

Regular Article

Micelles directed preparation of ternary cobalt hydroxide carbonate-nickel hydroxide-reduced graphene oxide composite porous nanowire arrays with superior faradic capacitance performance

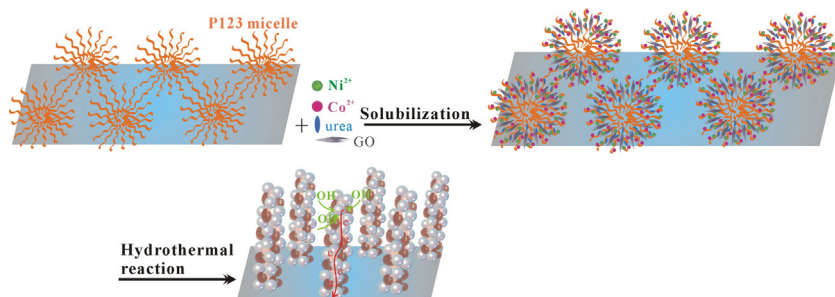


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GRAPHICAL ABSTRACT



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ABSTRACT

Electrode material is the key component of a supercapacitor, the highly accessible surface area, efficient electrons/ions migration channels, robust structural stability and redox activity of electrode material are pivotal prerequisites for harvesting optimal capacitive performance. Herein, a ternary cobalt hydroxide carbonate-nickel hydroxide-reduced graphene oxide composite (CN-rGO) with porous nanowire arrays architecture was deposited onto Ni foam substrate through confined hydrothermal reaction directed by surfactant micelles. The as-prepared CN-rGO nanowire arrays exhibit mesoporous texture with high specific surface area, which allows sufficient soaking of electrolyte with short diffusion path length. Additionally, the vertically aligned nanowires with incorporation of reduced graphene oxide offer efficient channels for migration of electrons generated by faradic components. Both features enable the sufficient faradic reactions and charge storage of the CN-rGO electrode. Under optimal Co:Ni feeding molar ratio of 7:3, the battery typed faradic CN-rGO electrode offers superior specific capacitance (2442 F g^{-1} at 1 A g^{-1}), good rate capability (65% capacitance retaining ratio within $1\text{--}20 \text{ A g}^{-1}$) and cycling stability (70% maintaining ratio after 2000 charge-discharge cycles). When used as faradic electrode of hybrid supercapacitor (HSC), balanced energy density ($42.9\text{--}26.2 \text{ Wh kg}^{-1}$), power density ($393\text{--}3519 \text{ W kg}^{-1}$) and cycleability (80% initial capacitance maintaining ratio undergoes 5000 charge-discharge cycles) can be delivered simultaneously, highlighting the potential of the micelles directed CN-rGO nanowire arrays electrode in efficient energy storage device.

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1. Introduction

Supercapacitors represent a significant category of energy storage and management devices, which operate through the electrostatic sorption of charged ions at porous electrode surface (electric double layer or EDL- capacitance) and/or the superficial redox reactions of active electrode (faradic capacitance). Because of the fact that only surface layers of electrode are involved in the electrochemical reactions, supercapacitors own higher power densities (P_{cell} s), charge-discharge rates whereas lower energy densities (E_{cell} s) relative to other secondary batteries. Electrode material is the key component of a supercapacitor, the accessible surface area, redox activity and conductivity of electrode material directly determine the specific capacitance (C_s) and further E_{cell} of the pertinent supercapacitor. Hence, the enhancements of electric double layer (EDL-) and faradic capacitances by rational composition and structure design are currently the major tasks in supercapacitor fields.

Relative to the chemically inert carbon materials with EDL- feature, the battery typed faradic materials can experience multiple redox reactions reminiscent to traditional batteries, therefore enable one order of magnitude higher C_s . Hence, different faradic materials, including transition metal oxides [1,2], sulfides [3,4], as well as conductive polymers [5] are widely investigated to improve the charge storage capacities of supercapacitors. Co, Ni hydroxides and hydroxide carbonates are significant faradic materials that can be easily synthesized by hydrolysis of precursor salts whilst own high redox activities and reversibilities, which cater for the notion of low cost and efficient energy storage. The binary composites composing of Co, Ni hydroxides and hydroxide carbonates can further enhance the faradic activities by coupled faradic contributions of both components [6,7], hence own great promise in high performance supercapacitor. On this basis, the construction of porous architecture with more exposed surface sites and more efficient ions infiltration channels is a potential strategy to substantially maximize the capacitive performance of Co, Ni hydroxides (hydroxide carbonates) based composites. Various porous architectures, such as interconnected nanoflakes [8] and porous nanowires [9] of Co, Ni hydroxides and hydroxide carbonates were designed to boost the faradic capacitances *via* optimized ions diffusion channels and surface utilization ratios. As for the porous faradic composite nanowires electrode, if the nanowires can be vertically aligned and firmly grown onto current collector, electrolyte ions can easily fill into the abundant interwire voids and infiltrate into the inner surface of nanowires along radial directions with short path length, and the vertical nanowire arrays also shorten the electrons migration distance to outer circuit, thus ensures high capacitive performance. Despite this, the intrinsically low conductivities of these Co, Ni based faradic materials cause severe energy loss, especially operated at high operation current densities, and the rigid structure of these inorganics is incapable of enduring the volumetric variations during charge-discharge cycles, both factors limit the rate capabilities and cycleabilities of the pertinent supercapacitors. These shortages can be mitigated by incorporating of conductive and flexible carbonaceous substrates into the faradic Co, Ni hydroxide and hydroxide carbonates porous nanowire arrays [10–12]. Reduced graphene oxide (rGO) is a singly atom layer carbon material with high electric conductivity, specific surface area and robust mechanical strength, which can be easily prepared by solution processable reduction of graphene oxide (GO) precursor. Hence, rGO can be homogeneously incorporated into the faradic Co, Ni hydroxide-hydroxide carbonate composite nanowire arrays as a flexible and conductive scaffold to improve the conductivity and structural tenacity, which necessitate elaborate structural design.

Micelles are ordered congeries assembled by radially/parallelly arrayed surfactant chains or blocks of copolymers. The prominent solubilization characteristics of micelles promote the enrichment of ions and polar/nonpolar molecules within the ordered inter-chain cavities to prepare molecular sieves and ordered mesoporous materials. Benefited by the ordered structure and the solubilization effect of micelles, herein, porous nanowire arrays of ternary CN-rGO composites were synthesized and deposited onto Ni foam substrate through confined hydrothermal assembly directed by block copolymer surfactant micelles. The resultant CN-rGO electrode can offer outstanding faradic capacitance, good rate capability and cycleability by further tuning of Ni:Co feeding molar ratio. When used as faradic electrode of hybrid supercapacitor (HSC), high E_{cell} , P_{cell} and good cycleability can be delivered simultaneously, showing the potential of the micelles directed ternary CN-rGO porous nanowire arrays electrode in efficient energy storage devices.

2. Experimental

2.1. The preparation of CN-rGO porous nanowire arrays electrodes

In a typical process, 200 mg of polyethylene oxide-polypropylene-polyethylene oxide triblock nonionic copolymer (P123, $M_w = 5800$, Saen Chemical technology co. LTD) surfactant and 0.61 g (10 mmol, purity: 99%, Sinopharm Group) urea were ultrasonically dispersed in 40 mL deionized water to form a homogeneous suspension. Thereafter, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (purity: 98.5%, Sinopharm Group) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (purity: 98%, Sinopharm Group) with total dosage of 2 mmol whereas different Co:Ni molar ratios were dissolved in the above mixture under vigorous stirring for 20 min. Meanwhile, 40 mg of GO (prepared by modified Hummer's method [13]) was ultrasonically dispersed in 20 mL of deionized water and then centrifuged to afford homogeneous GO suspension with concentration of 2 mg mL^{-1} . The GO suspension was poured into the Co, Ni salts solution and stirred for 1 h, the reaction mixture was then transferred into a 50 mL Teflon lined autoclave, a piece of Ni foam pre-cleaned in turn with diluted HNO_3 and deionized water was immersed vertically in the reaction system. The autoclave was sealed and heated at 100°C for 5 h to hydrothermally deposit the CN-rGO composite active layer onto Ni foam substrate. After being cooled to room temperature, the Ni foam coated with a layer of deep pink active layer was rinsed ultrasonically to eliminate the redundant portion and then dried at 60°C overnight. The afforded CN-rGO electrodes with Co:Ni feeding molar ratio of 3:7, 5:5, 7:3 and 9:1 were abbreviated as $\text{CN}_{3:7}$ -rGO, $\text{CN}_{5:5}$ -rGO, $\text{CN}_{7:3}$ -rGO and $\text{CN}_{9:1}$ -rGO electrodes, respectively. The hydrothermal temperature of $\text{CN}_{7:3}$ -rGO electrode was also altered to 90 and 110°C , the resulted electrodes were denoted as $\text{CN}_{7:3}$ -rGO₉₀ and $\text{CN}_{7:3}$ -rGO₁₁₀, respectively. The binary composite composing of $\text{Co}_2(\text{OH})_2\text{CO}_3$ and $\text{Ni}(\text{OH})_2$ was also prepared following the procedure for $\text{CN}_{7:3}$ -rGO but in absence of GO, which was labeled as $\text{CN}_{7:3}$.

rGO for EDL- electrode was prepared by hydrothermal reduction of GO suspension at 180°C for 12 h. The corresponding rGO electrode was fabricated by spreading the slurry composing of rGO, acetylene black and tetrafluoroethylene binder with a mass ratio of 85:10:5 onto stainless steel mesh current collector.

2.2. Characterizations

The morphologies and microstructures of the products were characterized by scanning electron microscopy (SEM, Hitachi SU-8000) coupled with X-ray energy dispersive spectroscopy (EDS) and transmittance electron microscopy (TEM, JEOL JEM-2100).

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