

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

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*Supplementary information available*

## **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 seconds for bleaching and 4 seconds for coloration.

## **Keywords**

Thin film, dip-coating, nickel hydroxide, SILAR, layer-by-layer, electrochromics

### **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 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 co-precipitation, 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 minutes each. UV-Ozone treatment using Novascan UV Ozone Cleaner at 100 °C for 10 minutes 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, 0.01M 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 minutes. The sputtering power was maintained at 300W. The electrodeposition was carried out by using a Metrohm Autolab potentiostat with a standard

3M 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 minutes.

## **2.2 Electrochromic characterization**

The chronoamperometry (CA) measurements were carried out using a Metrohm Autolab potentiostat with a standard 3M 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 450S 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 284.6eV 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 nm to 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  $H_2O_2$ [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 chalcogenite 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  $H_2O_2$  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.

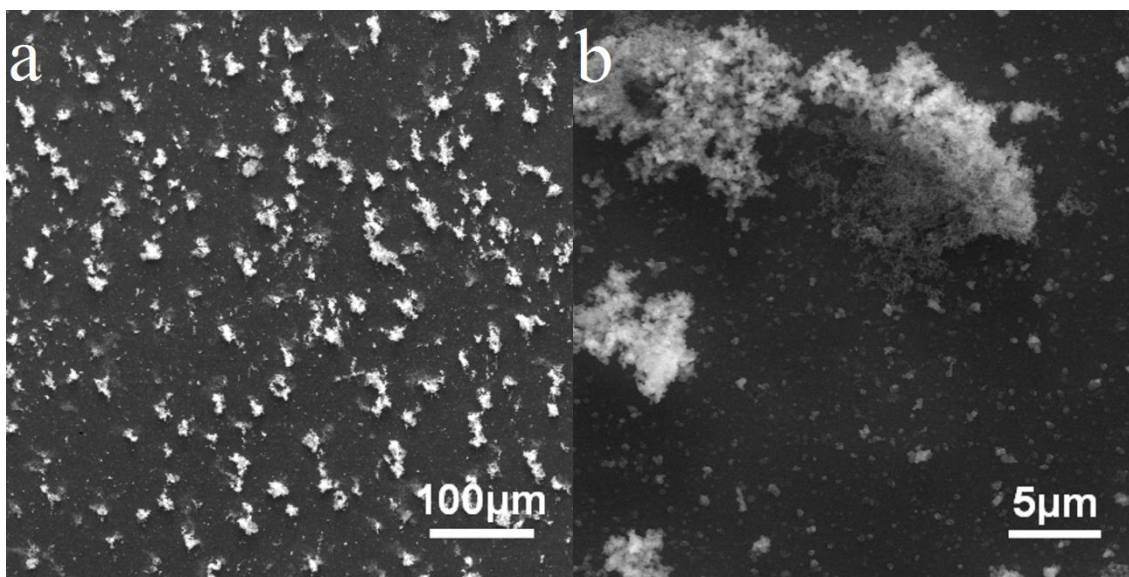
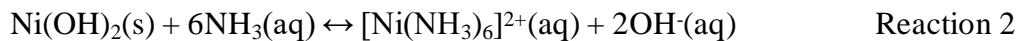
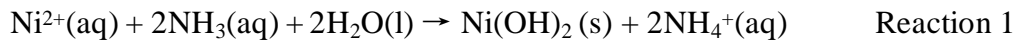


Figure 1 SEM micrograph with a) low magnification and b) high magnification of nickel hydroxide thin film produced using nickel ammonia complex and  $H_2O_2$  as SILAR precursor solutions, and using water as rinsing solution.

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 hexamminenickel 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 ammonia and this reverses reaction 2 and produce insoluble Ni(OH)<sub>2</sub>. In the context of SILAR process with water as the rinsing solution, instead of washing away the residue precursor solution, water is reacting with the carried over precursor solution. As illustrated in Fig. 2, the immediate consequence of having a reactive rinsing solution is the formation of homogeneously grown particles within the residue precursor solution during the rinsing step. The formation of these particles explains our observation of the rinsing solution becoming milky after more than 20 dipping cycles. In the worst case, some of the particles formed anchors on the thin film surface and will continuously grow in the subsequent dipping cycles to form big cluster of agglomerations as shown in Fig. 1. We emphasize again that uniform thin film can only be produced through heterogeneous growth, in which the reaction process happens only for the adsorbed precursors during the reaction dip after residue solution is effectively rinsed off.



To remove homogeneously grown particles, other work proposed an addition of sonication process[37] to prevent the particles from attaching on the substrate. We believe this could be a partial solution to the problem, but sonication process may increase fabrication cost and limit the scalability of the coating process.

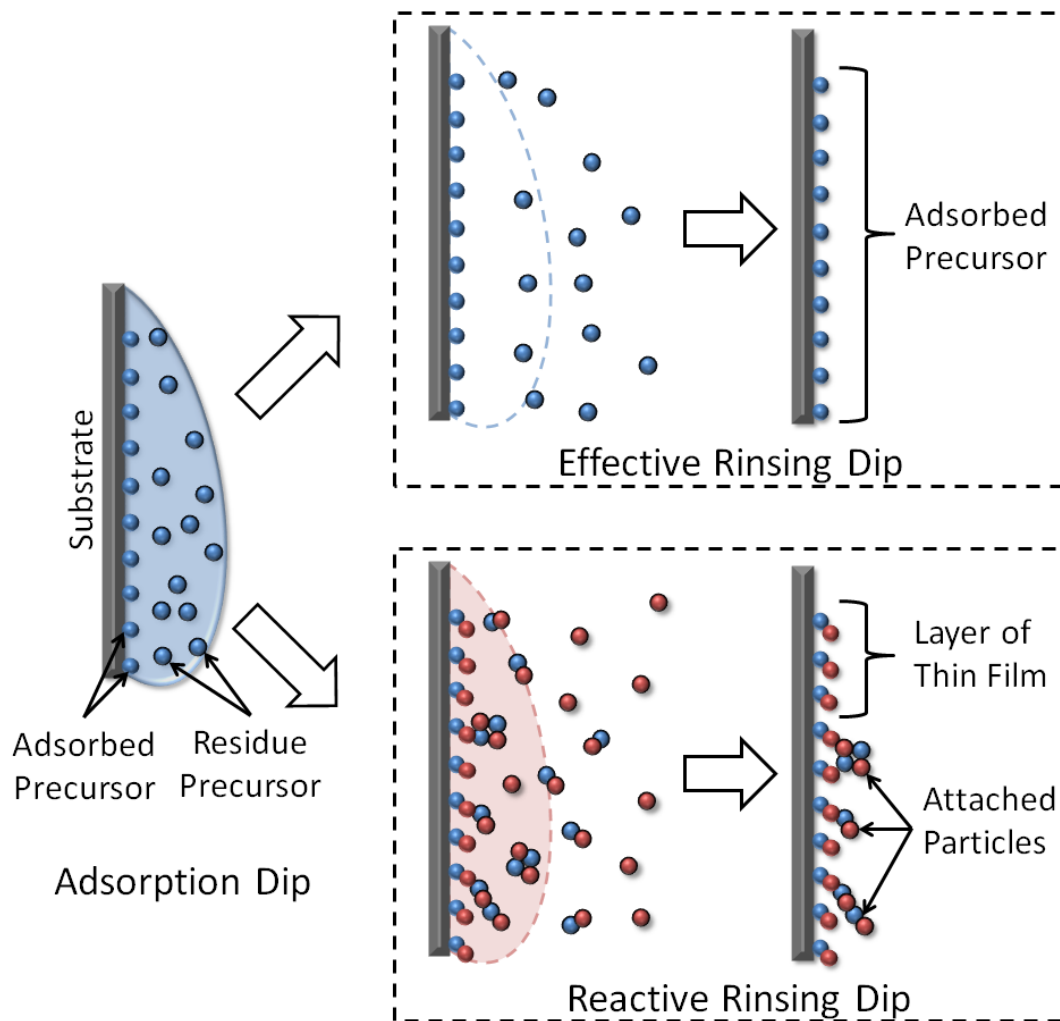


Figure 2 Schematics demonstrate the formation of homogeneously grown particles on the surface of the SILAR thin film due to ineffective rinse. An effective rinsing process removes residue precursors carried over from the adsorption dip, and leaves only adsorbed precursors ready for heterogeneous thin film growth in the subsequent reaction dip. A reactive rinsing solution triggers reactions for both adsorbed precursors and residue precursors. The later reaction results in homogenous growth of particles within carried over solution and produces structured film if the particles attach on thin film surface.

### 3.2 Modified SILAR recipe



In view that the ineffectiveness of the rinsing solution is hindering the layer-by-layer growth of the nickel hydroxide film, we propose to replace water with a new rinsing solution to address the root of the problem. The proposed rinsing solution should meet a few criteria. Most importantly, it should be non-reactive with the metal complex solution. The rinsing solution should also have no reaction with the anodic precursor solution and be of no or little corrosiveness to the hydroxide film that is already formed during previous dipping cycles. We also propose to have the non-reactive rinsing solution dip both before and after the adsorption dip. This is to prevent the carried over rinsing solution from triggering homogeneous precipitation in the adsorption solution. In this work, for nickel hydroxide thin film growth, ammonia solution with tuned pH was proposed as a suitable candidate to address the above requirements.

An optimum pH for the ammonia rinsing solution is critical in satisfying the 3 criteria listed above. To this end, we tested the reaction of 0.1 M nickel complex solution with ammonia solution of different concentrations. We found that 1% is the minimum concentration of ammonia solution to be the optimum in achieving the criteria. There are two reasons for not using higher concentration ammonia as rinsing solution. The first reason is to avoid the rinsing solution from corroding the already grown hydroxide thin film via reaction 2, and the second reason is to avoid the desorption of the already adsorbed metal complex ions due to competitive adsorption of the ammonia. Because of above reasons, we found that ammonia solution with concentration higher than 1.5% results in insignificant film growth. A lower ammonia concentration in turn may result in precipitate formation over the long run. Table 1 summarizes the modified SILAR recipe for nickel hydroxide growth through replacing the conventional rinsing solution with 1% ammonia. As mentioned earlier, rinsing dip should be carried out both before and after the adsorption dip to prevent homogeneous precipitation. Therefore, the very first deposition dip should begin with a rinsing solution as labelled in Table 1. We highlight that since water is reactive to Ni complex ions at room temperature, it can be used as a low-cost reaction precursor solution for hydroxide growth. For oxide growth,  $H_2O_2$  or hot water can still be used as reaction precursor (not covered in this work).

Table 1 Modified SILAR process for coating nickel hydroxide thin film.

Solution Name	Conventional recipe	Modified recipe	Dip duration (sec)
1 Adsorption	Metal complex (start)	0.1M NiSO <sub>4</sub> in excess NH <sub>4</sub> OH	10
2 Rinsing	DI water	1% NH <sub>4</sub> OH	5
3 Reaction	Hot water / H <sub>2</sub> O <sub>2</sub>	DI water	10
4 Rinsing	DI water	1% NH <sub>4</sub> OH (start)	5

The SEM micrograph of a bare ITO before and after 50 cycles coating of nickel hydroxide thin film using proposed SILAR recipe is shown in Fig 3. The existing topography of the ITO can still be observed after the coating process demonstrating good conformal coverage. This is also evidenced by the atomic force microscope (AFM) analysis of the surface topology before and after film coating as shown in Fig. S1 (in the supplementary information). The surface roughness before and after coating is similar and has a value of 4.3 nm and 3.9 nm respectively. As shown in the low magnification SEM micrograph in Fig. S2, precipitate on the film surface is not observed, demonstrating successful elimination of homogeneous reaction.

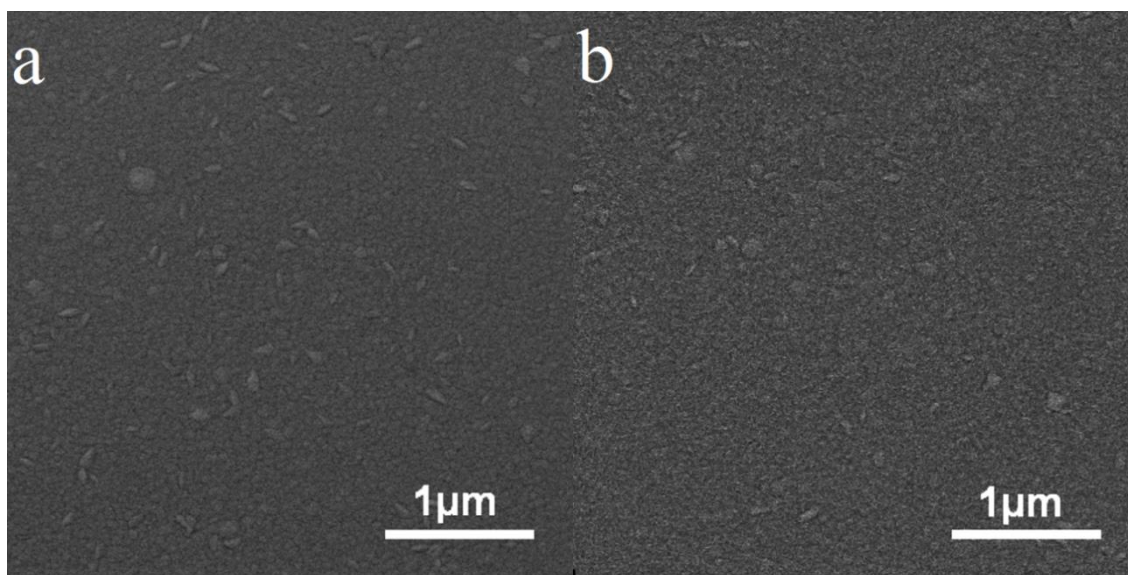


Figure 3 SEM micrograph of (a) Bare ITO and (b) 50 cycles coated nickel hydroxide thin film

The transparent nickel hydroxide thin film can be electrochemically cycled to its color state as shown by the transmittance spectra in Fig. S3. Therefore, visual proof of thin film thickening with more dipping cycles is observable after coloring the film in 0.1 M KOH solution through reaction S5 in the supplementary information. The films were fully colored by applying constant voltage of 0.65 V until no further change in transmittance was observed. The photograph of colored 10, 20, 50, 100 cycles coated nickel hydroxide is shown in Fig. 4a. Based on Beer's law and neglecting reflectivity due to similar surface condition, the thickness of the film should be proportional to the transmittance modulation of electrochromic film in the natural log scale. We measured the transmittance of the colored film produced by different dipping cycles (shown in Fig. S4) and plot the transmittance modulation at wavelength of 480 nm over dipping cycles (shown in Fig. 4b). As can be seen, the thickness of the film is linearly proportional to the number of dipping cycles, demonstrating a layer-by-layer coating mechanism. We obtained the thickness of thicker film using step profiler and estimate the growth rate of the film to be about 0.5 nm per dipping cycle. XRD analysis of the samples shows only substrate peaks indicating an amorphous nature of the coating film.

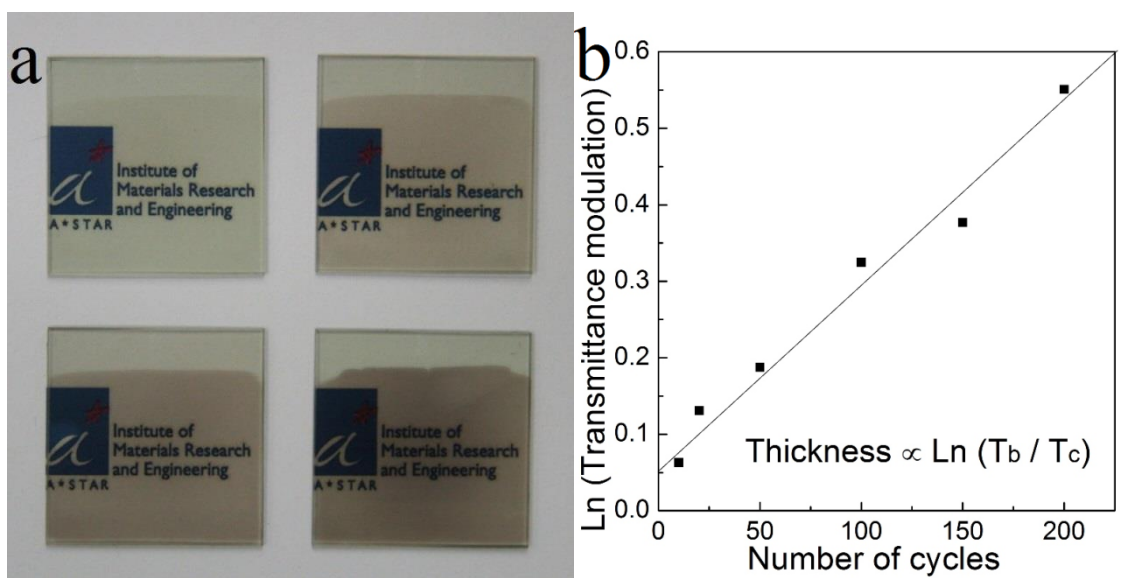


Figure 4 (a) Photograph of colored nickel hydroxide film grown by 10 (top left), 20 (top right), 50 (bottom left), 100 (bottom right) dipping cycles. b) Plot of transmittance modulation (480 nm) in natural log scale against number of dipping cycles, showing a linear increase of film thickness with number of dipping cycles.

### 3.3 Incorporating Al in nickel hydroxide thin film

In order to demonstrate the capability of our proposed SILAR process in incorporating additional element into the film, we added a simple modification to the proposed recipe with additional two dipping solutions for Al incorporation. The assigned name, composition, and dipping duration of each dipping solutions are listed in table 2. The first four dipping solutions are identical to the earlier proposed recipe for coating nickel hydroxide, while solution 5 and 6 are responsible for Al incorporation.

Table 2 Modified SILAR process for coating Al incorporated nickel hydroxide thin film

	<b>Solution Name</b>	<b>Composition</b>	<b>Dip duration (sec)</b>
<b>1</b>	Rinsing (start)	1% NH <sub>4</sub> OH	5
<b>2</b>	Ni complex Adsorption	0.1M NiSO <sub>4</sub> in excess NH <sub>4</sub> OH	10
<b>3</b>	Rinsing	1% NH <sub>4</sub> OH	10
<b>4</b>	Reaction	DI Water	20
<b>5</b>	Al complex adsorption	0.005M Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> in excess NaOH	10
<b>6</b>	Rinsing	DI Water	20

The surface of cleaned ITO substrate and the 20 cycles coated Al incorporated nickel hydroxide thin film are shown in the SEM micrograph in Fig. S5. Similar to the nickel hydroxide coating shown in Fig. 3, the Al incorporated film is thin and has conformal coverage which follows the surface structure of ITO substrate. For XPS analysis of the Al incorporated film, the survey, Al 2p and Ni 2p scan shown in Fig. S6 confirms the presence of only Al and Ni in their oxidized and hydroxide form respectively. FTIR analysis shown in Fig. S7 confirms the presence of mostly  $\alpha$  phased nickel hydroxide in both pure and Al

incorporated nickel hydroxide films with small amount of  $\beta$  phase presented in the pure film.[38] The TEM and EDX line profiling in Fig. 5 shows a uniform distribution of Al within the nickel hydroxide. Based on the EDX intensity, the ratio of Al:Ni is about 1:4. Similar to nickel hydroxide, no diffraction peak was observed by XRD analysis which indicates the film is amorphous.

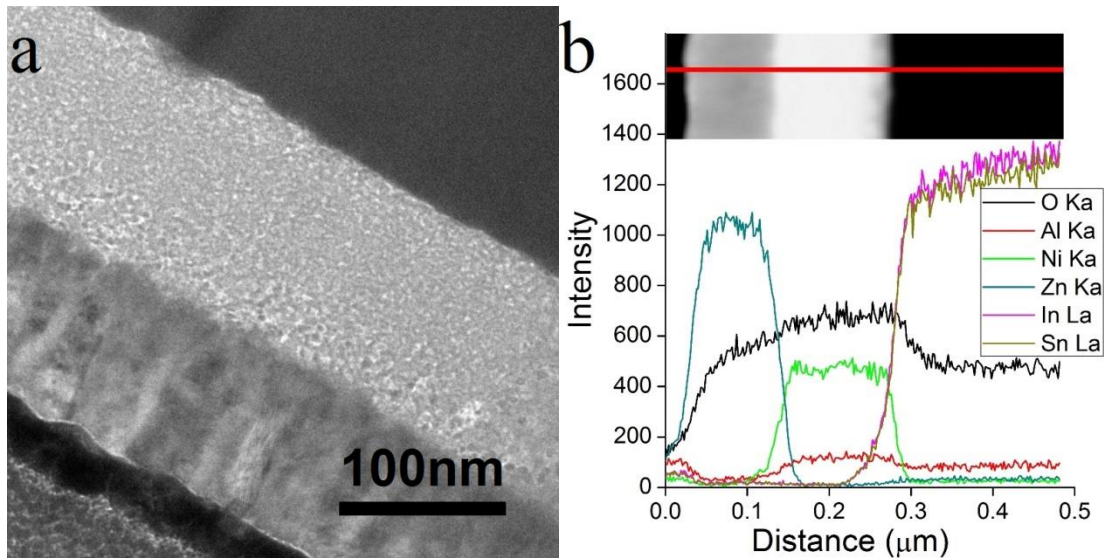
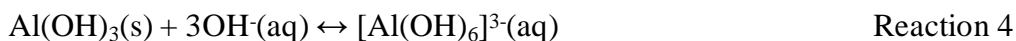


Figure 5 TEM image of the cross section of the as-deposited Al incorporated nickel hydroxide film. EDX line profiles of the cross section using STEM showing the relative counts for Ni, Al and O.

We also investigated the Al incorporation mechanism. We would like to highlight that the attempt to achieve  $\text{Al}^{3+}$  ion adsorption using  $\text{Al}_2(\text{SO}_4)_3$  as precursor solution does not work out because the acidic nature of the solution causes corrosion of the deposited nickel hydroxide film from earlier dipping cycles. Therefore, alkaline Al complex solution containing 0.005M  $\text{Al}_2(\text{SO}_4)_3$  and excess NaOH was used which results in 0.01M hexahydroxoaluminate complex ions (through reaction 3 and 4). The Al complex adsorption dip was followed by a rinse dip in DI water. Here, unlike the Ni complex solution which reacts with water as discussed earlier, reversibility of reaction 4 depends only on the concentration  $\text{OH}^-$  ion. This is why, in a separate experiment on diluting Al

complex solution with water, we found that no  $\text{Al(OH)}_3$  precipitation is formed through the dilution process unless acid is introduced. As a result, rinsing in water is suitable to remove the residual Al complex solution and left with only adsorbed Al complex on the surface.



In order to prove that Al incorporation is through adsorption of Al complex, several controlled experiments (summarized in table S1) were conducted with different combination of dipping solutions and on different substrates (a detailed explanation of the experiment can be found in the supporting information). The trace material presented on the substrate surface as a result of adsorption can be studied using XPS analysis shown in Fig. S8. The experiments conducted indicate that Al complex may only be able to adsorb on surface of nickel hydroxide instead of metal oxide. The adsorption of metal complex on hydroxide surface has been discussed elsewhere.  $\alpha$ - $\text{Ni(OH)}_2$  is a hydroxyl-deficient phase with the hydroxalite-like structure which consists of stacks of positively charged  $\text{Ni(OH)}_2$  layers and contains intercalated anions and water molecules in the interlayer space to restore charge neutrality. The interlayer distance is about 7.6 Å.[39] The structure of  $\alpha$ - $\text{Ni(OH)}_2$  displays more disorder because the layers are oriented randomly.[40] Since our film contains  $\alpha$ - $\text{Ni(OH)}_2$ , the  $[\text{Al(OH)}_6]^{3-}$  anions can be adsorbed into the interlayers. The driven force could be the electrostatic force and hydrogen bond between nickel hydroxide layers and intercalated species.

### **3.4 Improved electrochromic cycling stability using Al incorporated nickel hydroxide**

The electrochemical property of the dip coated films with comparable optical modulation was studied using cyclic voltammetry in 0.1 M KOH electrolyte between -0.1 V to 0.7 V as shown in Fig. 6a. Figure 6b shows the percentage transmittance change (at 635 nm wavelength) of pure and Al incorporated nickel hydroxide film during chronoamperometry (CA) measurement. A shift in both oxidation and reduction peak is observed which

suggests that the Al incorporated film may have higher film resistance than pure nickel hydroxide film. The higher redox peak current of the Al incorporated film also suggests a higher charge consumption to produce similar optical contrast as compared to pure nickel hydroxide film. The coloration efficiency is calculated as 26.4 and 23.1  $\text{cm}^2/\text{C}$  for pure and Al incorporated film respectively. For 80% color change, the response time of pure nickel hydroxide film is 3 seconds for bleaching and 2 seconds for coloration, while the response time of Al incorporated film is 4.5 seconds for bleaching and 4 seconds for coloration. For 90% color change, the response time of pure nickel hydroxide film is 10 seconds for bleaching and 2.5 seconds for coloration, while the response time of the Al incorporated film is 11 seconds for bleaching and 4.5 seconds for coloration. The slightly slower response for Al incorporated film may be due to its higher film resistance.

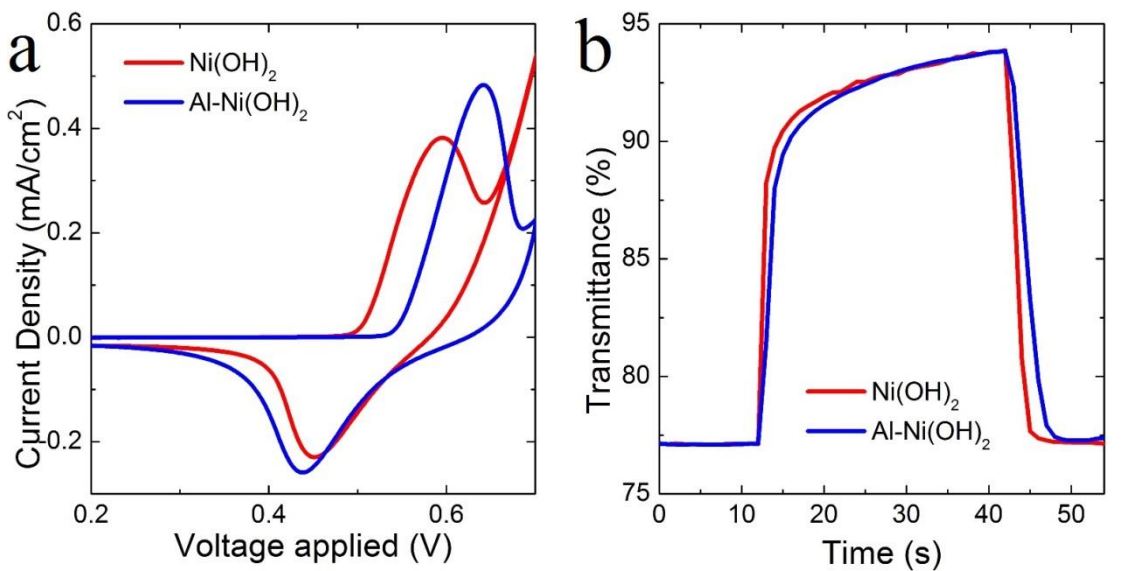


Fig. 6 (a) CV cycle (5th cycle) of nickel hydroxide film and Al incorporated nickel hydroxide film in 0.1 M KOH electrolyte. (b) The percentage transmittance change of nickel hydroxide film and Al incorporated nickel hydroxide film during CA cycle demonstrating their response behavior.

The electrochemical cyclic stability of the Al incorporated film was investigated through the CA method and *in situ* transmittance measurement at 635 nm in 0.1 M KOH electrolyte. A dip coated pure nickel hydroxide film using proposed SILAR recipe was used as the

control sample. The thickness of the nickel hydroxide film was carefully tuned to match the initial modulation of the 20 cycle coated Al incorporated nickel hydroxide film. The reduction process is set at -0.2 V for 20 seconds and the oxidation process is set at 0.65 V for 30 seconds. The *in situ* variation of the optical transmittance and the corresponding charge variation for both films are shown in Fig. 7a and 7b, respectively. With the addition of Al, the cyclic stability of the film is improved significantly together with a higher charge density. The coloration efficiency of pure nickel hydroxide film decreases by 46% from 26.4 to 14.2 cm<sup>2</sup>/C, while the coloration efficiency for the Al incorporated film decreases by only 6% from 23.1 to 21.7 cm<sup>2</sup>/C. The degradation phenomenon is generally attributed to the conversion of  $\beta$ -Ni(OH)<sub>2</sub> to  $\gamma$ -NiOOH which is accompanied by a large volumetric change. This may result in loss of contact between the active material and the conductive ingredients.[1, 21, 22] As a result, the internal resistance of the material rises with cycling, thus leading to the electrochemical **degradation of the film. Since the  $\gamma$ -NiOOH phase formed is colored, if isolated, it will result in irreversible reduction in the bleach state transmittance, i.e. electrochromic degradation of the film.** Aluminum is known to be able to help in pulling the layers together and maintain the interlayer spacing[41] thus improve the stability of the electrochromic device. As for the slower degradation of the colored state that is not improved by Al incorporation, this may be due to the partial dissolution of nickel hydroxide film in KOH electrolyte [42], resulting in mass and optical modulation loss.



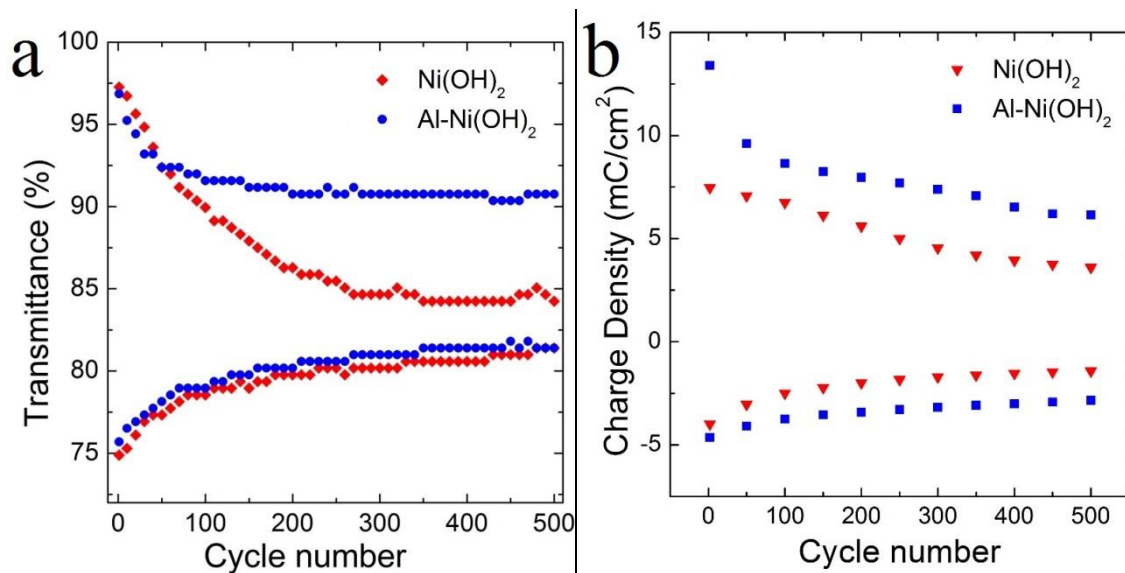


Fig. 7 (a) The percentage transmittance (at 635 nm) of nickel hydroxide film and Al incorporated nickel hydroxide film during CA cycling in KOH up to 500 cycles. (b) The charge density involve in each oxidation an reduction cycles during the CA cycling.

#### 4. Conclusions

In conclusion, we successfully identified the problem of conventional SILAR recipe and proposed a novel SILAR recipe to successfully produce, for the first time, layer-by-layer coated uniform nickel hydroxide thin film. The process is optimized for the sake of scalability and cost reduction. We also demonstrate the versatility of proposed process in producing metal incorporated nickel hydroxide. The Al incorporated film demonstrated improved cycling stability in alkaline electrolyte. The deposition mechanism and proposed SILAR recipe can be easily generalized for synthesizing uniform films of other metal hydroxide and third metal incorporated metal hydroxide. The scalability and versatility of the proposed coating process will be of great interest and importance to the functional coating community at large.

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