



# Nickel/silicon core/shell nanosheet arrays as electrode materials for lithium ion batteries



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## ABSTRACT

Ni/Si core/shell nanosheet arrays are proposed to enhance the electrochemical lithium-storage properties of silicon. The arrays are characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The arrays are micro-sized in height, which are constructed by interconnected Ni nanosheet as the core and Si coating layer as the shell. The electrochemical properties as anode materials of lithium ion batteries are investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge tests. The arrays can achieve high reversible capacity, good cycle stability and high rate capability. It is believed that the enhanced electrochemical performance is attributed to the electrode structure, because the interconnected Ni nanosheet can act as a three-dimensional current collector, and it has the ability of improving the electrode conductivity, enlarging the electrochemical reaction interface, and suppressing the electrode pulverization.

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## 1. Introduction

Silicon is one of the most promising next-generation anode materials of lithium ion batteries. It has a high theoretical capacity up to  $4200 \text{ mAh g}^{-1}$ , about ten times over that of traditional graphite [1–5]. However, for most unmodified silicon anode materials, they not only deliver actual capacities much lower than this theoretical value, but also exhibit very poor cycling performances and rate capabilities. These problems are attributed to the poor conductivity of silicon and the significant volume expansion (over 300%) during its lithiation process. These factors increase the electrode polarization and accelerate the electrode pulverization, respectively.

Two methods, i.e., forming composites by introducing secondary materials and preparing nanostructures, are often used together in order to improve the electrochemical properties of lithium ion batteries and other energy storage devices. The secondary materials, such as carbon [6–8], metals [9,10] and conductive polymers [11], often have good conductivity and ductility. They can reduce the electrode polarization, and meanwhile, act as the buffer to alleviate the particle pulverization. The nanostructured materials have large opening surfaces, which can enlarge the electrochemical reaction interfaces and shorten the diffusion paths of lithium ions. Therefore, according to the two

methods, many Si-based composites with mesoporous [12–14], spherical [15,16], array [17–23] and core/shell [24–28] nanostructures have been prepared, and they exhibit enhanced electrochemical performances when used as anode materials of lithium ion batteries.

Apart from above mentioned approaches, binder-free electrodes are often designed for further improvements of electrochemical performance. In this electrode, the active particles grow directly on the conductive substrate. No additives, such as conductive agent and binder, are used. As a result, more active materials can be accommodated in the limited space inside the electrode, and this can undoubtedly increase the capacity of the whole electrode. As far as we know, many of the binder-free electrodes have array nanostructures, and the frequently studied Si-based nanowire arrays is a typical example [29–31]. They show enhanced electrochemical properties due to their one-dimensional array nanostructures, in which each nanowire can touch firmly with the substrate, leading to a much better electrical contact than those of conventional powder electrodes. However, the point contact between the nanowire and the substrate may limit the speed of charge transfer. Therefore, it is natural to think about that the nanosheet arrays having larger contact interface with the substrate should exhibit enhanced electrochemical performance.

In this present work, Ni/Si core/shell nanosheet arrays with micro-sized height have been designed. In this composite array, the interconnected Ni nanosheet acts as a three-dimensional current collector, and is coated by the Si layer. The micro-sized arrays can certainly provide larger amounts of active materials

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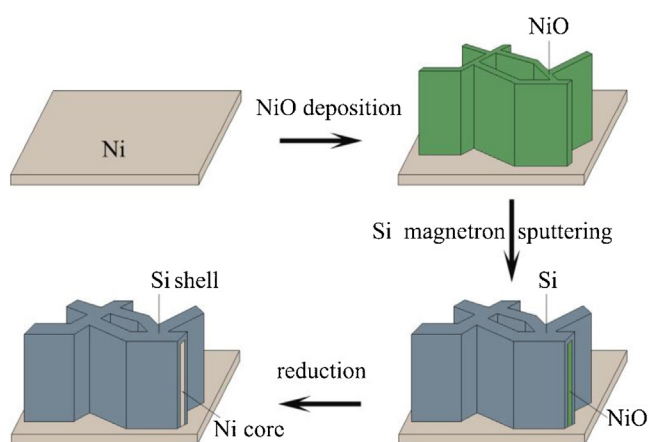
than those of nano-sized arrays, which is the key factor to improve the actual capacity of the whole electrode. Based on these analysis, the arrays have been prepared and its electrochemical performance is studied in detail.

## 2. Experimental

The preparation process of Ni/Si core/shell nanosheet arrays can be illustrated in Fig. 1. The first step is the fabrication of NiO nanosheet arrays by chemical bath deposition that has been reported in our previous work [32–35]. Briefly, 10.51 g nickel sulfate hexahydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), 2.03 g potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) and 10 mL concentrated ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) were dissolved in 90 mL distilled water. A clean nickel foil was used as the substrate. The deposition continued for 1 h at  $30^\circ\text{C}$ , and NiOOH nanosheet arrays formed on the substrate. Afterwards, the arrays were calcined in a quartz-tube furnace under flowing argon at  $350^\circ\text{C}$  for 1 h to decompose it into NiO. The second step is the Si deposition by radio-frequency magnetron sputtering technique (DETech DE500). The target was a polysilicon wafer (99.9999%) with a diameter of 6 cm, and its distance to the substrate was 20 cm. The chamber was firstly pumped to a base pressure of  $4.7 \times 10^{-7}$  Torr, and then introduced with pure Ar (99.999%) to keep the working pressure at  $8 \times 10^{-3}$  Torr. At a constant radio-frequency power of 60 W, the Si layer was deposited on the NiO nanosheet arrays for 1 h. To analyze the areal density of silicon in the film, the film was weighed by the high-precision balance with the accuracy of  $0.1 \mu\text{g}$  equipped in a simultaneous thermal analyzer (Netzsch, STA 449 F3). The final step is the reduction process of this NiO/Si composite film. The film was placed in the quartz-tube furnace, and heated under flowing Ar- $\text{H}_2$  mixture (5%  $\text{H}_2$ ) at  $400^\circ\text{C}$  for 3 h.

The materials were characterized by means of X-ray diffraction (XRD, Bruker D8 advance; Cu  $\text{K}\alpha$  radiation), scanning electron microscopy (SEM, Hitach S4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20) equipped with energy dispersive spectrometer (EDS).

Half cells were assembled in an argon-filled glove box (Mikrouna Super). In a CR2025 coin-type cell, the film was used as the working electrode, a pure lithium foil was used as the counter electrode, and a Celgard 2400 membrane was used as the separator. After adding the electrolyte, that is,  $1 \text{ mol L}^{-1}$   $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 in volume), the cell was sealed in the glove box and placed for 12 h before electrochemical tests.

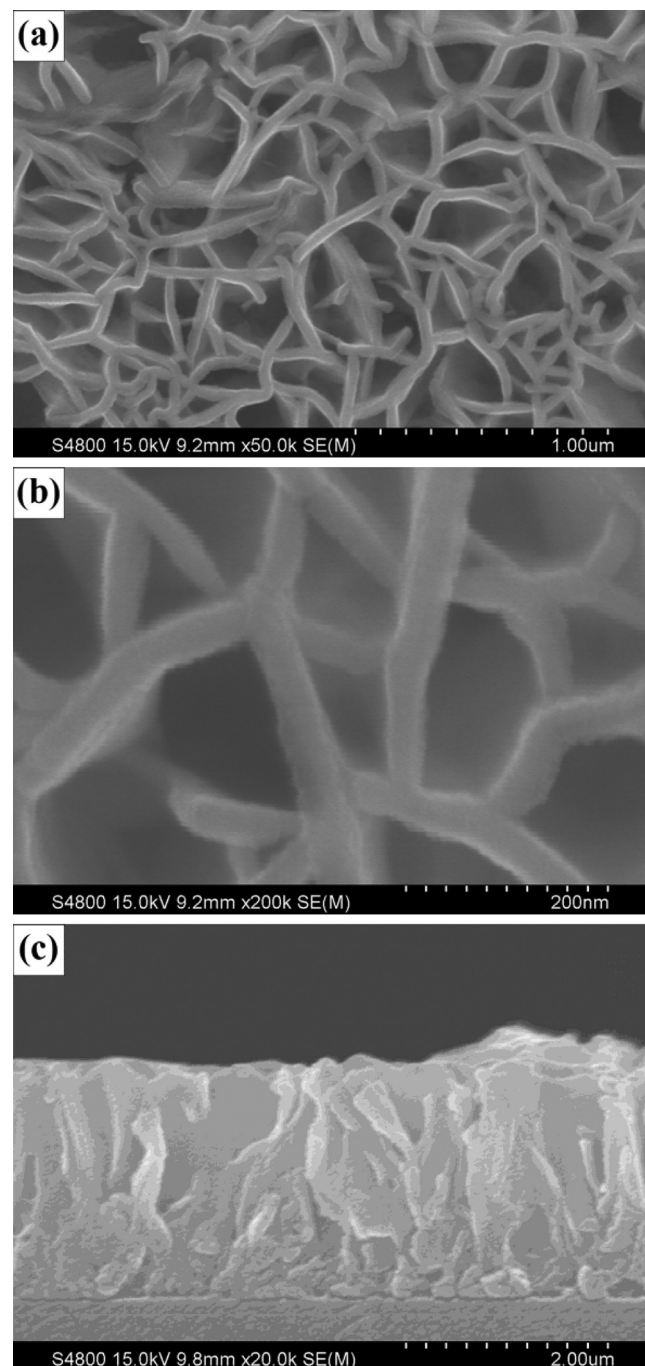


**Fig. 1.** Schematic diagram of the preparation process of Ni/Si core/shell nanosheet arrays.

Galvanostatic charge and discharge tests were conducted on a program-controlled battery analyzer (LAND CT2001A). The cells were cycled at different current rates between the two cut-off potentials of 0.02 and 1.5 V, respectively. Cyclic voltammetry (CV) analysis was performed on an electrochemical workstation (Metrohm Autolab PGSTAT302N) at a scan rate of  $0.1 \text{ mV s}^{-1}$  between 0 and 1.5 V.

## 3. Results and discussion

The formation mechanism, microstructure and morphology of the NiO nanosheet arrays prepared by this chemical bath deposition method have been studied in detail in our previous



**Fig. 2.** SEM images of the Ni/Si film, (a) the overall morphology, (b) the high-magnification image and (c) the cross-sectional image.

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