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A novel oxidation–reduction route for successive ionic layer deposition of $NiO_{1+x}\cdot nH_2O$ nanolayers and their capacitive performance

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ABSTRACT

Successive ionic layer deposition (SILD) of $NiO_{1+x}\cdot nH_2O$ nanolayers was first performed by an oxidation–reduction route using a $Ni(NO_3)_2$ and $K_2S_2O_8$ aqueous solutions. The obtained nanolayers were characterized by SEM, EDX, XRD, XPS, UV–vis and FTIR spectroscopy and electrochemical techniques. The results showed that the as-synthesized product is formed by nanosheets with a thickness of 6–12 nm, having cubic crystal structure of NiO and rhombohedral structure of γ-NiOOH. Electrochemical characterization of the sample prepared by 100 cycles of SILD indicated a capacitive behavior with the specific capacitance value of 1015 F/g at a current density of $1\ A\,g^{-1}$ in $1\ mol\,L^{-1}$ KOH aqueous solution. Repeated cycling for 3000 charge–discharge cycles demonstrate 10% capacitance fade relative to the initial values. The presented convenient route of synthesis may be used for the preparation of $NiO_{1+x}\cdot nH_2O$ nanolayers with high surface area and a large capacitance.

1. Introduction

Supercapacitors, also known as electrochemical capacitors (EC) derive capacitance as a result of charge separation at the electrode and electrolyte interface. They are already widely used in many fields of electronics and electrical engineering due to their unique properties, such as high power density, long cycling life, short charging time and high efficiency [1].

According to charge storage mechanisms, EC can be divided into two types, electrochemical double-layer capacitors (EDLC) and pseudocapacitors. Pseudocapacitors get their charge from the fast and reversible Faradic reaction that takes place at the electrode–electrolyte interface. Faradaic processes allow pseudocapacitors to achieve greater capacitances (10–100 times higher) and energy densities than EDLC [2].

As electrode materials for pseudocapacitor have been widely used metal oxides such as RuO_2 [3,4], MoO_3 [5], Co_3O_4 [6], MnO_2 [7,8], V_2O_5 [9] etc., because they possess high specific capacitance at low resistance [10]. Recently, nickel oxide attracted much attention as electrode material for supercapacitor in alkaline electrolytes due to its easy synthesis, relatively high specific capacitance, high chemical stability, environmental friendliness, and low cost [11–13].

Currently, several methods for the preparation nanostructured NiO various shapes and values have been presented. Thin layers of NiO are obtained by sol–gel techniques [14–16], electrochemical preparation [17–19], CBD (chemical bath deposition) [20], hydrothermal [21] and solvothermal [22] method and SILAR (Successive Ionic Layer Adsorption and Reaction) method [23] with using solution of $Ni(NO_3)_2\cdot 6H_2O$ and aqueous ammonia.

New possibilities of thin film NiO synthesis rose after development of Layer-by-Layer (LbL) synthesis techniques that makes possible to deposit NiO layers on the surface of samples with irregular shape, providing exact thickness of the layer [24]. As reagents to LbL synthesis commonly been used of charged inorganic substances, including colloidal nanoparticles, heteropolyacids, metal nanoparticles and polyelectrolyte solutions. The LbL self-assembly technique offers an excellent opportunity for the interface engineering of multilayer thin film structures or nanostructured building blocks, which can result in significantly improved electronic conductivity and high electrochemical performance of supercapacitors. LbL has quickly received growing attention as an effective, simple and environmentally benign way to develop advanced surface coatings, novel materials with nanoscopically controlled structure and nanopatterns, mesoporous and nanoparticles based materials for catalytic applications. The major advantage of the LbL self-assembly is its simplicity and low cost [25]. The LbL self-assembly provides a simple and effective method for preparing thin-film electrodes for electrochemical capacitors. One of the methods of LbL synthesis is the method of Successive Ionic Layer Deposition (SILD) [26–28] or in

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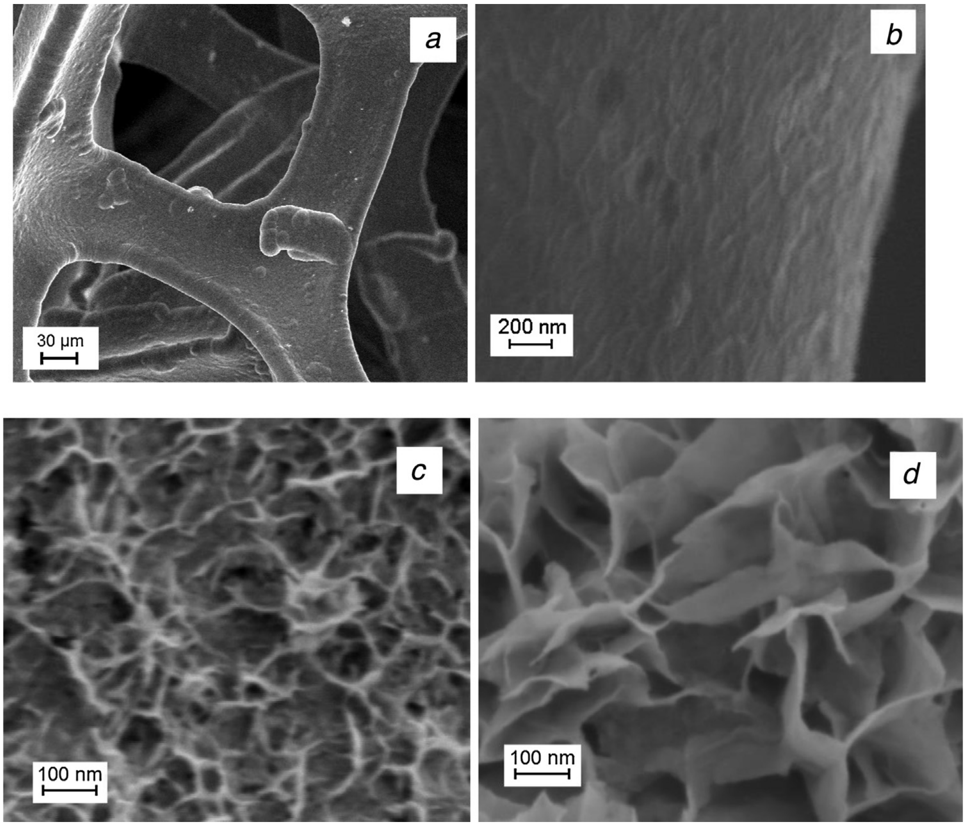

Fig. 1. SEM images (a,b) – the surface of origin nickel foam, (c) – as-prepared $NiO_{1+x}\cdot nH_2O$ layer on the surface of nickel foam synthesized after 100 SILD cycles and (d)—$NiO_{1+x}\cdot nH_2O$ layer on the surface of nickel foam after 3000 charge–discharge cycles.

other terminology SILAR. The synthesis of SILD method is performed without the use of polyelectrolyte solutions and this makes it possible to significant by simplify the procedure and get the coating that contains only inorganic compounds, which is important for many tasks.

In this article, we report the synthesis of $NiO_{1+x}\cdot nH_2O$ thin films by simple SILD method from solutions of nickel salt and potassium persulfate, and its application to create of supercapacitors electrode materials.

2. Experimental

As a substrate for nanolayers synthesis 5 × 25 mm polycrystalline nickel foam (NF) plates (110 PPI) were used, on which electrochemical experiments were preformed, and also 10 × 25 × 0.35 mm single-crystal silicon plates with <1 0 0> orientation, and a plate of fused quartz with size of 10 × 30 × 1 mm were used for physical characterization. Extra pure water (Mili-Q) was used in all experiments. Substrates of silicon were cleaned in an ultrasonic bath filled with acetone for 10 min. Then plates were sequentially treated for 10 min in concentrated HF, water, 70% HNO_3, water, 1 M KOH and than flushed out by water. NF plates were treated according to the technique described in [29] for 15 min in 6M HCl solution, then several times rinsed by water and dried on air at 120 °C for 30 min.

Aqueous 0.01 M solutions of analytical grade $Ni(NO_3)_2\cdot 6H_2O$ (pH 6.5) and $K_2S_2O_8$ (pH 10) were used. pH of these solutions was controlled by addition of KOH solution.

For synthesis of $NiO_{1+x}\cdot nH_2O$ substrate plates were sequential immersed for 30 s into solution of nickel salt, water, solution of potassium persulfate and again water. The sequence corresponds to one SILD cycle, which is repeated 100 times to obtain desired film thickness. Then sample was annealed on air at 150 °C for 10 min at a heating rate of 5 °C/min.

FTIR transmission spectra of synthesized films on silicon surface were registered by Shimadzu IR Prestige-21 spectrophotometer using differential technique with respect to spectra of bare silicon plate.

XRD patterns were obtained using a Rigaku Miniflex II diffractometer. The measurement conditions were Cu Kα radiation, 30 kV voltage, and 10 mA current.

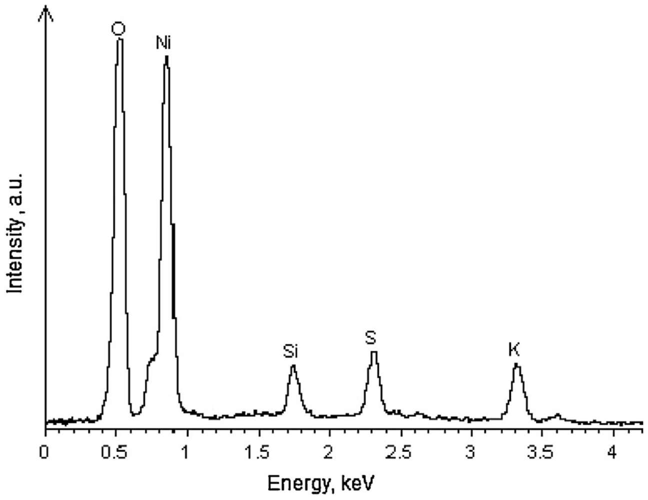

Fig. 2. EDX spectrum of $NiO_{1+x}\cdot nH_2O$ layer on silicon surface.