



# Solution layer-by-layer uniform thin film dip coating of nickel hydroxide and metal incorporated nickel hydroxide and its improved electrochromic performance

Junyi Liu<sup>a,b,1</sup>, Sing Yang Chiam<sup>b,1</sup>, Jisheng Pan<sup>b</sup>, Lai Mun Wong<sup>b</sup>, Sam Fong Yau Li<sup>a,\*</sup>, Yi Ren<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543 Singapore, Singapore

<sup>b</sup> Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 2 Fusionopolis Way, 138634 Singapore, Singapore

## ARTICLE INFO

### Keywords:

Thin film  
Dip-coating  
Nickel hydroxide  
SILAR  
Layer-by-layer  
Electrochromics

## ABSTRACT

In this work, we identified the problem faced by conventional successive ionic layer adsorption and reaction (SILAR) process in producing uniform nickel hydroxide films as the homogeneous precipitation reaction in water. Subsequently we proposed a novel SILAR recipe with a modified rinsing step and successfully demonstrated, for the first time, a layer-by-layer coating of uniform nickel hydroxide thin film without surface structures or agglomerated precipitates. In addition, we explored and demonstrated the capability of the proposed SILAR process in incorporating additional element such as aluminum into the nickel hydroxide film. The aluminum incorporated nickel hydroxide film shows improved electrochromic stability evidenced by reducing the degradation in coloration efficiency from 46% to 6%. The average coloration efficient is reported as 22 cm<sup>2</sup>/C and the response time is 4.5 s for bleaching and 4 s for coloration.

## 1. Introduction

Nickel hydroxide has received increasing attention in recent years for applications such as commercial alkaline secondary batteries [1–3], supercapacitors [4–6], catalysis [7,8], chemical sensor [9,10] and electrochromic devices [11–13]. The high power density, good cyclability, high specific energy and good optical modulation of nickel hydroxide make it very competitive for an extended range of applications. For many of these applications, especially for optical usage such as electrochromic smart window, a uniform, scalable and low-cost coating of nickel hydroxide thin film with controllable thickness is always preferred. However, none of the existing synthesis methods can address all of above aspects. For instance, solution based precipitation [14] and hydrothermal process [15] can only produce structured thin film that composes either fin or rod like surface structures, or surface bounded particles, not mentioning the poor control over thickness that does not increase linearly with time due to the depletion of the reactants. Physical vapor deposition [16] can produce uniform film but the level of hydration and the scalability is limited by the nature of the sputtering process. Electrodeposition, especially the nitrate based cathodic deposition process, is able to produce uniform nickel hydroxide film, but the process only works on conductive substrates [17,18].

The unrecyclable deposition solution and the needs of high pressure, temperature or power in above processes also inevitably increase the fabrication cost. Comparatively, solution dip coating method is a better approach because of its simplicity and scalability. Among various types of dip coating process, layer-by-layer dip coating enables fine tuning of the film thickness by a simple control of the number of dipping cycles. Notably, the dipping solutions can normally be recycled to save production cost. Successive ionic layer adsorption and reaction (SILAR) process is an emerging and well known layer-by-layer dip coating method that is used to produce many metal chalcogenide, oxide and hydroxide thin films [19]. SILAR process itself is a modified chemical bath deposition (CBD) process and is invented to avoid the homogeneous growth of particles within the deposition bath. Homogeneous reaction does not only complicate the morphology of the thin film produced, but also causes fast depletion of the non-recyclable deposition solution. In the conventional SILAR process, substrate is immersed into separated precursor solutions with rinsing in deionized (DI) water between every immersion [19]. The layer-by-layer thin film growth relies on the reaction of only adsorbed precursor ions on the substrate surface, what is known as heterogeneous growth. The water rinsing step removes excess precursor solution left on the substrate which will cause homogeneous growth of particles if carried over to the next precursor

\* Corresponding authors.

E-mail addresses: [chmlifys@nus.edu.sg](mailto:chmlifys@nus.edu.sg) (S.F.Y. Li), [renyi@imre.a-star.edu.sg](mailto:renyi@imre.a-star.edu.sg) (Y. Ren).

<sup>1</sup> Authors contributed equally to this work.

solution. However, to the best of our knowledge, uniform nickel hydroxide thin film using SILAR process has not been reported so far. In this work, we identified the problem of the conventional SILAR recipe and proposed modified process, so that a uniform nickel hydroxide thin film can be produced.

Moreover, many of the existing deposition methods, such as coprecipitation, hydrothermal and electroplating, are capable of producing mixed metal hydroxide materials. Such capability is very useful in producing functional thin films with enhanced performance. For instance, in the redox  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH system that are commonly used in battery and electrochromic applications,  $\gamma$ -NiOOH is easily formed when  $\beta$ -Ni(OH)<sub>2</sub> is overcharged. This results in a volume swelling or expansion of the material by the intercalation of water and ions, causing a rapid capacity or modulation fading during electrochemical cycles [2,3,20–22]. Therefore, improving material stability has become the highest priority for enhancing the performance of the nickel hydroxide based electrochromic and electrochemical devices. According to Bode diagram [23], the capacity limitation and the volume swelling will be solved if the long-time cycle between  $\alpha$ -Ni(OH)<sub>2</sub> and  $\gamma$ -NiOOH could be realized. However, pure  $\alpha$ -Ni(OH)<sub>2</sub> is labile in strong alkaline medium and rapidly transforms itself into  $\beta$ -Ni(OH)<sub>2</sub>. Many efforts have been focused on the preparation of stabilized  $\alpha$ -Ni(OH)<sub>2</sub> by incorporating Co [24,25], Al [3,26], Fe [27], Mn [28] and Zn [29] into nickel hydroxide. Among these metals, Aluminum is considered to be the most effective element to stabilize  $\alpha$ -Ni(OH)<sub>2</sub> and improve its electrochemical and electrochromic performance [3]. Recently, aluminum containing nickel hydroxide materials prepared by electrodeposition [28,30], hydrothermal process [26,31] and precipitation at elevated temperature [1,32–34] have been reported showing superior cycling reversibility and improved capacity compared with  $\beta$ -Ni(OH)<sub>2</sub> for battery and supercapacitor applications. However, thin films grown by above methods may not provide a clear view due to light scattering by the structured surface morphology which may affect their application as window devices. In this work, we demonstrated the versatility of the proposed SILAR process in obtaining uniform Al incorporated nickel hydroxide thin film. We studied the Al incorporation mechanism and demonstrated the improved cycling stability of our films.

## 2. Material and methods

### 2.1. Sample preparation

Tin-doped indium oxide (ITO) coated glass with a resistivity of 8–12  $\Omega/\square$  was used as the substrate and was cleaned by sonication in Acetone, IPA and deionized (DI) water for 10 min each. UV-Ozone treatment using Novascan UV Ozone Cleaner at 100 °C for 10 min was used to remove the remaining organic residual on the surface. For the nickel hydroxide coating, the ITO substrate was sequentially dipped into solutions containing 1% of aqueous ammonia, 0.1 M of nickel complex solution (0.1 M of nickel sulfate in excess aqueous ammonia), 1% of aqueous ammonia and DI water at room temperature. The above process was repeated to achieve desired film thickness. For Al incorporated nickel hydroxide film, the substrate was sequentially dipped into solutions containing 1% of aqueous ammonia, 0.1 M of nickel complex solution, 1% of aqueous ammonia, DI water, 0.01 M of hydroxoaluminate solution (0.005 M Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in excess NaOH) and DI water at room temperature. The above process was repeated to achieve desired film thickness. For control experiments used to understand growth mechanism, several dipping solutions were selectively removed from the dipping cycle. Nickel based thin films produced by other deposition processes were also employed in this work. This includes sputtered nickel oxide thin film and electroplated nickel hydroxide thin film. Sputtering deposition was achieved through unbalanced magnetic sputtering system using Ni target with oxygen and argon ratio of 1:1 for 20 min. The sputtering power was maintained at 300 W. The

electrodeposition was carried out by using a Metrohm Autolab potentiostat with a standard 3 M Ag/AgCl reference electrode and a Pt foil counter electrode in a 0.5 M Ni(NO<sub>3</sub>)<sub>2</sub> electrolyte. The nickel hydroxide film was electroplated under  $-0.9$  V for 2 min.

### 2.2. Electrochromic characterization

The chronoamperometry (CA) measurements were carried out using a Metrohm Autolab potentiostat with a standard 3 M Ag/AgCl reference electrode and a Pt foil counter electrode in a 0.1 M KOH electrolyte. An in situ monitoring of the transmittance at 635 nm during the CA cycling was accomplished using a Thorlab laser with Si diode detector setup.

### 2.3. Materials characterization

The X-ray diffraction (XRD) was performed using a General Area Detector Diffraction with a Cu X-ray source while the JEOL Nova Nanosem 230 was used for the SEM analysis. Focused ion beam cross-sectioning was performed using a Helios NanoLab 450 S dual beam Focused Ion Beam instrument from FEI. A strip of Pt was deposited using in-situ ion beam assisted deposition prior to ion milling to protect the area of interest from ion beam damage. X-ray photoelectron spectroscopy (XPS) was performed using a VG ESCA LAB -220i XL XPS with a monochromatic Al K $\alpha$  (1486.6 eV) X-ray source. The adventitious carbon C 1s peak at 284.6 eV was used as the charge correction reference. The UV-Vis transmittance measurements of the sample were performed using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer in the wavelength range of 200–800 nm. The readings were taking in 2 nm wavelength intervals. Atomic force microscope (AFM) analysis was performed using Bruker Dimension Icon system at scan rate of 1.5 Hz.

## 3. Results and discussion

### 3.1. Understanding the problem of conventional SILAR process in producing uniform hydroxide thin film

For metal oxide and hydroxide coating using SILAR process, the cationic precursor solution commonly used is metal complex solution in alkaline medium. The anionic solution commonly used is hot water [35] or H<sub>2</sub>O<sub>2</sub> [36] solution. The proposed chemical reactions during the anionic precursor dip or the reaction dip using zinc as an example is shown as reaction S1-S4 in the Supplementary information. Despite that the adsorption-reaction mechanism of SILAR process has successfully produced many smooth and uniform metal chalcogenide films [19], all the reported metal hydroxide films using SILAR are often complicated by structured surface morphology and agglomerated particles, not resembling a layer-by-layer growth of uniform thin film. We faced the same problem when we tried to produce nickel hydroxide thin film using nickel ammonia complex solution and H<sub>2</sub>O<sub>2</sub> solution with water as rinsing solution. We observed a lot of agglomerated particles formed on the film surface as shown in the SEM micrograph in Fig. 1. Apparently, the adsorption and reaction process is not clearly segregated using the conventional SILAR recipe, and the homogeneous growth of particles is not prevented. We believe this is due to the ineffectiveness of the rinsing step. We conducted a quick assessment of the suitability of water as the rinsing solution by drop casting nickel complex solution into water. We observed precipitates formed immediately after the nickel complex solution is in contact with water.

To understand the cause of above precipitation reaction, we studied the metal complexation process. The nickel complex solution contains 0.1 M NiSO<sub>4</sub> solution with excess aqueous ammonia. The resulting solution contains 0.1 M hexaamminenickel complex ion according to reaction 1 and 2. However, complexation reaction 2 is reversible if the relative concentration of NH<sub>3</sub> and OH<sup>-</sup> ion is changed. Dilution of the nickel complex solution with water will decrease the concentration of

Download English Version:

<https://daneshyari.com/en/article/6533951>

Download Persian Version:

<https://daneshyari.com/article/6533951>

[Daneshyari.com](https://daneshyari.com)