



Novel insight toward engineering of arrayed Cu@Sn nanoelectrodes: Rational microstructure refinement and its remarkable “harvesting effect” on lithium storage capability



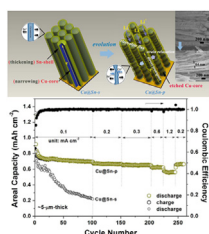
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HIGHLIGHTS

- Facile protocol for microstructure tailoring of Cu-cored nanowire array is described.
- The electrode shows high areal capacity, superior rate capability and ultralong cycling life.
- Surface roughening of Cu nanowire enhances the interfacial adhesion between Cu and Sn.
- Microstructure refinement makes the Cu@Sn electrode competitive for micro-energy storage.

GRAPHICAL ABSTRACT



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ABSTRACT

The impact of morphological and compositional evolutions of arrayed Cu@Sn nanoelectrodes on their lithium storage capability is investigated in this work. Strikingly, it is found that the diameter of Cu nanowire-core, inter-wire spacing, as well as Sn/Cu ratio of such nanohybrids could be directly adjusted through a synchronous electrochemical dissolution/deposition strategy in a single bath. In line with expectation, nanoarchitecture tailoring of the array-type electrode brings in expanded space available and enhanced interfacial adhesion, which can not only effectively enable high loading of conformal Sn nanolayers on per unit footprint area but also help in suppressing capacity fading, and thus harvesting outstanding areal capacity ($\sim 1.46 \text{ mAh cm}^{-2}$ at 0.2 mA cm^{-2}) and rate capability. It is envisioned that such work will shed light on ways to facilitate tune the characteristic parameters of a series of Cu-cored hybrid nanowire arrays with desired functionalities for nanodevice applications.

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1. Introduction

One of the most important issues in development of next-generation Li-ion microbatteries is to achieve high areal energy and power densities within limited footprint area (e.g., $<1 \text{ cm}^2$)

because these characteristics allow integration with micro-electromechanical systems (MEMS) and to supply enough energy for them [1–7]. Owing to its high theoretical capacity (994 mAh g^{-1} or 7234 mAh cm^{-3} for $\text{Li}_{4.4}\text{Sn}$) and low lithium-uptake potential [8–15], metallic Sn could be considered to be a potential anode material for Li-ion microbatteries. Nonetheless, its practical application is greatly bottlenecked by the substantial volume changes (more than 200%) inducing severe pulverization and electrical disconnection from the current collector during charge/discharge

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processes, eventually leading to dramatic capacity fading upon cycling. Recently, a robust design concept for constructing nano-architected electrodes has shown that combining active materials with well-aligned metallic (Cu or Al) nanorods can greatly improve their cycling stability, owing to the intimate contact of the active components with the nanoarchitected current collector providing reliable electrical connection and mechanical support [16–18]. In particular, metallic Sn was integrated with short Cu nanorods or nanowires (1–2 μm in length) through electrodeposition or magnetic sputtering route for the purpose of improving its cycling performance [19,20]. However, limited Sn loading on the low-aspect-ratio Cu nano-matrix determines low areal capacity within the small footprint area, the structural instability induced by weak interfacial adhesion and low quality of Sn layer, still posing the ultimate hindrance for its possible application in Li-ion microbatteries [2].

In order to overcome those shortcomings, both the diameter and surface roughness of the Cu nanowire (NW) (functioning as implanted “nanoelectronic wire” and supporting matrix) have to be adjusted or optimized further. In principle, a direct way to fabricate arrays of Cu-NW with desired geometric parameters is to use dimensionally compatible nanoporous anodic alumina membranes (AAMs), nevertheless, the complexity in controllably preparing sophisticated AAMs with ultra-small pores and large inter-pore distance still makes it a challenge [21,22]. Moreover, another knotty problem also existed with the normal collapse of high-aspect-ratio Cu-NWs with large inter-wire spacing into an entangled mess after removal of the template [23]. In this regard, exploring flexible protocols for engineering hybrid NWs with tailored Cu-core and favorable inter-wire spacing would be a meaningful but challenging work.

Although some of the methods reported so far highlight the possibility to adjust more than one structural parameter [24,25], it is often challenging to synchronously control several of the parameters, defining characteristics of arrayed hybrid NWs, such as diameter, inter-wire spacing, and composition. Aiming at exploring more available space for increasing electroactive component loading and harvesting high reversible Li^+ storage capacity on limited footprint area, we developed, for the first time, the successful engineering of an arrayed Cu@Sn nanoelectrode with shrinking Cu-NW core and elevated Sn/Cu ratio through a facile and straightforward electrochemical dissolution/deposition strategy. Undoubtedly, further reducing the diameter of the Cu-core along the parallel direction could ensure that the space left after loading of active material is sufficient for liquid electrolyte penetration or conformal integration of solid-state electrolyte throughout the electrode [1,2]. Besides, the induced surface roughening of Cu-core can also enhance interfacial adhesion between Sn-sheath and Cu-nano-matrix, which is essential for ensuring good cycling stability. Moreover, since no complex processes are involved, and more importantly, the synchronous etching is capable of evading the easy structural damage or even collapse of the nanoscaled Cu-skeleton by taking independent but uncontrollable etching processes, the innovative concept and approach presented here may provide new possibilities for fabricate other Cu-NW based hybrid arrays with optimized microstructure and composition.

2. Experimental section

2.1. Fabrication of arrayed Cu-NW matrix

AAMs with a pore diameter of 50–80 nm, and a thickness of $\sim 20 \mu\text{m}$ were fabricated by adopting the reported processes [26]. Prior to performing the experiment, the polished cathode Cu foil, AAM, cellulose paper separator, and the anode Cu foil were tightly

packed in sequence, and then assembled using two stainless steel clamps. Afterwards, electrodeposition of Cu-NW array was achieved using a current pulse approach with a cathodic pulse (-50 mA , 25 ms), and a relaxation time (0 mA, 250 ms) in a conventional acid copper sulfate based solutions ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 200 g l^{-1} , H_2SO_4 90 g l^{-1}) at room temperature. Finally, vertically aligned Cu-NWs were released from AAM by dissolving the template in 1 M NaOH solution for the sequential electrodeposition.

2.2. Assembly of Cu@Sn nanoelectrodes

A 36 mM Sn(II)-citrate solution was prepared by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ solution (the citrate was used to stabilize Sn^{2+} species in solution and avoid the precipitation of tin hydroxide), and the resulting pH was ~ 6 . The following two conditions are adopted for the conformal coating of Sn on Cu-NW matrix: (i) galvanostatic electrodeposition (GD) was conducted, while stirring, at a cathodic current density of -2 or -4 mA cm^{-2} ; (ii) periodically reversed step deposition was adopted with anodic current $+1 \text{ mA cm}^{-2}$ lasting 100 ms and -10 mA cm^{-2} as cathodic current for 50 ms, accompanied by rigorous magnetic stirring. The deposition temperature was fixed at $35 \text{ }^\circ\text{C}$. Afterwards, post-annealing treatments at $180 \text{ }^\circ\text{C}$ in vacuum were employed to enhance the interfacial bonding strength and reduce the microstructural discontinuities or defects among hybrid NWs. The fabrication of nanoelectrodes was performed on a PARSTAT 2273 potentiostat/galvanostat with a three-electrode configuration, in which Pt foil was used as counter electrode and saturated calomel electrode (SCE) as a reference electrode. Specifically, the nanoelectrodes obtained by galvanostatic deposition (GD) and pulsed galvanostatic deposition (PGD) are denoted as Cu@Sn-s and Cu@Sn-p, respectively.

Morphology and phase analysis were performed using FESEM (Hitachi S4800, 5 kV), TEM (JEOL JEM 2010), X-ray diffraction (Rigaku Dmax-2000, Cu Ka) and energy dispersive X-ray (EDX) analysis, respectively. Test cells were assembled in an argon-filled glove box (MBRAUN) with Cu@Sn nanoelectrodes as working electrode, Li foil as counter/reference electrode, polypropylene film (Celgard 2300) as separator, and 1 M LiPF_6 in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as electrolyte. Charge/discharge cycles of the cells were measured by using a Neware battery tester in the voltage range of 0.02–1.2 V or 0.02–1.5 V. Cyclic voltammograms (CVs) measurement were performed using an electrochemical workstation (Zahner Elektrik IM6ex). Note that the accurate mass loading of the active material is difficult to measure because of the partial oxidation or dissolution of Cu-core and thus the capacity unit has to be selected as $\mu\text{Ah cm}^{-2}$ or mAh cm^{-2} , accordingly [6,7].

3. Results and discussion

The entire procedure and concept for geometry-controlled engineering of arrayed Cu@Sn NWs are schematically illustrated in Fig. 1. For comparison purpose, the CV analysis shown in Fig. 2a were used to describe the redox characteristics of Sn^{2+} and Cu ions in the operation potentials. As is observed in the first scan, the anodic peak located at $+0.4 \text{ V}$ (vs. SCE) should be attributed to the dissolution of Cu in mildly acidic environment: $\text{Cu (s)} - \text{e}^- \rightarrow \text{Cu}^{2+}$ or Cu^+ (aq). According to previous literature [27,28], dissolution of SnCl_2 in citrate solution leads to different soluble Sn(II)-citrate chelated species, whereas only a very small fraction of Sn^{2+} ions is in the form $[\text{Sn}(\text{H}_2\text{O})_6]^{2+}$ because of the effect of citrate ligands in inhibiting the tendency of Sn^{2+} hydrolysis. As seen in Fig. 2a, a broad cathodic peak centered around -0.5 V should be ascribed to the reduction of Sn(II)-citrate complexes, and anodic peaks

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