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Red-ox reactions in aqueous solutions of $Co(OAc)_2$ and $K_2S_2O_8$ and synthesis of CoOOH nanolayers by the SILD method

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CoOOH nanolayers were first prepared by the successive ionic layer deposition (SILD) method using aqueous $Co(OAc)_2$ and $K_2S_2O_8$ solutions. The obtained nanolayers were investigated by SEM, EDX, XRD, FTIR spectroscopy and electrochemical techniques. SEM images showed that the layers formed by nanosheets of size approximately 80-100 nm which had a hexagonal crystal structure. Electrochemical study of nickel foam electrodes modified by CoOOH layer prepared by 50 SILD cycles demonstrates that specific capacitance of the film is 1520 F/g at current density 1 A/g. Repeated cycling for 1000 charge-discharge cycles demonstrates 2% capacitance fade, so such electrodes may be used as pseudocapacitor electrodes.

Keywords: cobalt oxyhydroxide, nanolayers, SILD, electrochemical properties.

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1. Introduction

Cobalt oxide is known to be a transition metal oxide with intriguing electrocatalytic, optical, magnetics, electronic and electrochemical properties. In recent years, cobalt oxyhydroxide and oxides have found wide applications as materials for electrochemical sensors [1], catalysts [2], drug delivery systems [3] and lithium-ion batteries [4]. In particular, cobalt oxyhydroxide attracts special attention as a material for pseudocapacitors because they showing large specific capacitance, low cost, natural abundance and environmental friendliness [5].

Previously, cobalt oxyhydroxide was obtained by electrodeposition [6], CBD [7], hydrothermal [8] and chemical precipitation [9] methods.

In this work, we describe a new simple route for synthesis of cobalt oxyhydroxide nanolayers by the successive ionic layer deposition (SILD) method from aqueous solutions of a cobalt (II) salt and potassium persulfate and investigate its electrochemical properties as electrode materials for pseudocapacitors. The SILD method is based on the sequential adsorption of anions and cations onto a substrate surface with the formation of a nanolayer of insoluble compounds [10].

The problem of achieving irreversible reactions at each stage of processing reagents is one of the main problems for this method of nanolayer synthesis. For the synthesis of metal oxide layers by this method, the obtained layer is most commonly formed by oxidation-reduction reactions, e.g. a layer of $SnO_2 \cdot nH_2O$ is formed by the interaction of the Sn (II) cations and a slightly alkaline solution of H_2O_2 [11], a layer of $TiO_2 \cdot nH_2O$ – solutions of $Ti_2(SO_4)_2$ and $NaNO_2$ [12], the layer of nanoparticles Ag - $AgNO_3$ solutions and N_2H_5OH [13;14], etc.

The major advantage of this method is its simplicity and equipment, its suitability for coating of most surfaces, the application to substrates with irregular shapes and sizes

and precision control of the multilayer thickness. These advantages for the SILD method permit one to obtain nanolayers based on a wide range of substances which may be used in optics, microelectronics, energy storage devices. The SILD method provides a simple and effective means for creating metal oxide nanolayers for thin-film electrodes, which may result in significantly improved electronic conductivity and high electrochemical performance of pseudocapacitors. The possibility of creating electrode materials on the basis of thin-film nanolayers of layered double hydroxides, which showed a good electrochemical performance, has been shown in our previous work [15,16].

2. Experimental methods

As substrates for nanolayer synthesis, single-crystal silicon plates ($10\times30\times1$ mm with $\langle100\rangle$ orientation) and polycrystalline nickel foam (NF) plates (110 PPI, $10\times25\times0.35$ mm) were used. The layers, obtained on the silicon plates, were characterized by physical methods, while those formed on NF plates were characterized by electrochemical methods. Substrates of silicon were cleaned in an ultrasonic bath filled with acetone for 10 minutes. Than plates were sequentially treated for 10 minutes in concentrated HF, water, 70% HNO_3, water, 1 M KOH and then flushed with water. NF plates were treated for 15 minutes in aq. 6 HCl, then rinsed several times with deionized water and dried aerobically at 120°C for 30 minutes.

For SILD synthesis, the following solutions were used: aqueous 0.01 M $Co(OAc)_2$ with (stable pH) and aq. 0.01 M $K_2S_2O_8$ with pH 9.5, which was achieved by addition of a KOH solution. All the reagents used were of analytical grade. Deionized water with resistively 18.2 MΩ·cm (Mili-Q) was used for solution preparation.

CoOOH films were synthesized on silicon and NF substrates by SILD techniques. First, plates were sequentially immersed for 30 seconds into a solution of cobalt salt, then washed in distilled water. Next, plates were dipped for 30 seconds in a potassium persulfate solution and again washed in water. This sequence corresponds to one SILD cycle, which is repeated 50 times to obtain the desired film thickness. Finally, the sample was annealed in air at 150°C for 10 minutes at a rate of 5°C/min.

The morphology and composition of the CoOOH films were investigated by scanning electron microscope (SEM) at an accelerating voltage 20 kV on Zeiss EVO-40EP microscope and energy-dispersive X-ray spectroscopy (EDX) used detector Oxford INCA350. FTIR transmission spectra of synthesized films on silicon surface were registered by FSM 2201 spectrophotometer using a differential technique with respect to the spectra for the bare silicon plate. X-ray diffraction (XRD) was carried out on Rigaku Miniflex II diffractometer with Cu K_α radiation, 30 kV voltage, and 10 mA current.

The electrochemical measurements of NF electrodes with the synthesized CoOOH layer were carried out in a three-electrode electrochemical cell in aq. 1M KOH as an electrolyte using Elins P-30I potentiostat. After 50 SILD cycles, the NF electrode was used as the working electrode. For the reference electrode, a Ag/AgCl (aq.KCl sat.) electrode was used, while a platinum plate served as the counter electrode. Electrochemical characterization of the films was made by cyclic voltammetry (CV) and galvanostatic charge-discharge (CD) techniques. The CVs were performed in a voltage window between -100 and 800 mV at different scan rates of 5, 10 and 20 mV/s. The CDs were carried out in a voltage window between 0 and 600 mV under different current density from 1 to 5 A/g. Specific capacitance (C) values were calculated using following equations:

$$C = I\Delta t/\Delta V m,$$

where I(mA) is a galvanostatic current, ΔV(mV) is the potential window, Δt(s) is the discharge time of a cycle and m(g) is the mass of the active material in the film electrode. The electroactive mass of CoOOH for the working electrode was measured using an OHAUS Pioneer^{TM} PA54C microbalance.

3. Result and discussion

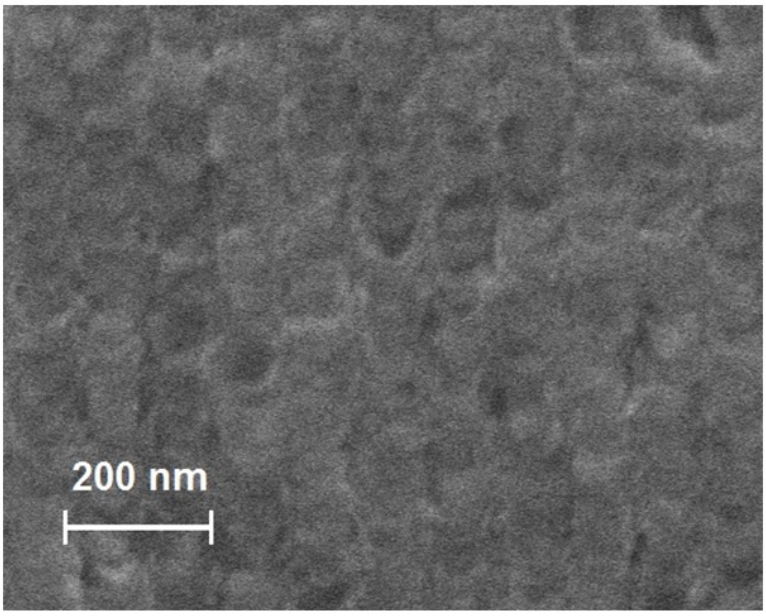

FIG. 1. SEM image of CoOOH layer on a silicon surface

SEM investigation of the synthesized sample shows that they formed by nanosheets of size approximately 80–100 nm (Fig. 1). The results of the dispersive X-ray spectroscopy showed significant energy signal intensity of the Co, O, and C elements in the sample. Average content of K and S in layer was no more than a few percent.

The XRD patterns of sample by XRD are shown in Fig. 2. Sample represents typical diffraction peaks (003), (101), (012), (015), (110), (113), which correspond to hexagonal crystal structure of β-CoOOH (JCPDS 14-0673) [8].

Fig. 3 shows the FTIR absorption spectrum of the CoOOH nanolayer. The broad band at 3400 cm^{-1} is attributed to O-H valence vibrations of the hydroxyl groups. The band at 1640 cm^{-1} attributed to O-H deformation vibrations [17]. The bands with peaks at 1472 and 1364 cm^{-1} corresponds to the valence vibrations of carbonyl group of acetate contained in CoOOH [18]. In this spectrum, one can identify the absorption band with peak at 1107 cm^{-1}, corresponding to valence vibrations of S-O in impurity ions of $S_2O_8^{2-}$ and SO_4^{2-}, which is probably adsorbed onto the surface of CoOOH nanoparticles [19]. The band observed at 594 cm^{-1} was ascribed to Co-O vibrations in CoOOH [20].

In order to explain the obtained results, a scheme of chemical reactions, occuring on the surface, can be suggested. During the first step, after dipping in the cobalt acetate solution and wash for remove excess of salt on the surface, a layer of cobalt(II) hydroxide is formed:

$$\text{-Ni-OH} + \text{Co(OAc)}_2 + \text{H}_2\text{O} \rightarrow \text{-NiOCoOH} + 2\text{HOAc}, \tag{1}$$

Then, after treatment with excess $K_2S_2O_8$ solution, an atoms of cobalt (II) from adsorbed hydroxide is transfered in the oxidation state 3+ and form insoluble oxyhydroxide

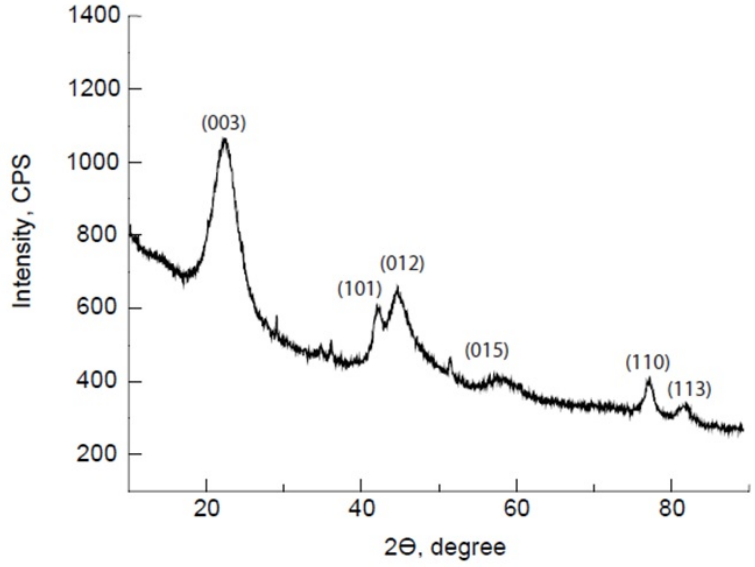

FIG. 2. XRD pattern of synthesized sample

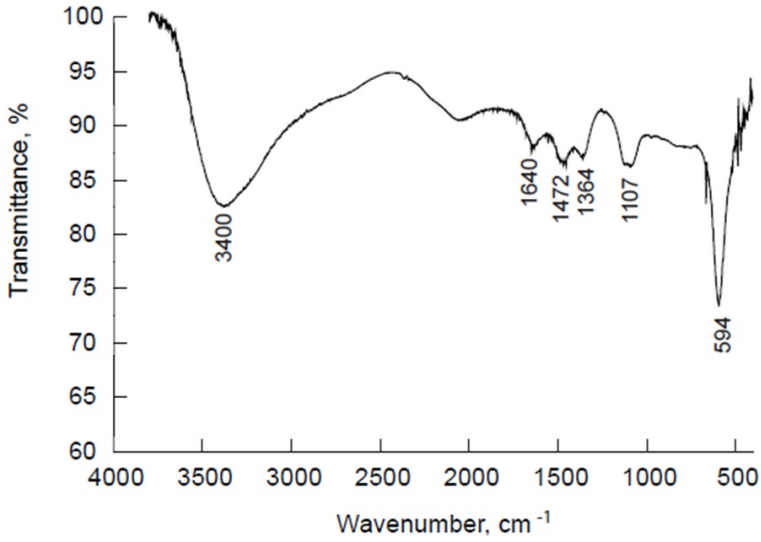

FIG. 3. FTIR transmission spectrum of CoOOH layer on silicon surface

CoOOH.

$$\text{-NiOCoOH} + S_2O_8^{2-} + H_2O \rightarrow \text{-NiOCo(OH)}_2 + 2HSO_4^-. \quad (2)$$

On the second SILD cycle, during the treatment with cobalt acetate solution, cobalt (II) cations are also adsorbed onto the surface of this layer, and then subsequently react with $S_2O_8^{2-}$ anions in the processing of the following solution, thus, the thickness of the synthesized layer increases. On the second and all subsequent cycles, when the layer is forming, the bonds of Co-O-Co form, and as result, the crystal lattice of CoOOH is generated.

Important results were obtained by electrochemical study of NF electrode with SILD synthesized CoOOH layer. As demonstrated in Fig. 4, at a scan rate 5 mV/s, two redox processes takes place in the layer, including the $Co^{3+} \rightarrow Co^{4+}$ transformation at 670 mV and the $Co^{4+} \rightarrow Co^{3+}$ at 170 mV [5]. The proportionality of currents to the square root of scan

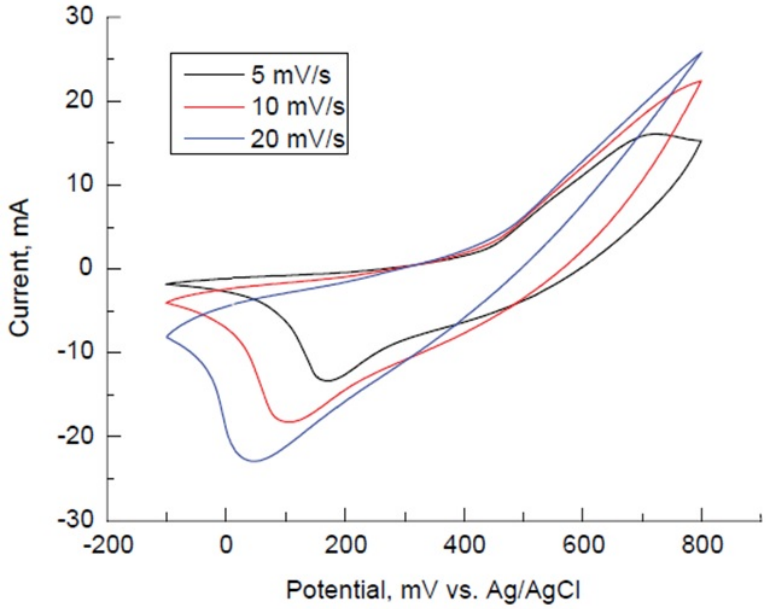

FIG. 4. Cyclic voltammogramms of nickel foam electrode, covered by CoOOH layer, recorded at different scan rates

rate provides information that the film is thick enough, and charge transfer rate is limited by diffusion of charge carriers in the film.

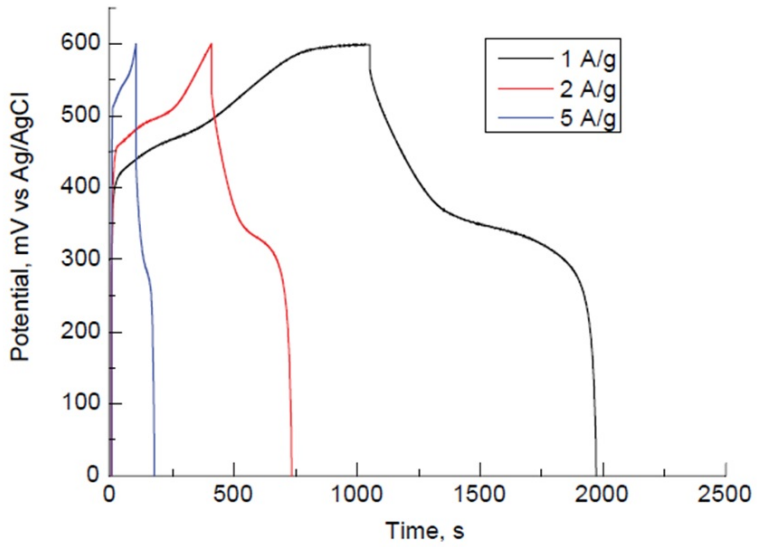

FIG. 5. Galvanostatic charge-discharge curves of nickel foam electrode, covered by CoOOH layer, recorded at different current densities

Charge-discharge curves of CoOOH-NF electrode at different currents (Fig. 5) allow one to determine its capacitance. For instance, specific capacitance of a sample, formed by 50 SILD cycles, is 1520 F/g at a current density of 1 A/g. The long-term cycle stability of the CoOOH-NF electrodes was evaluated by repeating the charge-discharge tests at 5 A/g for 1000 cycles. A capacitance retention ratio of 98% was obtained after 1000 charge-discharge cycles, illustrating the long-term electrochemical stability of the CoOOH-NF electrodes.

4. Conclusion

In this paper, we obtained CoOOH nanolayers with hexagonal crystal structure of β-CoOOH. The SILD method used $Co(OAc)_2$ and $K_2S_2O_8$ aqueous solutions. The electrochemical study of CoOOH nanolayer-modified nickel foam electrodes, prepared by 50 SLID cycles, demonstrates that the specific capacitance of the film is 1520 F/g at a current density of 1 A/g. Repeated cycling for 1000 charge-discharge cycles demonstrate a relatively small 2% capacitance fade. The results illustrate the long-term electrochemical stability of the system, and thus its potential application as materials for electrode of pseudocapacitors.

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References

[1] Muhammad Mehmood Shahid, Perumal Rameshkumar, Alagarsamy Pandikumar, at all. An electrochemical sensing platform based on a reduced graphene oxide–cobalt oxide nanocube@platinum nanocomposite for nitric oxide detection. *J. Mater. Chem. A*, 2015, **3**, P. 14458–14468.

[2] Xiaohui Deng, Harun Tüysuüz. Cobalt-Oxide-Based Materials as Water Oxidation Catalyst: Recent Progress and Challenges. *ACS Catal*, 2014, **4**, P. 3701–3714.

[3] Karimi Z., Karimi L., Shokrollahi H. Nano-magnetic particles used in biomedicine: Core and coating materials. *Mater. Sci. Eng. C Mater*, 2013, **33**, P. 2465–2475.

[4] Mengmeng Zhang, Rong Li, Xiaoxuan Chang, Chao Xue, Xinglong Gou. Hybrid of porous cobalt oxide nanospheres and nitrogen-doped graphene for applications in lithium-ion batteries and oxygen reduction reaction. *Journal of Power Sources.*, 2015, **290**, P. 25–34.

[5] Kian Keat Lee, Wee Shong Chin, Chorng Haur Sow. Cobalt-based compounds and composites as electrode materials for high-performance electrochemical capacitors. *J. Mater. Chem. A*, 2014, **2**, P. 17212–17248.

[6] A.D. Jagadale, D.P. Dubal, C.D. Lokhande. Electrochemical behavior of potentiodynamically deposited cobalt oxyhydroxide (CoOOH) thin films for supercapacitor application. *Materials research bulletin.*, 2012, **47**(3), P. 672–676.

[7] Eiji Hosono, Shinobu Fujihara, Iraru Honma, Masaki Ichihara, Haoshen Zhou. Synthesis of the CoOOH fine nanoflake film with the high rate capacitance property. *Journal of Power Sources*, 2006, **158**, P. 779–783.

[8] Jinhu Yang, Takehiko Sasaki. Synthesis of CoOOH hierarchically hollow spheres by nanorod self-assembly through bubble templating. *Chem. Mater.*, 2008, **20**, P. 2049–2056.

[9] Zhaorong Chang, Huaji Li, Hongwei Tang, Xiao Zi Yuan, Haijiang Wang. Synthesis of γ-CoOOH and its effects on the positive electrodes of nickel batteries. *International Journal of Hydrogen Energy*, 2009, **34**(5), P. 2435–2439.

[10] V.P. Tolstoy. Successive ionic layer deposition. The use in nanotechnology. *Russ. Chem. Rev.*, 2006, **75**(2), P. 161.

[11] Korotcenkov Ghenadii, Cho Beongki, Tolstoy Valeri. SnO_2-based thin film gas sensors with functionalized surface. *Advanced Materials Research.*, 2010, **93-94**, P. 145–148.

[12] Konstantin Semishchenko, Valeri Tolstoy, Artem Lobinsky. A novel oxidation-reduction route for layer-by-layer synthesis of TiO_2 nanolayers and investigation of its photocatalytical properties. *Journal of Nanomaterials*, Volume 2014, Article ID 632068, 7 pages.

[13] L. B. Gulina, G. Korotcenkov, B. K. Cho, S. H. Han, V. P. Tolstoy. Ag nanoclusters synthesized by successive ionic layer deposition method and their characterization. *Journal of Materials Science*, 2011, **46**(13), P. 4555–4561.

[14] G. Korotcenkov, B.K. Cho, L.B. Gulina, V.P. Tolstoy. Gas sensor application of Ag nanoclusters synthesized by SILD method. *Sensors and Actuators B: Chemical.*, 2012, **166-167**, P. 402–410.

[15] A.A. Lobinsky, V.P. Tolstoy, L.B. Gulina. Direct synthesis of $Co_2Al(OH)_{7-2}\boldsymbol{x}(CO_3)\boldsymbol{x}\cdot\boldsymbol{n}H_2O$ layered double hydroxide nanolayers by successive ionic layer deposition and their capacitive performance. *Appl. Surf. Sci.*, 2014, **320**, P. 609–613.

[16] V.P. Tolstoy, A.A. Lobinsky, O.V. Levin, L.I. Kuklo. Direct synthesis of $Ni_2Al(OH)_{7-}x(NO_3)x \cdot nH_2O$ layered double hydroxide nanolayers by SILD and their capacitive performance. *Materials letters*, 2015, **139**, P. 4–6.

[17] J. Xie, H. Cao, H. Jiang, Y. Chen, W. Shi, H. Zheng, Y. Huang. Co_3O_4-reduced graphene oxide nanocomposite as an effective peroxidase mimetic and its application in visual biosensing of glucose. *Anal. Chim. Acta*, 2013, **796**, P. 92.

[18] Zhangpeng Li, Jinqing Wang, Lengyuan Niu, Jinfeng Sun, Peiwei Gong, Wei Hong, Limin Ma, Shengrong Yang Rapid. Synthesis of graphene/cobalt hydroxide composite with enhanced electrochemical performance for supercapacitors. *Journal of Power Sources*, 2014, **245**, P. 224–231.

[19] Vanitha Duraikkan, Sultan Asath Bahadur, Shunmuganarayanan Athimoolam. Crystal growth and characterization of potassium manganese nickel sulphate hexahydrate— A new UV filter. *Journal of Minerals and Materials Characterization and Engineering*, 2012, **11**, P. 1121–1125.

[20] Chih-Wei Tang, Chen-BinWang, Shu-Hua. Characterization of cobalt oxides studied by FT-IR, Raman, TPR and TG-MS. *Chienc Thermochimica Acta*. 2008, **473**, P. 68–73.