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Component-controllable (Ni, Co)$Se_{2(1-x)}S_{2x}$ ($0 \leq x \leq 1$) acanthospheres for high-performance binder-free supercapacitors

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ABSTRACT

Component-controllable (Ni, Co)$Se_{2(1-x)}S_{2x}$ ($0 \leq x \leq 1$) acanthospheres on typical biomass carbon tube (CTs) are successfully fabricated through a simple chemical vapor deposition method. These composites, which are directly used as electrode materials for binder-free supercapacitors, exhibit excellent electrochemical properties and other different characteristics.

1. Introduction

Hierarchically complex micro/nanostructured materials elicit considerable research interest because they can provide a large surface area, fast electron transfer channels, and many active sites [1–3]. Accordingly, many researchers have applied these materials in the energy storage field [4,5]. Among them, supercapacitors are attracting increased attention because of their high specific power density, fast charge-discharge rates, long durability, and environmental friendliness [6–8].

Transitional-metal dichalcogenides are important potential electrode materials for supercapacitors because of their good conductivity, comparatively high electrochemical activity, earth abundance, and low cost [9–13]. However, it's still a challenge that controlled synthesis of nanostructured transition-metal dichalcogenides. In the present study, we designed and fabricated high-quality, three-dimensional, acanthosphere-like (Ni, Co)S_2, (Ni, Co)Se_2, and (Ni, Co)$Se_{2(1-x)}S_{2x}$ ($0 < x < 1$) microspheres on a low-cost, lightweight, and environmentally friendly biomass carbon tubes (CTs) through a chemical vapor deposition (CVD) method. The hierarchitectures were used as supercapacitor materials and found to exhibit superior pseudocapacitor performance with high specific capacitance and excellent cycle life.

2. Experimental

2.1. Synthesis of acanthosphere-like Ni-Co/CTs precursors

In a typical synthesis, biomass CTs were initially prepared by a method that we have recently reported (the detailed processes are shown in the Supporting Information). Then, 0.7276 g of $Co(NO_3)_2{\cdot}6H_2O$, 0.7270 g of $Ni(NO_3)_2{\cdot}6H_2O$, and 0.6006 g of urea were dispersed in a mixed-solvent system containing 4 mL of anhydrous alcohol and 16 mL of deionized water. The solution was stirred for 40 min and placed in a 30 ml Teflon-lined autoclave, after which 0.02 g of CTs was added to the solution. The autoclave was heated in an electrical oven at 120 °C for 15 h, and then the products were collected, washed with water and ethanol three times each, and dried in a vacuum oven at 60 °C.

2.2. Synthesis of acanthosphere-like Ni-Co-S/CTs microspheres

CTs covered with Ni-Co precursors were placed on the downstream side of the tube furnace, and 0.3 g of S powder was placed on the upstream side. To create an oxygen-free environment, the tube furnace was flushed three times under Ar flow. After being flushed with Ar, the tube-furnace temperature was quickly raised to 450 °C, which was held for 30 min. Throughout the entire process, Ar flow was maintained at a rate of about 100 sccm. For comparison, Ni-Co-Se-S/CTs and Ni-Co-Se/CTs were also synthesized through the same method. The characterization processes are detailed in the Supporting Information.

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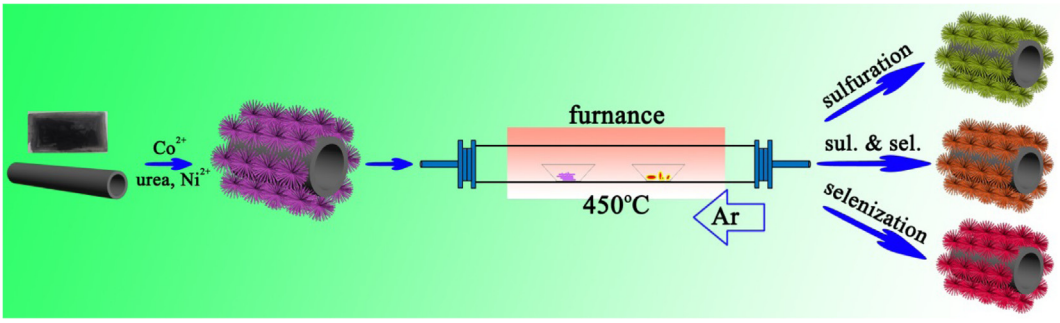
3. Results and discussion

We used an easy CVD method to convert Ni-Co/CTs precursors into Ni-Co-S/CTs, Ni-Co-Se-S/CTs, and Ni-Co-Se/CTs through sulfurization, selenization, or simultaneous sulfurization & selenization, as shown in Scheme 1. Fig. 1a–c show the typical SEM images of products, whose morphology completely inherited from Ni-Co/CTs precursors (Fig. S1a). Large-scale acanthosphere-like microspheres consisting of nanowires about tens of nanometers in size are tightly cover the surface of CTs. Fig. 1d–f present the powder X-ray diffraction (XRD) patterns of Ni-Co-S/CTs, Ni-Co-Se-S/CTs, and Ni-Co-Se/CTs, respectively. Notably, all diffraction peaks of Ni-Co-S/CTs and Ni-Co-Se-S/CTs are consistent with the standard card of CoS_2 (JCPDS No. 41-1471), and the diffraction peaks of Ni-Co-Se/CTs match well the standard card of $CoSe_2$ (JCPDS No. 9-234). However, compared with CoS_2 (JCPDS No. 41-1471) and $CoSe_2$ (JCPDS No. 9-234), we find that all characteristic diffraction peaks in the products shift owing to the multiple heteroatom doping [14,15]. As shown in Fig. 1g–i, EDX demonstrates the presence of S and Se elements with no other discernible heteroatoms further confirming the successful conversion of Ni-Co/CTs precursors into the desired products. Moreover, the inset tables of Fig. 1g–i reveal that the atomic ratio of nonmetallic (S and Se) to metallic (Ni and Co) elements is close to 2:1, in accordance with the above XRD results. Additionally, elemental mapping was conducted for a single acanthosphere scraped from the corresponding products (Fig. 2a–c). Results clearly indicate that all elements are still



Scheme 1. Schematic diagram of the preparation of Ni-Co-S/CTs, Ni-Co-Se-S/CTs, and Ni-Co-Se/CTs.

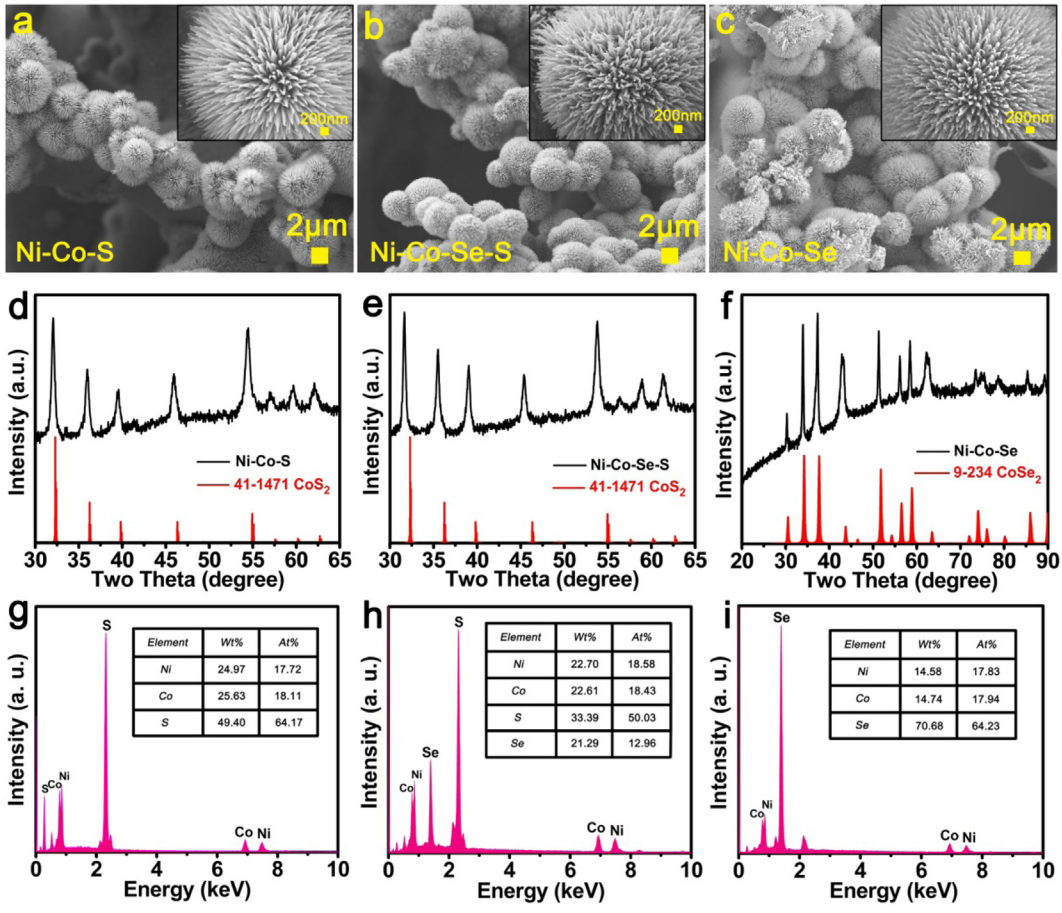


Fig. 1. SEM images of (a) Ni-Co-S/CTs, (b) Ni-Co-Se-S/CTs, and (c) Ni-Co-Se/CTs. XRD patterns of (d) Ni-Co-S/CTs, (e) Ni-Co-Se-S/CTs, and (f) Ni-Co-Se/CTs. EDX patterns of (g) Ni-Co-S/CTs, (h) Ni-Co-Se-S/CTs, and (i) Ni-Co-Se/CTs.

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