



Investigation of the electroactive capability for the supercapacitor electrode with cobalt oxide rhombus nanopillar and nanobrush arrays



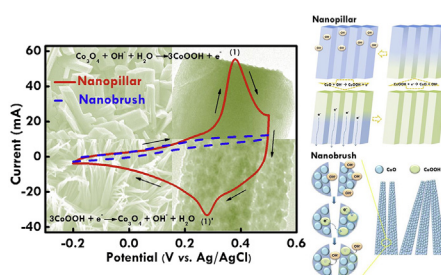
Yu-Bin Liu¹, Lu-Yin Lin^{*,1}, Ying-Yu Huang, Chao-Chi Tu

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology (Taipei Tech), Taipei 10608, Taiwan

HIGHLIGHTS

- One-dimensional cobalt oxide nanobrush and rhombus nanopillar arrays are made.
- Growth mechanism and structure-dependent supercapacitor performance are discussed.
- The nanopillar-based supercapacitor shows a specific capacitance of 509 F/g.
- The nanobrush-based supercapacitor shows a specific capacitance of 169 F/g.
- The nanopillar array has larger active surface area and less recombination sites.

GRAPHICAL ABSTRACT



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ABSTRACT

Well-defined nanostructures of the cobalt oxide are designed intensively to pursue large surface area and high conductivity as the electroactive material for supercapacitors (SCs). Instead of merely fabricating effective electroactive materials, two kinds of the cobalt oxide nanostructures synthesized directly on nickel foam to achieve good contact between the material and the substrate are compared to clarify the growth mechanism and the structure-dependent SC performance. The nanobrushes are completely composed of nanoparticles while the rhombus nanopillars present integrated structure by the recrystallization of single nanopillars. A higher specific capacitance (C_F) of 509 F/g is obtained for the SC electrode with CoO rhombus nanopillar array at a scan rate of 10 mV/s, comparing to that of 169 F/g for the CoO nanobrush array-based SC electrode, due to the larger electroactive surface area and less recombination sites for the former case. The C_F value is enhanced by 38% as compared with the initial value after 3000 cycles of repeated charge/discharge process for the CoO rhombus nanopillar array-based SC electrode due to the activation of the material. The results provide a blue print for achieving highly efficient SC electrode by carefully designing the well-established electroactive material to attain facile and long-lasting faradic reactions.

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1. Introduction

Energy-storage devices with high energy and power densities as well as long lifecycle can be realized by constructing the electrochemical supercapacitor (SC), which is classified into two types,

* Corresponding author.

E-mail address: lylin@ntut.edu.tw (L.-Y. Lin).

¹ The authors contributed equally.

electrochemical double layered capacitors (EDLCs) and pseudo-capacitors [1]. The EDLCs store electrostatic energy by separating charges in a Helmholtz double layer at the interface between the active material surface and the electrolyte, while the pseudo-capacitors store electrical energy by reversible faradaic redox reactions of the adsorbed ions at the electrode surface. Much attention has been paid on pseudo-capacitors due to its larger capacitance and fast redox kinetics, among which the cobalt oxides are considered as one of the most promising materials to accumulate charges *via* faradic reactions [2–4]. Wang et al. prepared multi-shelled cobalt oxide hollow microspheres and achieved a specific capacitance (C_F) of 360 F/g at a charge/discharge current density of 10 A/g [5]. Jiang et al. synthesized three-dimensional (3D) cobalt oxide/carbon flower-like nanostructures *via* a facile solvothermal strategy and obtained a C_F of 330 F/g at a charge/discharge current density of 0.5 A/g [6]. Wang et al. synthesized 3D-nanonet hollow structured cobalt oxide by a facile and eco-friendly route. A C_F value of 656 F/g measured by the cyclic voltammetry (CV) plot at a scan rate of 30 mV/s and a superior charge/discharge stability of 90.2% maintenance of its initial capacitance after 1000 continuous charge/discharge cycles at a current density of 5 A/g were achieved [7].

In addition, to realize practical application, it is necessary to improve the energy density of SCs at high rates *via* enhancing the kinetics of ion and electron transport at the electrode/electrolyte interface and in electrodes, as well as involving sufficient electroactive species exposed on the surface for the faradaic redox reaction. Hence, the morphology variation of the electroactive materials on the electrode has been regarded as one of the most important factors to influence the SC performances [8–11]. During the process of the faradic reaction for pseudo-capacitors to accumulate charges, the surface area of the active material for ions to adsorb on and subsequently undergo faradic reactions, the diffusion path for ions to reach the active materials from the electrolyte, as well as the conductivity of the active materials for charge transportation, are considered as the main concerns for achieving highly efficient SCs [12]. Constructing vertical growth nanomaterials directly on the conductive substrates has been reported to exhibit superior electrochemical capacitance [13–16]. As compared to the system with nanoparticles as the active materials, the randomly packed structure may lead to longer diffusion path for the ions to reach the active material from the electrolyte, and the abundant boundaries existing at the interfaces between the nanoparticles may cause low conductivity for charge transportation as well. In addition, if the active material is synthesized separately from the substrate, the post-coating process should be applied to fabricate the SC electrode. The connection between the active material and the substrate may be worse than the SC electrode prepared by directly growing the active material on the substrate. Xu et al. prepared cobalt and manganese oxides nanowires on nickel foam by a simple template-free growth process and a heat treatment. The resulting SC electrode exhibited a C_F value of 611 F/g at a charge/discharge current density of 2.38 A/g in a 6 M KOH electrolyte [14]. Nguyen et al. fabricated hierarchical mesoporous $\text{NiCo}_2\text{S}_4/\text{MnO}_2$ core-shell structured arrays on the nickel foam using a facile hydrothermal method and obtained a C_F of 17.5 F/cm² at a charge/discharge current density of 100 mA/cm² for the resulting SC electrode [17]. Qorbani et al. applied facile and low cost synthesis methods to produce hierarchical cobalt oxide/hydroxide nanoflakes on top of porous anodized cobalt layer, and achieved a maximum electrochemical capacitance of 601 mF/cm² at a scan rate of 2 mV/s [18].

Most of the researchers devoted to fabricating vertical growing cobalt oxide nanowire [14,19,20] or nanosheet [21,22] arrays directly on the conductive substrate by using facile and simple

methods to realize highly efficient SC electrodes, or tuning lots of reaction parameters to investigate the morphology variations on cobalt oxides. However, there is limited literature focus on the influence of the configuration of cobalt oxide arrays on the active surface area, ions diffusion path, electron transfer length, as well as the corresponding SC performances. Therefore, in this study, two cobalt oxide nanostructures with considerably different morphologies were directly synthesized on the nickel foam in the vertical direction *via* a facile template-free hydrothermal synthesis method. By simply varying the hydrothermal and post-annealing parameters in a very small extent, the rhombus nanopillar and nanobrush configurations were successfully obtained. The cobalt oxide rhombus nanopillar array presents integrated structure with some of the formation for the rhombus pillar nanopillars by four or five single rhombus nanopillars, while the cobalt oxide nanobrush array shows needle-like morphology composed of tiny nanoparticles. The electroactive surface area of the cobalt oxide and the diffusion path for the ions in the electrolyte are affected by the morphology of the electroactive material in a large extent because the spaces existing between each rhombus nanopillar and nanobrush is quite different. In addition, the boundaries and the recombination sites are also varied due to the different elements comprising the nanostructures, namely, the rhombus nanopillar presents integrated structure without other small components existing in the structure but the nanobrush is completely composed of several small nanoparticles. The higher C_F of 509 F/g was achieved for the SC electrode with CoO rhombus nanopillar array as the electroactive material, evaluated by the CV technique at a scan rate of 10 mV/s, which is higher than that of the SC electrode with CoO nanobrush array (169 F/g). The great cycling stability was also attended with 38% enhancement as compared with its initial C_F after 3000 continuous charge/discharge cycling test at a current density of 2 A/g for the CoO rhombus nanopillar array-based SC electrode, while the CoO nanobrush array-based SC electrode presents 26% maintenance of its initial C_F under the same condition. The conductivity of the electroactive material and the interfacial resistance for the electrode and electrolyte were also evaluated by applying the electrochemical impedance spectroscopy (EIS) technique.

2. Experimental

2.1. Materials

Ammonium fluoride (NH_4F , $\geq 98.0\%$), hydrochloric acid (HCl, analytical grade), ethanol (EtOH , $\geq 99.8\%$), and urea ($\text{CO}(\text{NH}_2)_2$, BioReagent) were purchased from Sigma–Aldrich. Cobalt(II)nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98.0%) was obtained from Showa.

2.2. Preparation of electrodes with CoO nanobrush and CoO rhombus nanopillar arrays on nickel foam

The nickel foam was cleaned prior to be applied in the hydrothermal reaction. The nickel foam with the size of 1 cm in width and 3 cm in length was soaked in a solution containing 6 M HCl for 30 min under ultrasonic vibration, and subsequently washed by deionized water (DIW) and EtOH alternatively. The cleaned nickel foam was then dried in a vacuum oven for 1 h. In addition, the CoO nanostructures were synthesized using a template-free hydrothermal method. The synthesis of the CoO rhombus nanopillar array was shown as following. Solution A was prepared by dissolving 2 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 8 mmol NH_4F , and 10 mmol $\text{CO}(\text{NH}_2)_2$ in 36 ml DIW under stirring. The hydrothermal reaction was conducted by transferring 10 ml solution A and the cleaned nickel foam to a 110 ml Teflon-lined stainless steel autoclave, and

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