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Fabrication of cobalt oxide/carbon core-branch nanowire arrays as cathode materials for supercapacitor application

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ABSTRACT

Porous core-branch nanowire arrays are critical for developing advanced electrochemical devices. In this work, Co_3O_4/C core-branch nanowire arrays are successfully fabricated by combining hydrothermal synthesis and atomic layer deposition (ALD) methods. Interconnected amorphous carbon nanoflakes are homogeneously coated on the Co_3O_4 nanowire core forming Co_3O_4/C core-branch nanowires with diameters of ~280 nm. Supercapacitor electrodes based on the Co_3O_4/C core-branch nanowire arrays are tested. The Co_3O_4/C core-branch nanowire arrays exhibit excellent electrochemical performances with a high capacitance of 700 F g^{-1} at 2 A g^{-1} as well as good cycling stability due to the attractive characteristics such as good conductivity, porous structure and direct growth on the conductive substrates. Our synthetic approach may pave the way for fabrication of other metal oxides/carbon arrays for applications in electrochemical energy storage.

1. Introduction

Electrochemical supercapacitors based on nanostructured metal oxides are receiving considerable attention. High performance of supercapacitors relies largely on scrupulous design of nanoarchitectures and smart hybridization of bespoke pseudocapacitive materials. Although RuO_2 has been demonstrated with excellent pseudocapacitive performance, the high cost of RuO_2 limits its commercial application [1,2]. Therefore, it is highly desirable to search for alternative low-cost transition metal oxides with high capacitances [3].

Co_3O_4 and Co_3O_4-based composites have been extensively investigated as active materials for supercapacitors due to their high capacitances, good capability retention, low cost, and high stability [4–6]. The performance of supercapacitors is mainly determined by the electrochemical activity and kinetic feature of the electrode materials. To improve the performance of supercapacitors, it is crucial to enhance the kinetics of ion and electron transport in electrodes and at the electrode/electrolyte interface. To date, great efforts have been dedicated to designing nanostructured Co_3O_4 nanomaterials (such as nanowire, nanoflake, core/shell structures) [7–9], and Co_3O_4-based composites with conductive layers, which can improve the electron transfer leading to good high-rate capability [10,11]. Particularly, several works are focused on Co_3O_4–C composite materials and enhanced performances have been proven in these systems [7,12]. In addition, there are a few reports about Co_3O_4/C core/shell nanowire arrays for supercapacitor application. For example, Pan's group constructed cobalt oxide/carbon core/shell nanowires with dense CVD-carbon shell and Co_3O_4 nanowire and a high specific capacity of 116 mAh g^{-1} was obtained in this core/shell arrays [7], when they were applied for supercapacitors.

Different from the above Co_3O_4/C core/shell nanowire arrays, herein, we report novel nanostructured Co_3O_4/C core-branch nanowire arrays, in which carbon nanoflake shell is homogeneously coated on the Co_3O_4 nanowire core by combining hydrothermal synthesis and atomic layer deposition (ALD) methods. As cathode materials of supercapacitor, the as-prepared Co_3O_4/C CBNAs show excellent supercapacitor performance with a high capacitance of 700 F g^{-1} as well as good cycling stability.

2. Experimental

The Co_3O_4/C core-branch nanowire arrays were synthesized as follows. First, the precursor of $Co_2(OH)_2CO_3$ nanowires were synthesized by a hydrothermal process as described in the reference [13]. Second, the $Co_2(OH)_2CO_3$ nanowires were coated with Al_2O_3 of 120 cycles by ALD at 120 °C. Trimethylaluminum Al

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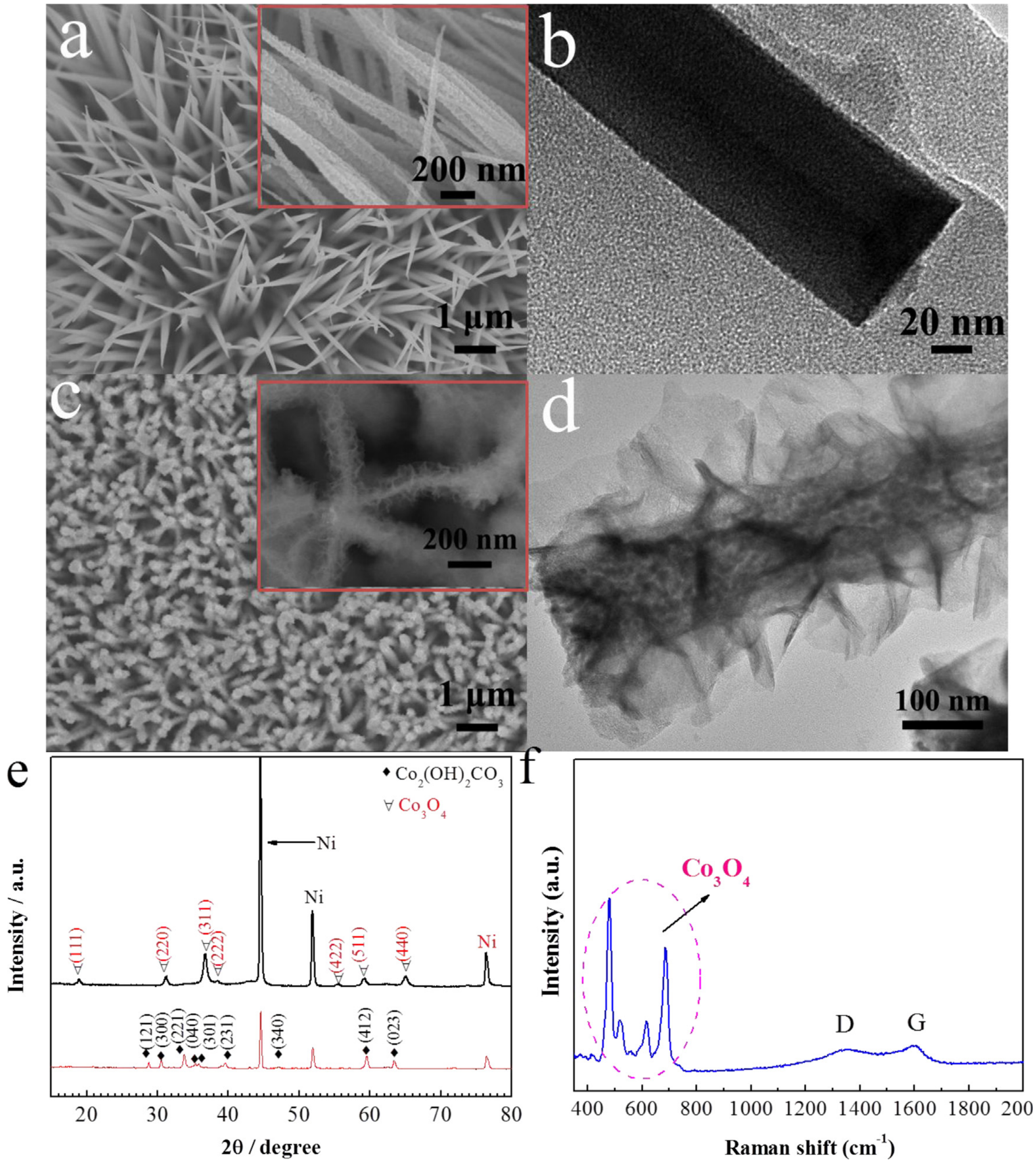

Fig. 1. SEM and TEM images of (a, b) $Co_2(OH)_2CO_3$ nanowire arrays and (c, d) Co_3O_4/C core-branch nanowire arrays. (e) XRD patterns of $Co_2(OH)_2CO_3$ and Co_3O_4/C core-branch nanowire arrays. (f) Raman spectrum of Co_3O_4/C core-branch nanowire arrays.

$(CH_3)_3$ and water were used as the aluminum and oxygen sources, respectively. Third, the $Co_2(OH)_2CO_3$–Al_2O_3 nanowires were immersed in 0.04 M glucose for 24 h and annealed in argon at 350 °C for 2 h. Finally, the Al_2O_3 was removed in 1 M KOH forming the Co_3O_4/C core-branch nanowire arrays. The weight of Co_3O_4/C core-branch nanowire arrays were ~1.7 mg cm^{-2}. The carbon in the core-branch nanowires accounted for ~3% analyzed by element analysis and Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo PQ3).

The morphologies and structures of the samples were characterized by X-ray diffraction (XRD, RIGAKU D/Max-2550 with Cu Kα radiation), field emission scanning electron microscopy (FESEM, FEI SIRION), transmission electron microscopy (TEM, JEOL JEM200CX) and Raman spectroscopy (LABRAM HR-800). The electrochemical measurements were carried out in a three-electrode electrochemical cell containing 2 M KOH aqueous solution as the electrolyte, Hg/HgO as the reference electrode and a Pt foil as the counter-electrode. Cyclic voltammetry (CV) and galvanostatic charge/discharge measurements were performed on CHI660c electrochemical workstation (Chenhua, Shanghai) and Neware program-control test system, respectively. The specific capacitance was calculated using the following equation:

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where C (F g^{-1}) and I (mA) represented specific capacitance and the current applied. ΔV (V), m (mg), and Δt (s) designated the potential drop during discharge, mass of the active materials, and total discharge time, respectively.

3. Results and discussion

SEM images of $Co_2(OH)_2CO_3$ nanowires and Co_3O_4/C core-branch nanowire arrays are shown in Fig. 1. After hydrothermal