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REVIEW

Hierarchical construction of core-shell metal oxide nanoarrays with ultrahigh areal capacitance

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Abstract
High areal capacitance of electrodes is highly desirable for practical supercapacitor applications, which requires a combination of high mass-loading and high utilization of electrochemically active material. In this work, we report the fabrication of hierarchical core-shell Co_3O_4@NiO nanowire@nanorod arrays where ultrathin NiO nanorods (~5 nm) were directly grown on the Co_3O_4 nanowire arrays via a two-step hydrothermal reaction followed by a calcination process. The hybrid nanoarrays exhibited a high specific capacitance of 2033 F g^{-1} at the current density of 5 mA cm^{-2} along with a mass loading as high as 19.5 mg cm^{-1}, leading to an ultrahigh areal capacitance of 39.6 F cm^{-2} as a supercapacitor electrode, much higher than that of pure Co_3O_4 nanowire arrays (6.7 F cm^{-2}). In addition, a remarkable rate capability (21.4 F cm^{-2} at the current density of 30 mA cm^{-2}) and excellent cycling stability (100% after 1000 cycles) were observed. Compared with the pure Co_3O_4 nanowire arrays, the greatly enhanced capacitive performance is mainly attributed to the unique hierarchical porous architecture and the synergistic effect of the individual components.

Contents

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Introduction

Recently, supercapacitors (SCs) have attracted significant attention due to their high power density, long life cycle, short charging time, and good safety record [1-3]. Their bridging function for the power/energy gap between traditional dielectric capacitors (which have high power output) and batteries/fuel cells (which have high energy storage) makes them potentially useful for powering HEVs and EVs [4]. In the last few decades, considerable efforts have been devoted to developing metal oxides electrodes, such as RuO_2 [5], IrO_2 [6], MnO_2 [7], NiO [8], Co_3O_4 [9-11], SnO_2 [12], V_2O_5 [13], Fe_2O_3 [14], and MoO_3 [15], because as faradaic materials for SCs, they can provide 10–100 times greater energy density than conventional carbon materials and better electrochemical stability than polymer materials [16-18]. Specially, most of these research works focused on achieving high specific capacitance of the electrode materials by building structures with small particles or thin film on the electrodes [19]. For instance, ultrathin mesoporous Co_3O_4 nanosheet arrays and $Ni(OH)_2$ on Ni foam were reported to show ultrahigh specific capacitance (2735 F g^{-1} and 2675 F g^{-1}) [20,21]. However, areal capacitance of the electrodes, as a critical requirement for a practical supercapacitor, is often ignored. A high areal capacitance requires a combination of high mass-loading of the electrochemically active material per area, and high utilization efficiency of this material (i.e. specific capacitance). In general, pursuing high mass-loading on conventional electrodes usually leads to an increase of "dead volume" in electrode materials which is not accessible to the electrolyte in the supercapacitor, and thus results in low utilization efficiencies of the materials [22]. As well known, the diffusion distance of electrolytes into pseudocapacitor electrodes is only ~20 nm in depth [23], which means that all the material included in such a depth can be considered as "on the surface", and can be involved in the redox reaction, while that underneath is "dead" or "inactive" material as far as electrochemical energy storage is concerned. Any attempt to increase the mass loading usually results in an increase of thickness of the material, which consequently leads to more inactive material being buried under the surface, and hence lower overall efficiencies. It is generally found that the specific capacitance decreases as the mass-loading of the electrode material increases, which results in their areal capacitance always being lower than ~15 F cm^{-2} [22].

In this regard, hierarchical design of complex core–shell nanoarrays with porous structures is considered as an effective approach to simultaneously achieve high mass-loading and high utilization of the electrode material, because they not only provide large active surface area and short diffusion path lengths to electrons and ions, but also show a potential synergistic effect of each component, leading to high capacitance, low internal resistance, remarkable rate capability, and excellent stability [24-27]. For example, Ni_3S_2 nanorod@Ni$(OH)_2$ nanosheet core–shell nanostructures [26] and cobalt monoxide nanowire@ultrathin nickel hydroxidenitrate nanoflake arrays [27] were reported to show areal capacitance of 4.7 F cm^{-2} and 2.4 F cm^{-2} with mass loading of 3.7 mg cm^{-2} and 3 mg cm^{-2}, respectively. We recently prepared hierarchical Co_3O_4@Ni-Co-O nanosheet@nanorod arrays, which showed very high areal capacitance of 25 F cm^{-2} with a mass loading of 12 mg cm^{-2} [28].

Herein, we designed and synthesized a hierarchical Co_3O_4@NiO nanowire@nanorod arrays (NWRAs) electrode with ultrahigh mass loading of the active materials (~20 mg cm^{-2}) to further enhance the areal capacitance to~~39.6 F cm^{-2} (2033 F g^{-1}) by growing ultrathin NiO nanorod (diameter of ~5 nm) on a Co_3O_4 nanowire array with high surface area (116 m^2 g^{-1}) through a two-step hydrothermal reaction. As far as we know, this value is much higher than the reported ones. Moreover, this electrode material also exhibits excellent rate capability (54% can be maintained when the current density increased 6 times) and cycling performance (100% after 1000 cycles). This hierarchical hybrid nanoarray, with short ion diffusion path and enlarged surface area, provides more efficient contact between electrolyte ion and active materials for Faradaic energy storage, paving a promising way to build high performance electrochemical electrodes.

Materials and methods

Synthesis of Co_3O_4@NiO nanowire@nanorod arrays (NWRAs)

All the reagents used were of analytical grade, purchased from Beijing Chemical Reagent Factory, and used as received without further purification. $Co_2(OH)_2CO_3$ nanowire arrays were firstly prepared by a reported method [29]. In a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ (2 mmol), NH_4F (8 mmol) and urea (10 mmol) were dissolved in 36 mL of distilled water and stirred to form a clear solution. Nickel foam (approximately 3 cm × 2 cm × 1.5 mm) was carefully cleaned with concentrated HCl solution (37 wt%), absolute ethanol, deionized water, consecutively. The aqueous solution and the nickel foam were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 120 °C for 12 h to prepare $Co_2(OH)_2CO_3$ nanowire arrays. To prepare the Co_3O_4@-NiO NWRAs, $Ni(NO_3)_2 \cdot 6H_2O$ (1–3 mmol) and urea (10 mmol)