# Alloyed Cu/Si core-shell nanoflowers on the three-dimensional graphene foam as an anode for lithium-ion batteries

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## Abstract

In this study, we demonstrate a facile method to fabricate a flexible alloyed copper/silicon core-shell nanoflowers structure anchored on the three-dimensional graphene foam as a current collector. This combination provides flexible and free-standing structure and three-dimensional conductive network, allowing unique properties for current collection and transmission. The copper oxide nanoflowers are synthesized on the three-dimensional graphene foam by a simple electrodeposition and etching, which serves as an outstanding template to retard the stress effects during the lithiation/delithiation of silicon. After the silicon coating uniformly deposited on the copper oxide nanoflowers, a simple hydrogen annealing was applied to reduce copper oxide nanoflowers and form the copper/silicon alloy, remarkably enhancing the conductivity of silicon. Moreover, this structure can be directly assembled without any conductive additive or binder. In electrochemical testing, the resulting copper/silicon core-shell nanoflowered electrode demonstrates a high initial capacity of 1869 mAh g-1 at 1.6 A g-1, with a high retention rate of 66.6 % after 500 cycles. More importantly, at a high current density of 10 A g-1, this anode still remains a high capacity retention >63% (compared with the highest capacity 679 mAh g-1), offering enormous potential for energy storage applications.

## Introduction

Lithium ion batteries (LIBs) have currently dominated the commercial market owing to the environmental benignity, suitable energy density, and long cycle lifetime. The commercial LIBs are commonly using graphite as anode materials, however, it has become clear that the theoretical capacity (~372 mAh g-1) of graphite has nearly reached the bottlenecks with little room for further exploration [1], and also the energy density and rate performance of existing LIBs are not sufficient for some advanced electronics equipment such as smart watch, and micro implantable biosensor system. With increasing demand and market potential, the worldwide academia researches and industrial community have been focused on investigating anode materials to achieve desirable power density, high rate performance, and long-term stability energy storage system, generating further impetus on flexible electrochemical applications, such as wearable devices, portable electronic devices especially for implant biological equipment [2, 3]. Alternative anode materials such as metal (Si, Ge and Sn) and metal oxide (Co3O4, SnO2 and GeO2) have been considered. Among them, element Si has the highest theoretical specific capacity of 4200 mAh g-1 (corresponding to Li4.4Si), which has been proposed as the best candidate for rechargeable battery anode [1]. Many important aspects of silicon anode in LIBs have been investigated. however, some challenges for the Si electrode are also obvious due to the low conductivity and large volume expansion (around 300%) during the usage of LIBs. This expansion problem causes the pulverization of Si or active materials and the repeated formation of the solid electrolyte interface (SEI) on Si anode, resulting in the loss of interparticle electrical contact, and consequently deteriorating the battery cycle lifetime and capacity performance.

To tackle these problems, numerous researches have been focused on the novel design of electrode structures including thin films [4], microparticles (MPs)[5], nanaoparticles (NPs) [6-9], nanowires (NWs) [10-12], and other composite structures [13-15]. Among them, depositing Si thin film on nanowires or nanoparticles substrates to form the hollow core-shell structure has been reported to be an effective way to release the strain caused by volume change during the lithiation [16-19]. Wang et al. used the highly cross-linked Cu NWs foams as templates, coated with a high quality amorphous Si (a-Si) thin film to achieve Cu/a-Si core-shell NWs, demonstrating an extremely electrical conductivity for the whole electrode and revealing ultra-long cycle life and high performance rate when used in LIBs [16]. Li et al. reported a scalable method to obtain the crystalline Ni3Si2 nanocone (NCs) and NWs on nickel foam as template. a-Si was then in situ coated on this template via an inductively coupled plasma (ICPCVD), The achieved electrode demonstrated good electrical conductivity and mechanical stability of this combination of the metallic core with the a-Si shell [20]. These examples confirmed the nanostructure metallic supporting core can provide a mechanically stable anchoring basis for Si film, which is helpful for the improvement of cycling performance.

More recently, a graphene-based flexible current collector has been considered as an alternative for the current collector [21, 22]. The unique structural and electronic characteristics of graphene make it attractive for LIBs applications, offering the fast electron and ion transport path for the whole electrode in energy storage system. Such 3D graphene interconnected network can be synthesized with a template of metallic foam by the hydrothermal method, layer-by-layer assembly, or chemical vapor deposition (CVD) method [23-26]. For instance, Chen et al. deposited a 3D flexible and conductive interconnected graphene foam by CVD method in which the nickel foam and methane (CH4) act as a template and carbon source [26]. The monolayer graphene produced by the CVD method has excellent quality and conductivity compared with other chemical methods. Followed on this work, many researches have been reported to use the 3D graphene foam as the current collector to develop flexible electrode with excellent conductivity for advanced energy storage system such as LIBs, super capacitor, and fuel cell [27-29]. Li et al. directly deposited the Si films on the flexible free-standing graphene foam and used that as high capacity anodes for LIBs [30]. Their results showed that this flexible structure could relax the strain of the Si during the volume expansion.

These studies provide significant insights on the design of the high-performance Si electrode. Several critical factors are essential and of important to be considered together: a high surface area to permit a high lithium-ion flux across the interface, a high conductively metallic doping to enhance the electron transport, the well-defined nanostructure and flexible current collector to accommodate the strain associated with the volume expansion. However, surprisingly most of the previous studies mainly focused on one aspect[16, 20, 30, 31]. A potential advantage here is to consider these critical aspects as many as possible, which can be expected to broaden the design of the LIBs and spread of the applications towards future market.

Here, we demonstrate a facile method to fabricate a flexible alloyed Cu/Si core-shell nanoflowers (NFs) structure located on three-dimensional graphene foam (3DGF) as an anode for LIBs. In this interconnected core-shell structure, the copper diffused into the Si NFs significantly improves the electrode conductivity and provides a pathway to allow the electron moving fast from the current collector to Si. Moreover, the use of 3DGF as the current collector not only offers a robust mechanical support for long-term cycle stability, but also significantly increases the mass loading of the Si due to its high specific surface area. By assembling this structure in CR2032 coin type half LIBs, the alloyed Cu/Si core-shell NFs anode achieves a final capacity of 896 mAh g-1 at current density of 3.2 A g-1 for 1000 cycles, with capacity retention of 54.4 %. Remarkably, this anode could even cycle at a high charging/discharging current density of 18 A g-1 for 30 runs, and then back to the 1.8 A g-1 with 77.7 % capacity retention. Our results reveal that the alloyed Cu/Si core-shell 3DGF nanostructure could be a promising anode material for lithium-ion batteries with superior capacity and cycling stability. Meanwhile, the 3DGF is extremely light and flexible, offering enormous potential to be used in the flexible batteries for future smart watch or micro implantable biosensor system.

## Experimental section

### Synthesis of 3DGF

A nickel foam (1.5 mm × 3.5 cm × 3.5 cm, purchased from Liyuan Novel Materials from Changde, China) was used as a template (Figure 1a) for 3DGF synthesis. Firstly, it was loaded into a vacuum tube in a low pressure chemical vapour deposition (LPCVD) machine under 10 mTorr pressure. Then the tube was heated to 1000 °C at a speed of 10 °C /min with the flow of Ar and H2­ (1000 sccm:500 sccm) at the atmosphere pressure. After that, a small amount (50 sccm) of CH4 was then introduced into the tube for facilitating the graphene deposition. After 10 min of gas mixture flow, the samples were rapidly cooled down to the room temperature with the same flow of Ar2 and H2­. Finally, the as-prepared Ni/GF samples were etched in 3M HCl aqueous solution at 80 °C for 240 min to fully remove all the nickel foam templates to get the 3DGF (Figure 1b). The resulting free-standing 3DGF has a mass density around 0.50-0.55 mg cm-2. Figure S1 shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the as-prepared 3DGF.

### Synthesis of CuO nanoflowers anchored on the 3DGF

To synthesize the CuO NFs on the 3DGF, Cu NPs were firstly electrodeposited on the as-prepared 3DGF with an electrochemical potential of –0.40 V for 30 s in 0.1 M Cu2SO4 and 0.3 M H2SO4 aqueous solution by an electrochemical workstation (Metrohm Autolab PGSTAT302N). Then the 3DGF covered with Cu nanoparticles was etched and oxidized in a mixed 0.05 M K2S2O8 and 1.5 M NaOH aqueous solution at 80 °C for 2 min to achieve the final 3GDF/CuO NFs.

### Synthesis of Cu/Si Core-Shell NFs on 3DGF

The plasma enhanced chemical vapor deposition (PECVD) was employed to deposit the Si shell over CuO NFs under the gas flow of 35.5 sccm SiH4 and 2 sccm H2 for 90 min at 100 °C. 11 W RF power under 0.2 Torr pressure was used. According to the difference in weight of the whole electrode before and after, the Si mass loading over the CuO NFs was measured to be 0.20-0.25 mg cm­-2. After that, the sample was heated to 450 °C in a vacuum tube with 45 sccm H2 under 1.4 Torr pressure for 4 hours. This procedure was aimed to reduce the CuO to Cu under the Si shell and alloy this Cu with Si. The final resulting alloyed Cu/Si core shell nanoflowered structure was used as the electrode in LIBs. Figure S2 shows the optical images of 3DGF, 3DGF/Cu NPs, 3DGF/CuO NFs, 3DGF/CuO/Si NFs, and 3DGF/Cu/Si NFs samples. These images exhibit the morphology evolution of samples in different experimental processes.

### Structural characterization

The structures and morphologies of the samples were observed by the field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700), high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 F30), and Raman spectrometer (Horiba HR800 Raman system with 532nm wavelength). The energy dispersive spectrometer (EDS) was performed to examine the elemental information. The X-ray powder diffraction (Burker Advance D8) was used to record the crystal structure of the resultant materials.

### Electrochemical measurements

To further characterize the electrochemical properties, CR2032-type coin cells were firstly assembled in an argon-filled glove box (H2O, O2 <0.5 ppm). In this half-cell test, electrode with Cu/Si NFs anchored on 3DGF was directly used as the working electrode without any binder and conductive additive. The Li metal was acted as the negative electrode. The electrolyte was 1M LiPF6 in a solution mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 vol%). The galvanostatic cycling test was carried out with cut-off voltages of 0.01 V and 2 V on a multichannel batteries test system (Neware BTS-4000). The cycling voltammetry was measured by using an electrochemical workstation (Metrohm Autolab PGSTAT302N) at the scanning rate of 0.1 mV s-1 in two-electrode system. The mass density of 3DGF and mass loading of Si were determined by a high precision electronic balance (Mettler Toledo, 0.01mg).

## Result and Discussion

Figure 2a-c show the SEM characterization of the as-prepared CuO NFs anchored on the 3DGF substrate by a facile electrochemical deposition process. The diameter of high-density distribution CuO NFs is estimated to be 3.5-4.5 µm from the enlarged images of Figure 2b and 2c. Each petal of NFs is measured to be approximately 200 nm width with 1 µm in length. The final achieved Cu/Si Core-Shell NFs on 3DGF are shown in Figure 2 d-f. The diameters of the Cu/Si core-shell NFs increase to around 4-5.5 µm. Figure 2f shows the partial view of a single Cu/Si NF. After depositing Si shell on NFs, the diameter of the core-shell Cu/Si petal becomes approximately 400 nm. Through a simple comparison with the CuO petal, the thickness of the sidewall-coated Si shell is around 100-150 nm. This NFs structure could effectively release the stress effect when the Si expands during lithiation processes. Figure S3 shows typical SEM images of Cu/Si NFs grown on 3DGF with different distribution at different magnifications. The number inserted indicates the concentration of CuSO4 and H2SO4 electrolyte used in electrochemical deposition electrolyte. It is clear that for 0.1 M CuSO4/0.3M H2SO4 electrolyte the morphology of Cu/Si NFs is the most optimal without any unexpected spikes and inhomogeneous distribution. To examine further details, the TEM image and EDS mapping of the unannealed CuO/Si core-shell NFs and annealed Cu/Si core-shell NFs on 3DGF are provided in Figure 3. As seen in figure 3a, before annealing a significant core-shell boundary between CuO and Si is observed. The Si shell and CuO core are identified separately by different gray levels. Most of CuO cores were uniformly coated with the Si shell by the PECVD system, which is also confirmed by the EDS mapping of Cu and Si elements with a single unannealed CuO/Si NF (Figure 3c). This boundary becomes ambiguous after H2 annealing at 450 °C for 4h, as shown in Figure 3b and 3d, suggesting that the Cu core is successfully diffused into Si shell by the annealing processes. Figure 4 shows the EDS carbon, copper, and silicon elements mapping of Cu/Si core-shell NFs grown on 3DGF. In Si mapping image, the element Si (cyan color) is mainly aggregated on the CuO NFs, indicating that the CuO NFs is more desirable for the deposition of Si to be coated on compared with the bare 3DGF, Large specific surface area of this NF structure may result in more active sites, therefore improving the Si mass loading and the conductivity of the whole electrode.

Figure 5a shows the XRD patterns for the CuO NFs, CuO/Si core-shell structure, and alloyed Cu/Si core-shell structure after being annealed at 350 °C and 450 °C for 4 hours. Regarding to the CuO NFs structure, a series of sharp diffraction peaks of CuO and Cu2O are observed in accordance with PDF #44-0706 and #35-1091, which is an evidence of the oxidation from Cu nanoparticles to CuO NFs by NaOH and K2SO4 solution. After the Si shell coating on the CuO NFs by PECVD, no obvious peak is observed in related to Si shell, suggesting the formation of amorphous Si film on the CuO NFs. It was reported that the amorphous Si demonstrates more effective lithiation/delithiation process than the crystallized Si [32]. After simple annealing at 350 °C under H2 for 4 hours, all the diffraction peaks associated with CuO and Cu2O disappear Several new sharp diffraction peaks located at 36.6°, 44.5°, 44.9°, 77.5°, and 82.2° appear, which are consistent with crystalline planes of Cu3Si (201), (012), (300), (430) and (003) (PDF #51-0916), respectively. With increasing the annealing temperature to 450 °C, no other new peaks were emerged, suggesting that the temperature 350 °C is favorite to activate the reduction of CuO to form the Cu-Si alloy. Figure 5b provides the Raman spectrum of the as-prepared 3DGF. Two bands locate at 1581 cm-1 and 2725 cm-1 correspond to G and 2D peaks of graphene. Based on the full width at half maximum (FWHM) of 2D and G band, and the intensity ratio of 2D to G band (I2D/IG = 0.59), the graphene film is estimated to be 4-5 layers [33] (see Table S1). It is also noted that no band occurs at 1350 cm-1, indicating the absence of defects for the as-prepared 3DGF.

For the electrochemical test of the alloyed Cu/Si core-shell NFs anode, we use a standard CR2032 coin cell to test the cyclic voltammetry (CV) and galvanostatic charge-discharge. In this test, the mass density of Si in Cu/Si core-shell NFs anode and bare 3DGF are measured to be around 0.20-0.25 mg cm­-2 and 0.50-0.55 mg cm‑2, respectively. The half-cell test of this composite anode shows an initial discharge capacity of 1868 mAh g-1 at current density of 1.6 A g-1, based on the Si mass. In comparison, the bare 3DGF without Si coating results in a discharge capacity of only 280 mAh g-1 in a control experiment (Figure 6c). Therefore, the mass of Si is approximately used in all calculations. Figure 6a shows the CV curves of the alloyed Cu/Si core-shell NFs anode measured with a scan rate of 0.1 mV s-1 over the potential window of 0.01 V to 1.1 V versus Li+/Li. During the first discharge of alloyed Cu/Si anode, a cathodic peak at ~ 0.7 V is observed, but disappears in subsequent cycles, implying that this peak relates to the formation of solid SEI. After that, two peaks occur at 0.15 V and 0.03 V at the first discharge process, corresponding to the formation of LixSi by the lithiation of Si. These two peaks are also observed in the second and third discharge processes, implying a similar reaction pathway of two-stage lithiation process in subsequent cycles. When the battery is charging, two sharp peaks are observed at 0.30 V and 0.46 V in the anodic scan, which suggests that the phase changes from Li15Si4 alloy back to the amorphous LixSi, and the Li ion release from the Si anode. The peaks located at 0.01V and 0.23V in the cathodic and anodic scan are attributed to the lithiation/delithtaion process of graphene in the 3DGF substrate. When compared the whole three CV cycles, it can be seen that the CV curves of subsequent cycles almost overlap the previous cycle except a slight difference probably be caused by the surface change during the lithiation of Si. These results demonstrate a good reversibility for the redox reaction of Si anodes.

Figure 6b shows the first three galvanostatic discharge/charge voltage profiles cycling at a current density of 0.35 A g-1. Two voltage plateaus around 30 mV and 200 mV are observed on the discharge curve, due to the lithiation of Si shell on Cu NFs. For the charge curves, the voltage plateaus around 300 mV and 450 mV can be found, in a good agreement with the peaks shown in the CV curves in Figure 6a. Meanwhile, in the first discharge cycle, an earlier voltage stage occurs ~700mV during the first lithium-ion insertion of alloyed Cu/Si anode, which is consistent with the cathodic peak associated with the surface formation of SEI shown in Figure 6a.

The cycling performance of the alloyed Cu/Si core-shell NFs anode at 1.6 A g-1 and 3.2 A g-1, and non-alloyed Cu/Si core-shell NFs anode at 3.2 A g-1 during their initial 500 cycles are shown in Figure 6c. The non-alloyed core-shell NFs structures were reduced to Cu before the Si deposition for a comparison purpose. After initial cycles for the formation of SEI layer and activation of the active materials, the alloyed Cu/Si NFs anode exhibits a specific capacity of 1868 mAh g-1 and 1647 mAh g-1 at a discharge/charge current density of 1.6 A g-1 and 3.2 A g-1, respectively. The capacity retention rates of these two current densities are about 66.6% and 65.1% from 6th to the 500th cycle, which is significantly higher than that of the non-alloyed Cu/Si core-shell NFs anode. This result highlights the benefits of alloyed Cu/Si core-shell nanostructure, which plays a significant role enhancing the reaction stability for anode electrodes.

The rate capability of alloyed Cu/Si core-shell NFs anode has been tested with an increase gradient of current density at 0.35 A g-1 , 1.8 A g-1, 3.5 A g-1, 7 A g-1, 9 A g-1, and 18 A g-1, corresponding to the discharge capacities of 2087 mAh g-1, 1315 mAh g-1, 931 mAh g-1, 592 mAh g-1, 511 mAh g-1, and 257 mAh g-1, respectively (Figure 6d). Remarkably, when the current density gradually decreases back to 1.8 A g-1, the capacity retention remains 101%, 92%, 95%, 81.4%, and 77.7% corresponding to the discharging/charging current densities at 18 A g-1, 9 A g-1, 7 A g-1, 3.5 A g-1, and 1.8 A g-1. This good rate performance and stability are likely due to the unique alloyed Cu/Si core-shell NFs structure that provides superior conductivity for the active materials. Another reason is probably related to the good conductivity of 3DGF as the flexible current collector in LIBs.

Furthermore, the alloyed Cu/Si core-shell NFs anode exhibits an exceptional long-term cycle performance (Figure 7). The capacity performance of the alloyed Cu/Si core-shell NFs anode sample achieves a high capacity retention (> 63 %) after 1000 runs at 10 A g-1 current density, compared with the highest capacity 680 mAh g-1 (at 270 cycles).

To further assess the stability and mechanical strength of this Cu/Si core shell structure performed in LIBs, Cu/Si NFs on 3DGF electrode after 50 cycles at 1.6 A g-1 current density were examined under SEM (as shown in Figure 8). Compared with the pristine Cu/Si NFs electrode, it is interesting to note that the Cu/Si core shell NFs are well preserved on 3DGF after cycling. This observation confirms the robust structural property of Cu/Si NFs, which is promising to relieve the stress and remain the structure after long cycling operations. Moreover, these unique NFs are still firmly anchored on the 3DGF during battery cycling, indicating a tight connection between Cu NFs with 3DGF. According to previous results, the achievement of high rate performance and long-term cycling stability of the alloyed Cu/Si anode could be ascribed to the alloyed Cu/Si core-shell NFs providing numerous fast pathways for lithium-ion during lithiation/delithiation processes. On the other hand, the 3DGF substrate acts as a significant role in supporting and holding the Cu/Si NFs to accommodate the contraction and expansion reversibly during the cycling process. This soft substrate could release the stress in Si to offer excellent mechanical stability for the whole electrode, which is an effective way to prevent the structural collapse and conductive loss after a long-term cycling [34].

## Conclusion

In summary, we have demonstrated a facile method to fabricate a novel alloyed Cu/Si core-shell NFs anchored on the 3DGF structure as an anode in LIBs. This structure could be directly assembled to batteries without any conductive additive or binder. The electrochemical performance of this anode reaches a high capacity of 1869 mAh g-1 at 1.6 A g-1, with a high retention rates of 66.6 % after 500 cycles. Even at a high current density of 10 A g-1, this anode exhibits a superior high capacity retention >63% over the 500 cycles (compared with the highest capacity of 679 mAh g-1). These improvements of electrochemical performance can be ascribed to the combination of flexible 3DGF and unique alloyed Cu/Si core-shell NFs. And this structure provides an effective strategy for next generation Si-based flexible anodes in LIBs.

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