements

Si@CNPs and Si@CF electrodes were cut into a disc with a diameter of 1 cm. Coin-type half cell (CR2032) were assembled in a glove box filled with argon with the electrodes as the anodes while lithium foil was used as both the counter electrode and the reference electrode. The anode and the cathode were separated by a separator of Celgard 2400 and an electrolyte of 1 M LiPF₆ in ethylene carbonate (EC)-dimethyl carbonate (DMC) (EC/DMC = 1:1, volume ratio). The cell was discharged and charged using NWEARE BTS-610 test system and its cyclic voltammograms (CV) test was carried out using a CHI 660D electrochemical workstation at a scan rate of 0.1 mV s⁻¹ both within the potential range of 0.01–3.0 V vs Li⁺/Li. Electrochemical impedance spectra (EIS) measurements were recorded on CHI 660D electrochemical workstation within frequency range of 100kHz–0.01 Hz and ac amplitude of 10mV.

3. Results and discussion

The synthesis procedure of Si@CNPs electrode is illustrated in Fig. 1. First, CNPs with controlled morphology and compositions was synthesized via electro-deposition method as 3D current collector by adjusting the Ni²⁺ and Cu²⁺ concentration ratio, electro-deposition potential and electro-deposition time. Then, the active Si film with the controllable thickness was deposited on CNPs 3D current collector by using magnetic sputtering to construct Si@CNPs composite electrode. It can be clearly observed that the 3D CNPs not only provides more effective void space for the active Si loading on CNPs current collector but also is easier to buffer the lateral stress of Si film due to volume effect.

Fig. 2 shows schematic illustration of formation mechanism of 3D CNPs. At the beginning of electro-plating, a dense layer of crystal grains form on the surface of substrate. Meanwhile, the thin layer near the surface of substrate temporarily form spent ion space regions due to the reduction of ions. As the electro-plating continues, the protrusions formed by more grain deposition will preferentially be reduced at these
sites due to the effect of the tip discharge. Therefore, the grain protrusions formed at the initial electro-depositions time can act as the growth core. When the current density is high, the smaller crystal grains are more easily formed due to the increasing nucleation speed of the ions, and the number of protrusions formed on the surface at the initial stage of electro-plating increase. These protrusions continue to grow and form smaller diameter nanoarrays. However, when the current density is small, the nucleation rate of the crystal grains slow down and form the larger crystal grains. Correspondingly, a small current density is applied to form larger diameter nano-pillars.

Fig. 3 displays the effect of different Ni\textsuperscript{2+} and Cu\textsuperscript{2+} concentration ratio on the morphology of 3D CNPs. The Ni\textsuperscript{2+} and Cu\textsuperscript{2+} concentration ratio is set 60:1, 50:1, 40:1 and 30:1, respectively. From the SEM images of 3D CNPs, it can be found that the tendency to generate nanopillars increases with the concentration of Cu\textsuperscript{2+} increasing. As the concentration ratio increases to 30:1, a more ordered arrangement of CNPs can be observed on the surface of copper foil. When the concentration of Cu\textsuperscript{2+} in the plating solution is low, the deposition rate is controlled by Cu\textsuperscript{2+} diffusion process and the tendency of Cu\textsuperscript{2+} reduction reaction is not very obvious. As the Cu\textsuperscript{2+} concentration increasing, more Cu\textsuperscript{2+} are reduced and rapidly accumulated in a specific position, forming a certain number of minute protrusions. Meanwhile, an ion depletion region is gradually formed around the protrusions, which further promotes the reduction reaction of ions at the tip of protrusion \[32\]. As the electro-plating continuing, these preferential discharge sites gradually grow to form a nanopillars structure. Therefore, the Ni\textsuperscript{2+} and Cu\textsuperscript{2+} concentration ratio in the subsequent experiments is set at 30:1.

The surface morphology of CNPs obtained at different deposition time were analyzed by SEM as shown in Fig. 4. The surface morphology of CNPs deposited for 10 s is shown in Fig. 4a. It can be observed that the surface of the coating is covered by nanoparticles due to the sharp increasing of current at the beginning of the electro-deposition process. Fig. 4b shows that there is an obvious growth trend of CNPs. Fig. 4c and d show the morphology of the CNPs after depositing for 200 s and 300 s respectively. It is found that the array is more orderly and has a relatively complete CNPs structure after 200 s of electrodeposition. At the same time, the void spaces between CNPs is in the range of ten to several hundred nm which reserve a certain space for the volume expansion caused by Si after lithium intercalation. However, the diameter of CNPs further increases after 300 s deposition, which displays combined growth and destroys the order and uniformity of CNPs. In the next experiment, the sample deposited for 200 s will be used as the experimental object to carry out the treatment and research of Si-loading.

CNPs obtained by electro-deposition was observed and shown in Fig. 5a. The distribution of nano-pillars with rough surface is relatively uniform and the average distance of nano-pillars is 100–200 nm. In order to further determine the height of nano-pillars, the surface of nano-pillars was observed obliquely at an angle of 45°. As shown in Fig. 5b, the height of nano-pillars maintain at about 200–300 nm.
nano-pillars with a certain aspect ratio not only improve the electron collection efficiency of two-phase interface, but also prevent Si films cracking and falling off.

Fig. 5c shows the XRD spectra of the two electrodes. When using Ni plate as substrate, the interference peak of the substrate Ni is excluded and a Characteristic peak corresponding to the Cu(111) crystal plane (FCC structure, JCPDS No. 04-0836) is observed at 2θ = 43.4°. Furthermore, XRD analysis of nano-pillars grown on copper substrate show that the characteristic peak of Ni (111) crystal plane (FCC structure, JCPDS No. 04-0850) appears at 2θ = 44.5° excluding Cu interference peak. It can be observed that nano-pillars prepared by constant-pressure electroplating contain both Cu and Ni elements. But no characteristic peak of the Cu-Ni alloy phase is formed and the existing characteristic peaks have no peak shift. The above results indicate that the Cu-Ni alloy phase is not formed in co-deposition process and Cu/Ni element is deposited separately on substrate. The elemental analysis of CNPs was carried out (see Fig. 5b) and showed that no O element was introduced.

Fig. 6(a–d) show the SEM images of Si@CNPs at different sputtering time (15 min to 2 h). It can be observed that Si@CNPs electrode retains the original morphology of nano-pillars after sputtering for 15 min, and the void space still maintain at about 100–200 nm. After sputtering for 30 min, the diameter of nano-pillars increases from the original 200 nm–450 nm. As the sputtering time increasing to 1 h, it can be clearly observed that the void space disappears and the nanoscale Si is sufficiently filled into the void space to form a continuous film. After sputtering for 2 h, the surface of electrode is almost covered by nanoscale Si. Therefore, 3D anode with sputtering of 30 min is used as the experimental object which not only ensures the loading of effective active Si, but also maintains the basic 3D structure of current collector. As a comparison, Si films deposited on 2D copper foil (Si@CF) was also prepared via magnetic sputtering technology (see Fig. 3e in EIS).

X-ray diffraction analysis was performed for the 3D Si@CNPs composite electrode. As shown in Fig. 6e, the characteristic diffraction peaks of the (111) and (200) crystal faces correspond to Cu (JCPDS No. 04-0836) and Ni (JCPDS No. 04-0850), respectively. The Raman analysis of sputtered Si in the literature [33] reveals that Si films prepared via magnetic sputtering are amorphous. In order to determine the thickness of deposited Si films, the as-prepared composite electrode was treated by ion thinning technique, and the cross section image of the composite electrode was obtained and shown in Fig. 6f, in which the white protrusions section represents the deposited CNPs and the grey layer is the Si sputtering film. The thickness of Si film is 180–200 nm measured by the scale bar.
It also can be seen from the cross-sectional view that the CNPs play a role in anchoring the Si layer, which not only enlarges the contact area of the two phases, but also plays an effective role in stabilizing the active Si layer. The path is copper foil substrate → CNPs → Si film, the red, green and blue lines represent the elemental distribution of Si, Ni and Cu, respectively. The linear elements analysis shows that the Si is mainly concentrated between 550 and 750 nm and the thickness is about 200 nm, which is consistent with the analysis results. Fig. s5 shows EDX analysis of Si@CNPs composite electrode, containing Cu, Ni, Si and O. The oxygen element may come from the oxidation of surface Si atoms.

Fig. 7a shows the cyclic voltammetry curves of Si@CNPs electrode for three cycles at a scan rate of 0.1 mV s⁻¹ (0.001–1.5 V vs. Li⁺/Li). It can be observed that a strong reduction peak appears at about 1.05 V during the first discharge cycle, which corresponds to the decomposition of electrolyte on surface of active material and formation of a solid electrolyte membrane (SEI). Two weak reduction peaks appear about 0.25 and 0.03 V due to different embedding depths of Li⁺ in nanoscale Si which form different alloy states LiₓSiᵧ. During the charging process, there are two distinct oxidation peaks at 0.38 and 0.5 V in the lower potential region, which correspond to the Li⁺ desorption reaction in the Li-Si alloy. It is worth to note that an obvious oxidation peak appeared at about 1.05 V during the charging process, which may be caused by the re-decomposition of the formed SEI film under the catalysis of the nickel substrate. No obvious changes are observed in the peak currents and potentials in the second and third cycles, indicating good reversibility of 3D Si@CNPs anode.

Fig. 7b shows the charge-discharge profiles of Si@CNPs with a sputtering time of 1 h at 0.2 C. The first discharge capacity of as-prepared 3D anode reaches approximately 4600 mA h g⁻¹, which exceeds the theoretical specific capacity of Si (4200 mA h g⁻¹) due to the consumption too much Li⁺ from the decomposition of electrolyte and the formation SEI film. At the same time, the charge-discharge curves of 2, 10, 50 and 100 cycles are given. These curves demonstrate that Si@CNPs electrode has good stability during charge-discharge cycling. It can be seen from the high-temperature phase diagram of Li-Si that four alloy phases of Li₁₂Si₁₅, Li₁₅Si₃, Li₁₃Si₄ and Li₁₂Si₄ are gradually formed as the amount of intercalation Li⁺ increasing [34,35]. While Si remains its amorphous state during the lithium insertion process. When the active Si film exceeds a certain thickness (about 500 nm), a new crystalline alloy Li₁₃Si₄ is formed at a low potential (about 0.07 V) and the transition from amorphous to crystalline occurs [36,37].
Fig. 7b does not show the corresponding voltage platform of lithium phase transition. The amorphous Si film prepared by magnetron sputtering can avoid the influence of lithium phase transition and ensure the stability of electrode during the de-intercalation lithium process.

Fig. 7c shows the cycle performance and coulombic efficiency of two 2D Si@CF and 3D Si@CNPs electrodes at 0.2 C (0.01–1.5 V vs. Li+/Li) for 60 cycles. It can be seen that the initial discharge capacities of Si@CF and Si@CNPs electrodes are 4120.5 mAh g−1 and 4655.7 mAh g−1, respectively, and the corresponding coulombic efficiencies are 46.6 % and 41.4 %, showing a relatively large first irreversible capacity. Two anodes reached a relatively stable charge-discharge state after the second cycle. The reversible capacity can be basically maintained at 1750 mAh g−1 before 20 cycles. However, it can be clearly observed that 2D Si@CF electrode has a significant capacity decay after 20 cycles, and the charge capacity dropped to about 906 mAh g−1 at 60 cycles. However, 3D Si@CNPs electrode has almost no discharge capacity decay (about 1766 mAh g−1) after 60 cycles, and its capacity retention rate exceeds 91.6 %. 3D CNPs can effectively maintain the microstructure of 3D Si@CNPs electrode, improving the diffusion rate of charge at the solid-liquid two-phase interface and the collection efficiency of electrons in the current collector.

Fig. 7d shows the rate performance of 3D Si@CNPs electrode. It can be seen that the charge and discharge capacities of the electrode are decreased as the rate increasing. At the rate of 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C, the charge capacity are 2161.8, 1997.7, 1642.3, 1375.9, and 1095.4 mAh g−1, respectively. When the rate returns to 0.2 C, 3D Si@CNPs electrode reversible capacity can still maintain at 1914.4 mAh g−1, which indicates that the electrode has good stability during the cycling. 3D Si@CNPs electrodes can still maintain above 1000 mAh g−1 at 2 C, which is much higher than the theoretical specific capacity of graphite materials (370 mAh g−1) and as-prepared 2D Si@CF electrode(740 mAh g−1) [38].

The lithium ions chemical diffusivity coefficient (DLi) is also calculated from the low frequency region of EIS spectra after 60 cycles (shown in Fig. s6) according to the literature [39]. Rs, Rf and Rct represent the solution resistance, resistance for Li+ migration through the SEI films and resistance of charge-transfer, respectively. As shown in Table 1, the lithium ions diffusion coefficients for Si@CNPs and Si@CF are 7.8 × 10−12, and 3.2 × 10−17. The larger lithium ions diffusion coefficients reveals that 3D Si@CNPs porous structure is able to shorten the Li+ migrate distance and improves the rate performance of 3D electrode.

Two Coin-type half cells after 60 cycles were disassembled and 2D Si@CF and 3D Si@CNPs electrodes were taken
Table 1 – The impedance parameters and the lithium ions diffusion coefficient for two electrodes.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>$R_s$ (Ω)</th>
<th>$R_F$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$R_{total}$ (Ω)</th>
<th>$D_{Li}$ (cm$^2$ S$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si@CNPs</td>
<td>13.9</td>
<td>110</td>
<td>221</td>
<td>344</td>
<td>$7.8 \times 10^{-17}$</td>
</tr>
<tr>
<td>Si@CF</td>
<td>22.4</td>
<td>204</td>
<td>390</td>
<td>616.4</td>
<td>$3.2 \times 10^{-17}$</td>
</tr>
</tbody>
</table>

Fig. 6 – SEM images of Si@CNPs at different sputtering time: (a) 15 min, (b) 30 min, (c) 1 h and (d) 2 h, (e) XRD patterns and (f) Cross section SEM image of Si@CNPs.

4. Conclusion

We have designed Si film deposited on 3D CNPs composite as the carbon/binder free anode for the application of lithium ion battery, resulting in improved cycle and rate performance.

out, washed with acetone and dried for SEM analysis. Fig. 8 shows the surface morphology of 2D Si@CF (a) and 3D Si@CNPs (b) after 60 cycles. It can be seen from Fig. 8a that the recycled 2D Si@CF electrode has severe cracking and splits from a single continuous film to island structures. Fig. 8b shows the morphology of 3D Si@CNPs, which can be observed that the electrode has no cracking due to the anchoring effect of CNPs. The results indicate that void space between nano-pillars can accommodate the volume changes of Si and prevent further deterioration of the active Si film.
Fig. 7 – (a) Cyclic voltammograms (CV) curves of Si@CNPs at a scan rate of 0.1 mV s\(^{-1}\) within the potential range of 0.01–1.5 V, (b) Charge-discharge profiles of Si@CNPs at 0.2 C (c) Cycle performances of the Si@CF and Si@CNPs electrodes and (d) Rate performances of Si@CNPs electrode.

Fig. 8 – SEM images of the two electrodes after 60 cycles: (a) 2D Si@CF electrode and (b) 3D Si@CNPs electrode.

3D Si@CNPs electrode displays high electrochemical performance due to the following reasons: First, thinner active Si film can effectively avoid the generation of large stresses. Second, CNPs increases the contact area between the active Si and the current collector, providing more channels for the fast and efficient collection of electrons. Third, CNPs play a significant role in anchoring the active Si film, buffering the interfacial stress and avoiding a large amount of active material falling off from current collector.
Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.11.081.

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