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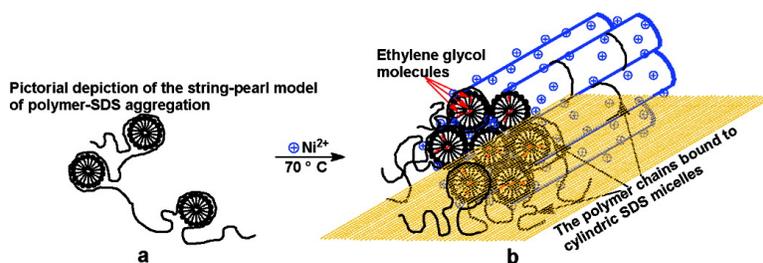# Electrochemical Deposition of Mesoporous Nickel Hydroxide Films from Dilute Surfactant Solutions

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Electrochemical Deposition of Mesoporous Nickel Hydroxide Films from Dilute Surfactant Solutions

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Abstract: A series of micelle-templated mesoporous nickel hydroxide films were prepared by electrochemical deposition from dilute surfactant solutions by using different types of template and by varying plating solvent composition. Lamellar mesostructured $Ni(OH)_2$ films are obtained with only anionic surfactant sodium dodecyl sulfate (SDS) as the template. In particular, a unique cooperative assembly fashion, that is, the combination between Ni^{2+} and a complex composed of the primary template SDS and a cosurfactant, such as triblock poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) copolymers and poly-(ethylene glycol), was explored, by which two-dimensional hexagonal mesoporous $Ni(OH)_2$ films were electrodeposited. Meanwhile, the deposition medium also plays a crucial role in determining the mesostructure of $Ni(OH)_2$ films. For the composite nickel hydroxide films deposited from aqueous solution or dilute aqueous solution of ethylene glycol (<20 wt %) in the presence of SDS or the SDS−poly(alkylene oxide) polymer complexes, a mixed lamellar phase with $d_{001} = 37.4$ Å and $d_{001^*} = 28.5$ Å was obtained. However, single lamellar phase with $d_{001} = 37.4$ Å was electrodeposited from concentrated aqueous solutions of ethylene glycol (≥20 wt %). Furthermore, such deposition baths have access to hexagonal mesoporous nickel hydroxide films with $d_{100} = 37.4$ Å at 70 °C with the SDS−poly(alkylene oxide) polymer complexes as the templates. Within the potential window for $Ni(OH)_2$, the morphology and quality of mesostructured films are significantly dependent on the deposition potential, while the mesostructures of the composite films always remain unchanged.

Introduction

The discovery of mesoporous materials (M41S) set up a prototype for the harmonious organization of inorganic and organic species into perfectly periodic geometric architectures in nature.[1,2] These kinds of mesoporous materials predominantly possess the long-range ordered arrays of uniform nanoscale channels and cages. Such crystallographic periodicities with nanoscale repeated units are formed by the cooperative organization of cationic surfactants, anionic surfactants, or nonionic block copolymers with target species, which is driven by various interactions, such as electrostatic, covalent bonding, hydrogen bonding, and van der Waals forces.[3−5] It has been noted that the crystallographic phases found for these materials are known to often (although not always) mimic the phases found for the surfactants in solution.[6−8]

Inspired by the templating procedure for the synthesis of the mesostructured M41S family, the extension of the surfactant templating routes to the formation of nonsiliceous mesoporous materials, including a wide range of minerals from carbon,[9] metals,[10] metal oxides,[11] and phosphates[12] to sulfides,[13] has been well documented. In many cases, these mesoporous materials display unique electronic, magnetic, and catalytic properties,[14−21]

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However, most of them were available until now by conventional chemical methods (sol−gel processes). Therefore, the exploration of new approaches to these materials is of great significance for facile and efficient preparation.

Among the existing synthetic approaches to mesoporous materials, electrochemical techniques show unique principles and flexibility in the control of the structure and morphology of mesoporous materials. Unlike the conventional sol−gel methods, electrochemical deposition provides the fabrication of mesoporous films or coatings rather than powders, which is required for a number of applications in batteries, fuel or solar cells, and sensors.[22−25] Over the past few years, a series of mesoporous metals and semiconductors, such as Pt,[26] Sn,[27] Ni,[28] Se,[29] as well as Pt/Ru alloy,[30] and oxides, including NiO,[28] ZnO,[31] and Cu₂O,[31b] have been prepared by electrodeposition in the presence of surfactants, where the templates could be lyotropic liquid crystalline phase formed by concentrated polyoxyethylene alkyl ether (>30 wt %) or anionic surfactant sodium dodecyl sulfate (SDS) at very low concentration (typically, less than critical micelle concentration). As shown previously, the structure of liquid crystal template is specifically hexagonal.[8,26c] Such templates can be regarded as "hard" templates. The templated nanostructures are in effect casts of the structures of the liquid crystalline phases themselves. Hence, the nanostructures of deposits are mostly consistent with that of templates, that is, hexagonal. In contrast, a very dilute anionic surfactant solution can template the nanostructure in a different way.[26d,31a] Actually, the effective templates are not the surfactants in the bulk solution but those adsorbed on the electrode surface where solid−liquid interface induces surface excess concentration of surfactant−inorganic ion aggregates because of electric field force and surface forces.

So far, a large amount of work concerning the electrodeposition of mesoporous materials has been restricted to lyotropic liquid crystalline phase, the binary system of oligopoly(ethylene oxide)s/water. Nevertheless, the existence of organic solvent can destroy the liquid crystalline order.[32] When the concentration of surfactant is higher than that required for the formation of liquid crystalline phase, the template structure is independent of the content of oligopoly(ethylene oxide)s. Therefore, different mesostructures have been somewhat difficult to obtain in such a system. Conversely, in the case of electrodeposition in dilute

surfactant solution, the templates for mesostructures are flexible because the surfactant assembly on electrode surfaces is extensively determined by many interactions. First, the electric field environment and solid−liquid interface induce a series of surface array patterns of surfactants, which is often different from the free and aggregated micelles in bulk solution.[33] Second, different surfactant templates, characterized by organic chain length, headgroup charge, and introduction of cosurfactants and other interactions, can form distinctive assembly patterns on electrode surface, leading to the generation of templates with various architectures. Third, solvent composition, electrolytes, solution pH, surfactant concentration, deposition potential, and even deposition temperature may affect the mesostructure of deposits. All these, along with varying the substrate for film deposition, make the assembly process of inorganic and organic species versatile and robust. Our intention in this research is to explore the potential coupled cooperative self-assembly in association with various parameters stated above at solid−liquid interfaces.

Nickel hydroxide has aroused increasing attention since it is a significant cathode material in alkaline rechargeable batteries, such as Ni/Cd, Ni/H₂, Ni/MH, and Ni/Zn systems.[34] The electrochemical applications and practical capacity of the Ni-(OH)₂ cathode are directly determined by its active surface area and morphology. Therefore, the application of nanostructured porous electrode material is expected to improve the high energy density batteries.

In this paper, we systematically investigate the electrochemical preparation of different mesostructured nickel hydroxide electrodes from dilute surfactant solutions. The different mesophases of Ni(OH)₂ were obtained by the choice of the template types and the adjustment of solvent composition in combination with applied potential. In particular, previous synthesis of mesoporous materials mainly focused on pure structure-directing agent. Here, we demonstrate for the first time an electric field induced synergistic organization between bicomponent surfactants and inorganic ions to fabricate ordered mesoporous Ni-(OH)₂ films. This new synthetic strategy is based on the strong interaction between the anionic surfactant SDS and nonionic poly(alkylene oxide) polymers (cosurfactants), leading to their co-adsorption on the electrode surface. Extensive studies describe that the strong interaction occurs in many polymer−surfactant aqueous systems, depending on many factors, including Coulombic interactions, the hydrophobicity of the polymer−surfactant pair, and the conformational features of the polymer.[35] On the other hand, the application of a bias voltage can simultaneously induce assembly of the anionic surfactant SDS and Ni²⁺ on the electrode surface through an intermediate form of S⁻I⁺ and reduce the inorganic ions.[3] Combination of both mechanisms above has been the idea for the cooperative organization of molecular inorganic and organic aggregates on electrode surface for the mesostructured Ni(OH)₂ films.

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Experimental Section

Chemicals and Apparatus. The anionic surfactant sodium dodecyl sulfate (SDS), nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O), and poly-(vinyl pyrrolidone) (PVP, M_w = 50 000) were purchased from Aldrich and used without any further purification. The triblock copolymers HO-(CH$_2$CH$_2$O)$_{20}$(CH$_2$CH(CH$_3$)O)$_{70}$(CH$_2$CH$_2$O)$_{20}$H (designated EO$_{20}$PO$_{70}$-EO$_{20}$, Pluronic P123), EO$_{106}$PO$_{70}$EO$_{106}$ (Pluronic F127), and poly-(ethylene glycol) (PEG, M_w = 6000) were commercially available from BASF and used as received. All solutions were prepared using high purity water (Millipore water, 18 MΩ). All glassware was cleaned in a mixture of Millipore water and nonionic detergent, followed by thorough rinsing with Millipore water and 2-propanol many times before drying in an oven at 70 °C.

The electrochemical experiments were conducted on a VMP2 Multi-Potentiostat, using a conventional three-electrode system in an undivided cell, composed of a gold plate working electrode, a large surface area platinum counter electrode, and a standard Ag/AgCl reference electrode in 4 M KCl saturated with AgCl. The gold or platinum plate electrodes were prepared by evaporating a gold or platinum film (∼50 nm thickness) onto glass slides with a thin (∼10 nm) adhesive underlayer of chromium or titanium. The electrodes were cleaned in an ultrasonic bath of 2-propanol for 10 min prior to use, rinsed with Millipore water, and dried under ambient conditions.

Electrodeposition. All electrodepositions of nickel hydroxide films were performed under both potentiostatic and thermostatic control. Nickel hydroxide films were deposited from 0.02 M nickel nitrate solution mixed with various weight percents of the anionic surfactant SDS, or a binary system composed of SDS and a poly(alkylene oxide) polymer P123, F127, or PEG at a different weight ratio. The mass of the Ni(NO$_3$)$_2$ bath was 40.00 g, and the cell temperature was maintained at 70 °C for all depositions.

SDS Templates: Potentiostatic deposition of Ni(OH)$_2$ films was carried out at −0.5, −0.6, −0.7, and −0.8 V versus Ag/AgCl from a SDS/Ni(NO$_3$)$_2$ solution, where the SDS concentration ranged from 0.5 to 5 wt %, and the solvent was water or a mixture consisting of water and ethylene glycol. To probe the effect of the amount of organic solvent on the nanostructure of the deposits, in the case of electrodeposition from the mixed solvent bath, the concentration of ethylene glycol in the mixing solvent was varied until it was as high as 50 wt %.

SDS/Poly(alkylene oxide) Polymers Complex Templates: The complex templates were prepared by carefully tuning the ratio of the two components in the SDS/poly(alkylene oxide) polymers systems in order to ensure that the system contained polymer-bound SDS micelles only (no free micelles). To obtain an appropriate concentration ratio, the SDS concentration was varied while the amount of a poly(alkylene oxide) polymer was kept constant. In a typical synthesis, 0.16 g of P123 was placed on the bottom of a beaker and mixed with 30.0 g of an aqueous solution of Ni(NO$_3$)$_2$ (0.02 M). The mixture was first heated to 70 °C and maintained at that temperature for 50 min. Then, the mixture was vigorously stirred at 70 °C for 1 h immediately after the addition of 10.0 g of a 0.02 M solution of Ni(NO$_3$)$_2$ in ethylene glycol, allowing complete solvation of P123 and the formation of a homogeneous mixture by the absence of small P123 particles suspended in solution. After initial stirring for 10 min, the solution became cloudy because high temperature gives rise to an increase in the hydrophobicity of the PO and EO block moieties.[36] This suggests that P123 was gradually dispersed in water. A small amount of water was added every ca. 10 min to compensate for the loss of water during the whole heating process. Afterward, to this solution were added 2.5 g of water and 0.60 g of SDS in sequence while vigorously stirring. Upon addition of SDS, the solution immediately acquired an absolutely clear appearance, indicating an apparent interaction between P123 and SDS and the solubilization of SDS. Finally, after the full adsorption of SDS onto the polymer chain together with the evaporation of excess of water, the electrodeposition was conducted.

For comparison, Ni(OH)$_2$ films were electrodeposited from the plating solution prepared in the same procedure as that described above, except heating at 40−50 °C. In addition, Ni(OH)$_2$ films were also deposited from aqueous solutions of Ni(NO$_3$)$_2$ in the presence of SDS/cosurfactant or a pure cosurfactant, which were prepared by an analogous procedure as that described above (just no addition of a Ni(NO$_3$)$_2$ solution in ethylene glycol or SDS, respectively).

After electrodeposition, the working electrodes were taken out of the cell and washed with water and 2-propanol several times to remove the surfactants adsorbed on the surface of the Ni(OH)$_2$ films.

Characterization. The film structure was characterized by low-angle X-ray diffraction and transmission electron microscopy (TEM). X-ray diffraction (XRD) measurements were performed on a Bruker D4 diffractometer with a Cu Kα (1.54 Å) X-ray irradiation source. X-ray diffractograms were recorded over the range of 1.0−10 in 2θ degrees. Specimens for transmission electron microscopy (TEM) images were prepared by scraping films from the working electrodes and directly transferring the films on a razor blade onto carbon-coated copper grids. The observations were undertaken with a Philips CM-10 transmission electron microscope operated at 80 kV. The film surface morphology was obtained by scanning electron microscopy (SEM) images, which were taken with a JEOL JSM-840 scanning electron microscope operated at 5 kV. The Ni(OH)$_2$ films were coated with Au and Pd before imaging in the SEM.

Results and Discussion

Cathodic deposition in a transition metal nitrate bath leads to the production of oxides or hydroxides depending upon the stability of resulting deposits. In the case of electroreduction of an aqueous solution of nickel nitrate, the generation of OH$^-$ at the working electrode raises the local pH. As a result, the nickel ion deposits in the form of Ni(OH)$_2$ on the cathode.[37] Upon the addition of anionic surfactants (for example, SDS) into an inorganic electrolyte solution (in this context, designated as Ni(NO$_3$)$_2$), the electrostatic interaction results in the formation of an interface (S$^-$I$^+$), comprised of metal cations and anionic headgroups of surfactants. Applying a potential between the working and counter electrodes is anticipated to induce the stacking of such an interface, layer by layer, with the interlayer spacing related to the length of surfactant chains, as illustrated by the bilayer model on the electrode surface. Most recently, nanostructured ZnO films with lamellar phase have been synthesized with this strategy.[31a] From the energetic point of view (including the packing of organic templates and charge density matching),[3] under such conditions, the surfactants usually pack parallel to each other to provide high possible charge density to balance inorganic cations adsorbed on the electrode surface. It is therefore plausible to postulate that for the analogous inorganic condensation at the surfactant−inorganic species interface to that of ZnO, the same lamellar phase is anticipated to be obtained based on this mechanism. Thus, the introduction of other interactions is necessary in order to vary the packing of anionic surfactants.

SDS Template. The low-angle XRD pattern (Figure 1a) of the as-deposited mesostructured Ni(OH)$_2$ films at −0.5 V versus Ag/AgCl from an aqueous solution of SDS (1.0 wt %) portrays two sets of evenly spaced reflections, which are unambiguously indexed as a couple of different lamellar phases, one with d_{001}

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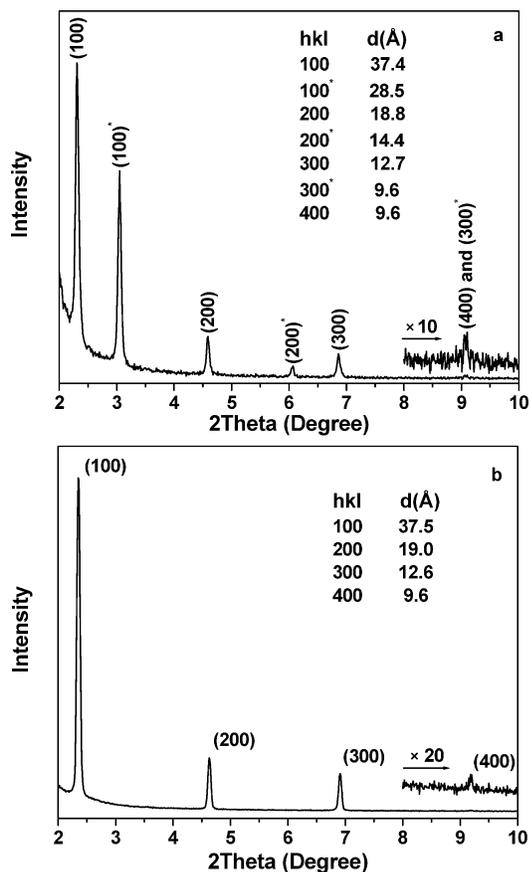
Figure 1. Low-angle X-ray diffraction patterns of the lamellar mesostructured nickel hydroxide films electrodeposited at −0.5 V versus Ag/AgCl from (a) aqueous solution and (b) 20 wt % aqueous solution of ethylene glycol by using 1.5 wt % SDS surfactant species as the template.
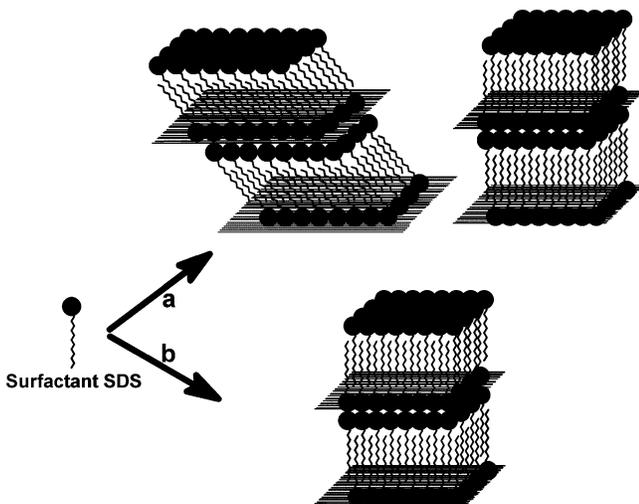

Figure 2. Schematic representation of the template configurations in (a) aqueous solution and dilute aqueous solution of ethylene glycol (<20 wt %) and (b) aqueous solution of ethylene glycol at a concentration equal to or greater than 20 wt % at the solid−liquid interface.

= 37.4 Å and the other with d_{001*} = 28.5 Å. The formation of a lamellar biphase suggests that two different geometrical orientations of SDS−Ni^{2+} bilayers are formed relative to the electrode surface, as depicted in Figure 2. Unlike the electrodeposition of lamellar ZnO films,[31a] the minimum SDS concentration (0.5 wt %) required for templating the mesostructure of Ni(OH)$_2$ films is greater than the critical micelle
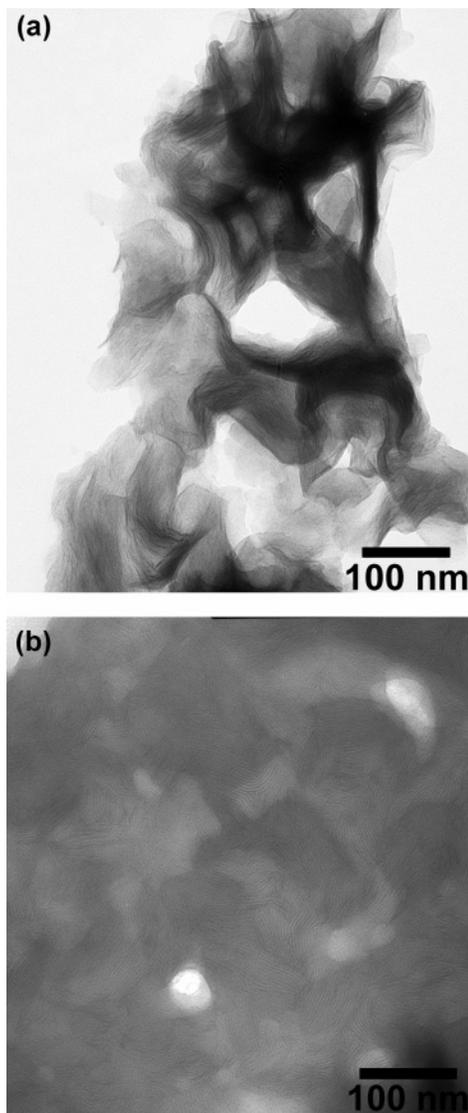

Figure 3. TEM images of lamellar mesostructured nickel hydroxide films electrodeposited at −0.5 V versus Ag/AgCl from (a) aqueous solution and (b) 20 wt % aqueous solution of ethylene glycol by using 1.5 wt % SDS surfactant species as the template.

concentration of pure SDS solution (0.23 wt %).[38] It is believed that the rate of SDS−Ni^{2+} interface formation is smaller than that of SDS−Zn^{2+} interface formation since the inorganic polymerization is presumably the same for both cases (NO$_3^−$ at the same concentration is reduced). Identical d spacing values are obtained by varying the deposition potential and the content of SDS in aqueous solution within the spectrum of this research, indicating that the interfacial assembly pattern of surfactant−inorganic intermediates does not depend on the deposition potential and bulk surfactant concentration. The layered structure of the electrodeposited composite nickel hydroxide films is also evident from the TEM images, presented in Figure 3a. A rough estimate of the periodicity and inorganic wall thickness gives values in the ranges of 2.1−4.8 and 1.4−2.9 nm, respectively. When the various stacking patterns and orientations of lamellar mesostructured Ni(OH)$_2$ films on the copper grid are taken into account, the d spacing values measured from the TEM image

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are substantially consistent with the repeat distance determined by XRD. The bending and folding of the inorganic walls and corrugated films are also revealed by the TEM images.

In general, solvent type can significantly affect the surfactant assembly. Organic solvents, such as 1,3,5-trimethylbenzene and ethanol, have been explored to modify the mesostructures by changing the packing of surfactant molecules.[1,2,39] To investigate the impact of solvent on the mesostructure of deposits, ethylene glycol is preferred because of its high boiling point and the good solubility of inorganic electrolytes in it. When the electrodeposition is carried out in dilute aqueous solutions of ethylene glycol ($<$20 wt %), the deposited $Ni(OH)_2$ films have the same lamellar structure constituted by biphase as that described just above, whereas a transformation to single lamellar phase takes place when more concentrated aqueous solutions of ethylene glycol ($\geq$20 wt %) are utilized as the electrodeposition media. Typically, Figure 1b shows the XRD pattern of as-deposited mesoporous $Ni(OH)_2$ films from a 20 wt % aqueous solution of ethylene glycol. Only one set of evenly spaced reflections with $d_{001} = 37.4$ Å is observed, corresponding to a more stable lamellar phase. The organic solvent molecules are believed to associate with the surfactants. This fact suggests that a single orientation of $SDS-Ni^{2+}$ bilayers is formed at the solid−liquid interface when a large amount of ethylene glycol replaces the water between surfactant tails (Figure 2). However, the mesostructure of $Ni(OH)_2$ films is independent of the SDS concentration and deposition potential if a fixed amount of ethylene glycol, required for the formation of single lamellar phase, is utilized as the deposition medium.

The TEM images obtained from the same mesostructured $Ni(OH)_2$ films confirm that the films are composed of lamellar nanostructure (Figure 3b). The stacking direction of the layers is wide distribution. The interlayer distance and the thickness of the wall system are estimated to be 3.5 and 1.8 nm, respectively, which is in good agreement with the value shown by the XRD pattern. Additionally, for the single phase lamellar nanostructured films, the stacking of layers is local order, as compared to the biphase lamellar nanostructure described above. This can be explained by the fact that the position of interface S^-I^+ is variable if two different orientations of the $SDS-Ni^{2+}$ bilayer coexist, whereas the single orientation of the $SDS-Ni^{2+}$ bilayer results in local positional order of interface S^-I^+. TEM analysis is also performed on the films deposited at different potentials and confirms that those deposited above −0.8 V versus Ag/AgCl have well-defined lamellar nanostructure.

The qualities of the layered nanostructured films were found to vary significantly with the deposition potential. For both types of lamellar mesostructured films discussed above, the X-ray diffractograms exhibit very strong diffraction peaks if deposited at −0.5 V versus Ag/AgCl. However, reducing the deposition potential from this optimum leads to a decrease in the X-ray diffraction intensity while maintaining the identical deposition period. The films deposited at −0.8 V versus Ag/AgCl exhibit no peak at all. The changes of film quality caused by the deposition potential can also be reflected from the surface morphology of lamellar composite nickel hydroxide films. At the same time, the surface morphologies of both types of
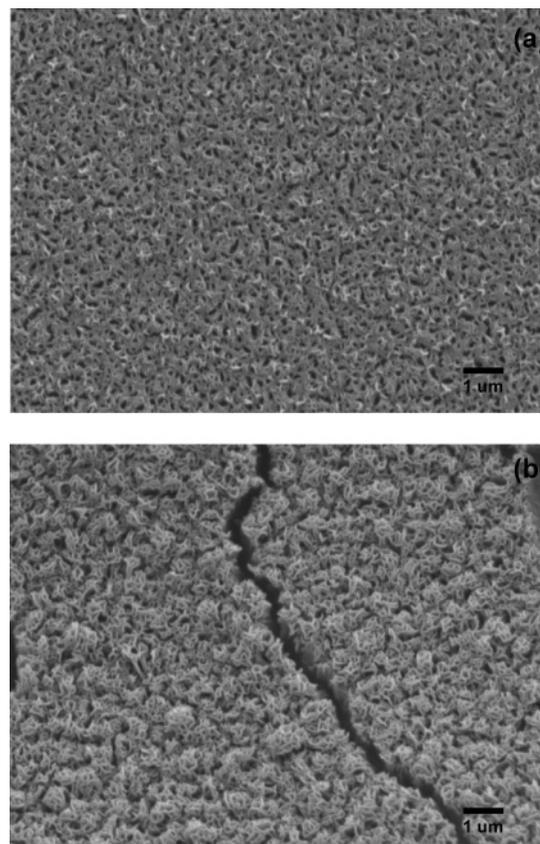
(39) (a) Huo, Q. S.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324. (b) Tolbert, S. H.; Landry, C. C.; Stucky, G. D.; Chmelka, B. F.; Norby, P.; Hanson, J. C.; Monnier, A. *Chem. Mater.* **2001**, *13*, 2247.

Figure 4. Surface morphologies imaged by SEM of lamellar nickel hydroxide films electrodeposited at (a) −0.5 V and (b) −0.7 V versus Ag/AgCl from 20 wt % aqueous solution of ethylene glycol with 1.5 wt % SDS surfactant species as the template.

lamellar mesostructured films show the same variation trend as that when varying the deposition potential. Typically, the film surface morphologies obtained from 20 wt % ethylene glycol aqueous solution at different potentials are imaged by SEM (shown in Figure 4). Figure 4a displays that the films deposited at a potential of −0.5 V versus Ag/AgCl present spongelike morphology and are relatively flat. However, the film surface becomes rough and is comprised of wormlike particles as decreasing the potential to −0.7 V versus Ag/AgCl (Figure 4b), which is well close to that of nonporous $Ni(OH)_2$ films deposited in absence of any surfactants (see Supporting Information Figure I). We thus conclude that the different film morphologies caused by the variation of potential are kinetically controlled. The growth of the nanostructured film is apparently driven by a balance (a competition process) between the inorganic polymerization and the cooperative assembly. Under strong reduction condition, inorganic polymerization is quickly triggered, leading to the formation of a large percentage of solid inorganic domains without any features. This elucidates the similarity of the surface morphology obtained at −0.7 V to that of nonporous films. Support for this idea is also found by a clear increase in the electrolysis current density (shown in Supporting Information Figure II) and the corresponding TEM images of the films which present a large number of featureless regions.

SDS/Poly(alkylene oxide) Polymers Complex Templates. As shown in Figure 5a, the X-ray diffraction pattern of the as-prepared mesoporous nickel hydroxide films deposited from a
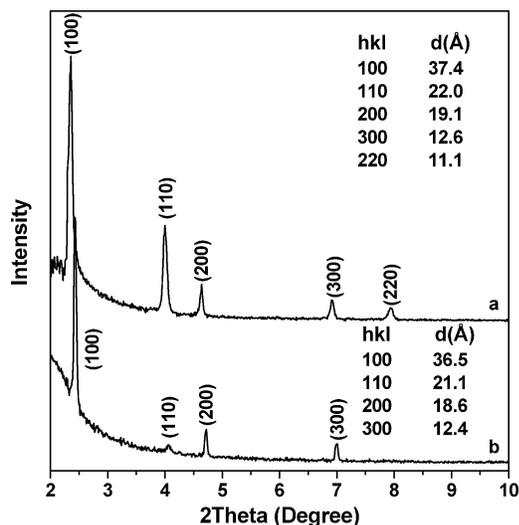
Figure 5. Low-angle X-ray diffraction patterns of (a) as-electrodeposited and (b) as-treated mesoporous nickel hydroxide films obtained at −0.5 V versus Ag/AgCl by using 1.5 wt % anionic surfactant SDS species and 0.4 wt % cosurfactant P123 as the template. The solvent for plating is 20 wt % ethylene glycol aqueous solution.

water−ethylene glycol (20 wt %) mixing solvent in the presence of SDS (1.5 wt %) and cosurfactant P123 (0.4 wt %) shows the first three strong well-resolved peaks with a 1, $\sqrt{3}$, 2 spacing pattern, which can be indexed as (100), (110), and (200) diffraction peaks associated with *p6mm* hexagonal symmetry. Two additional peaks appear in the 2θ range of 5−10° which can be indexed as (300) and (220) reflections, respectively. The intense (100) reflection gives a *d* spacing of 37.4 Å, corresponding to a unit cell parameter of $a = 43.2$ Å. The strong and narrow reflections are indicative of the long-range mesoscopic ordering of the pores. Further evidence for two-dimensional hexagonal mesostructure is provided by TEM images obtained at different orientations shown in Figure 6. The micrographs viewed from different directions reveal the well-defined hexagonal mesoporous structure, with one-dimensional channel structure and a well-ordered hexagonal mesopore array. The long-ranged ordered arrangement of channels is observed in part a of Figure 6. Selected area electron diffraction patterns recorded on the inorganic walls show that they are amorphous. The apertures of the mesopores have a small mean diameter of around 2 nm, as estimated by TEM images (see Figure 6b). Previous reports demonstrate that amphiphilic triblock copolymers tend to template large pore (i.e., $\varnothing_{pore} \geq 5$ nm) mesoporous materials.[6,7,11] It is therefore conceivable that the primary templating effect of small surfactant SDS molecules is associated with the formation of such small nanopores. The distance between mesopores is about 4.4 nm on the average, which corroborates well with the XRD data. From TEM images, the pore wall of the hexagonal mesoporous nickel hydroxide is estimated to be about 2.9 nm in thickness.

To remove the organic template, the as-deposited films are kept in the original plating solution. Concomitantly, the plating solution is cooled to ambient temperature naturally as soon as the electrochemical deposition stops. The XRD pattern of the as-treated hexagonal mesoporous films shows that the well-defined hexagonal mesostructure still remains although each peak becomes slightly weaker (Figure 5b). The appearance of each peak at higher angles implies slight contraction of the
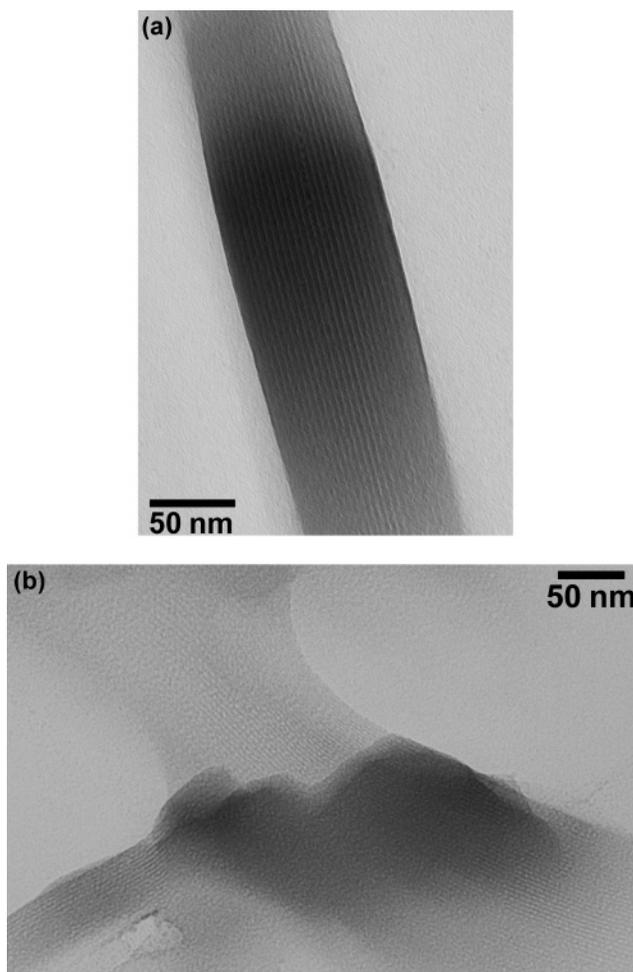

Figure 6. Transmission electron micrographs of hexagonal mesoporous nickel hydroxide films electrodeposited from 20 wt % ethylene glycol aqueous solution by using 1.5 wt % anionic surfactant SDS and 0.4 wt % cosurfactant P123 species as the template. Panel a represents a side view of the pore channels. Panel b represents a view of the hexagonal pores.

framework.[7] The FTIR spectrum reveals that there is no trace of the organic species in the as-treated hexagonal mesoporous films (see Supporting Information Figure III), suggesting that the removal of the templates is from the mesoporous nickel hydroxide films.

Figure 7 reveals the variation of film surface morphology obtained by varying deposition potential in the presence of SDS (1.5 wt %) and P123 (0.4 wt %). In a trend similar to that of lamellar films, at a cell potential of −0.5 V versus Ag/AgCl, the films surface is relatively smooth and composed of very small wormlike particles, as shown in Figure 7a. With a decrease in potential to −0.7 V, the surface particles self-organize into microspheres, with a puffy appearance likely due to the hierarchical template effect of the polymers (see Figure 7b). However, the corresponding XRD results and TEM images demonstrate that the composite films still have two-dimensional hexagonal mesostructure, whereas the intensities of the XRD reflections significantly decrease. In the case of SDS/P123 as the structure-directing agent, it is reasonable to assume that the deposition potential can possibly change the assembly fashion of SDS/P123 and the polymerization rate of mineral framework. Nevertheless, at lower deposition potential, the preservation of the two-dimensional hexagonal mesostructure rules out the
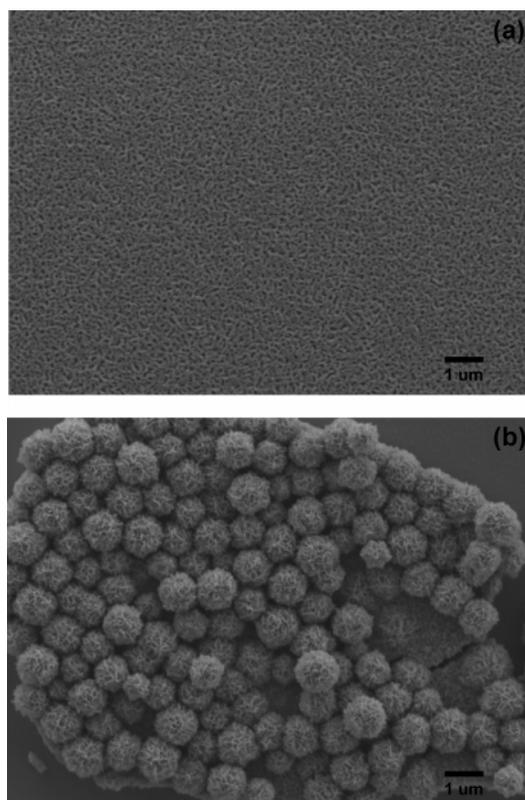
Figure 7. SEM images of Ni(OH)$_2$ films electrodeposited in the presence of 1.5 wt % SDS and 0.4 wt % cosurfactant P123 from 20 wt % ethylene glycol aqueous solution at potentials of (a) −0.5 V and (b) −0.7 V versus Ag/AgCl.

possibility of changes of the template structure. We thus conclude that the condensation rate of the inorganic material, Ni(OH)$_2$, increases under the stronger reduction conditions because low deposition potential similarly results in the greatly higher cell current density.

However, there is a point that should be addressed that crystalline Ni(OH)$_2$ films are electrodeposited in the presence of P123, F127, or PEG but in the absence of SDS, as judged from the wide-angle XRD pattern. For the films deposited under such a condition, the low-angle XRD pattern gives no peaks and TEM images present no features. Accordingly, the neutral polymers have no direct template effect on the formation of mesostructured films.

Further studies demonstrate that the other complexes composed of SDS/PEG or SDS/F127 can template the identical two-dimensional hexagonal mesoporous nickel hydroxide films to that presented above. Since the phase transformation from lamellar to hexagonal mesostructure occurs after the addition of cosurfactants poly(alkylene oxide) polymers, the essential template directing the formation of two-dimensional hexagonal mesophase (i.e., SDS molecules) must have a dramatically different profile from that for layered composite films described above. Water-soluble nonionic polymers, such as poly(alkylene oxide) polymers and poly(vinyl pyrrolidone) (PVP), are known to interact strongly with the anionic surfactant SDS in aqueous solution.[40] The incorporation of such polymers yields a complex with a string (for example, P123) of pearls (SDS) structure.
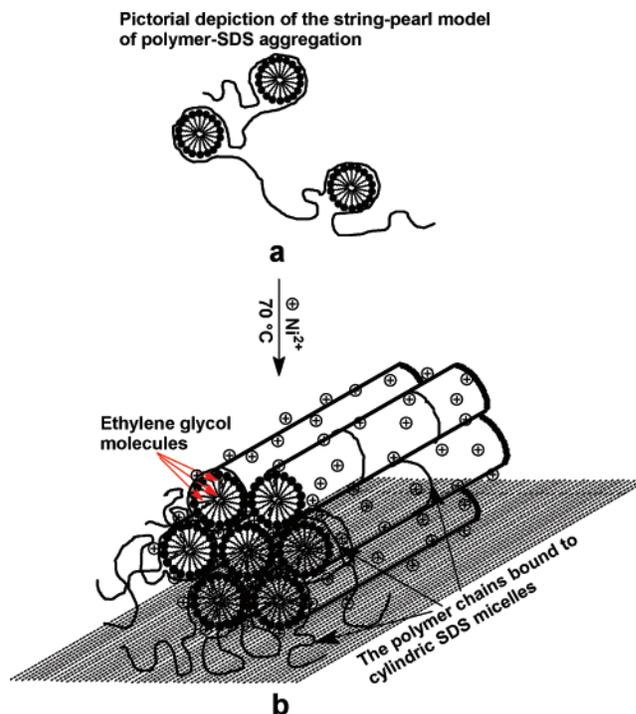

Figure 8. Cooperative templating model for the electrochemical synthesis of hexagonal mesoporous Ni(OH)$_2$ thin films on the surface of working electrode.

Concretely, according to the "necklace model", the polymer−surfactant aggregates in bulk solution are comprised of a series of spherical micelles surrounded by the polymer segments and connected by polymer strands,[41] where the surfactant headgroup dominates the interaction with the polymers. Figure 8a schematically represents a scenario of this interaction. Obviously, the sphere−cylinder micelle transformation occurs while the inorganic condensation is initiated by electrochemical reduction, allowing the hexagonal array of cylindrical SDS−Ni^{2+} interface. The neutral poly(alkylene oxide) polymers have great surface excess concentrations due to low electrostatic repulsion, resulting in an increase in the amount of polymer-bound SDS spherical micelles at the cathode surface. The high concentration of surfactants has be shown to be favorable for the transformation into rodlike micelles.[3] On the other hand, these polymer chains are bound to cylindrical SDS micelles, thereby, suppressing the formation of an SDS−Ni^{2+} bilayer. The corresponding geometric configuration of the complex template is proposed in Figure 8b. For clarity, only few polymer chains are portrayed around cylindrical SDS micelles in comparison with their surface excess. Here, the cooperative "templating" perspective accounts for the mechanism of generation of hexagonal mesophase. After the reduction of a nitrate group, inorganic condensation occurs around the cylindrical micelles, leading to the hexagonal mesopore array. At the same time, the organic medium (ethylene glycol) also plays a key role in adjusting the surfactant geometry as discussed below. In this cooperative assembly fashion, a certain amount of ethylene glycol ($\geq$20 wt %) is necessary to give rise to the generation of single two-dimensional hexagonal mesophase, which is analogous to the formation of the single lamellar phase.

(40) (a) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255. (b) Brackman, J. C.; Egberts, J. B. F. N. *Chem. Soc. Rev.* **1993**, 85.

(41) (a) Nikas, Y. J.; Blankschtein, D. *Langmuir* **1994**, *10*, 3512. (b) Braem, A. D.; Prieve, D. C.; Tilton, R. D. *Langmuir* **2001**, *17*, 883.

Table 1. Effect of the Composition of the Complex Templates Composed of SDS and Cosurfactants (P123, F127, or PEG) on the Mesostructure of Ni(OH)₂ Films Electrodeposited from 40.00 g of 20 wt % Ethylene Glycol Aqueous Solution

SDS (g)	cosurfactants (g)	deposition potential vs Ag/AgCl in 4 M KCl (V)	mesophase
0.20−0.60	0.16	−0.5, −0.7	H
0.80	0.16	−0.5, −0.7	H (half) + L (half)
1.00	0.16	−0.5, −0.7	H (minor) + L (major)
1.20	0.16	−0.5, −0.7	L
0.30−0.80	0.20	−0.5, −0.7	H
1.00	0.20	−0.5, −0.7	H (more) + L (less)
1.20	0.20	−0.5, −0.7	L
0.60−1.00	0.32	−0.5, −0.7	H
1.20	0.32	−0.5, −0.7	H (more) + L (less)
1.60	0.32	−0.5, −0.7	L

Nevertheless, not all interactions between polymers and SDS can give rise to hexagonal mesostructure. For example, the complex formed by stronger interaction between PVP and SDS still templates the same lamellar nanostructure as that obtained with only SDS as the structure-directing agent. The possible reason should be the different attraction between PVP segments and sulfate anions. Unlike the dipole−ion interactions between PEO or PPO and sulfate anion, the interaction between a PVP segment and a sulfate anion is electrostatic in nature and is, therefore, weakened due to the electrostatic screening induced by the presence of salt (Ni(NO₃)₂).[41a] In this case, the assembly of SDS−Ni²⁺ (bilayer) on the electrode surface cannot be changed. Similarly, the nanostructure of the composite Ni(OH)₂ films deposited from aqueous solution of dimethyl sulfoxide (DMSO, >20 wt %) shows the coexistence of lamellar (major phase) and hexagonal (minor phase) mesostructures due to the weak electrostatic interaction between SDS and DMSO.

Hexagonal mesoporous nickel hydroxide films can be available over a wide composition range of surfactants. Table 1 summarizes the effect of weight ratios of SDS to P123, F127, and PEG on the resulting mesostructure of nickel hydroxide films. When the surfactant concentration in increased at a fixed cosurfactant concentration, the amount of surfactant bound to polymer increases until a saturation concentration, C_{sat}, is reached. On the basis of the calculation of the value of C_{sat} on the SDS/F108 system by Tilton's group,[41b] we can estimate an approximate value of C_{sat} for the SDS/P123 system, this is, ∼0.6 g of SDS are bound to 0.16 g of P123. It was found that a decrease in the weight ratio of SDS:P123 to less than 2.5:1 results in a reduced productivity of hexagonal mesoporous composite films, as revealed by the dramatic decrease in XRD peak intensity.[42] Apparently, this can be attributed to a decrease in the concentration of in situ complex templates. However, any micelles that form beyond C_{sat} are certain to be free micelles. Thus, as the concentration of SDS is increased to above C_{sat}, the deposited films contain mixed hexagonal and lamellar phases, as shown in TEM images. This originates from the co-adsorption of the SDS−Ni²⁺ bilayer and hexagonally arranged SDS−Ni²⁺ cylinders on the working electrode surface. Finally, when SDS concentration is twice the value of C_{sat}, only lamellar phase is observed under TEM, suggesting that the SDS bilayer is a more stable surface assembly. Meanwhile, the corresponding

XRD pattern gives a set of evenly spaced peaks with a $d(100)$ spacing of 37.4 Å, which can be indexed to an identical single lamellar phase to that obtained with only SDS as the template.

Temperature is an important factor in determining the film mesostructure (organic array). In contrast, the deposition of Ni-(OH)₂ films was also carried out in the presence of SDS (1.5 wt %)/cosurfactants (0.4 wt %) at 40−50 °C. However, deposition at such low temperatures results in the low productivity of mesostructured films, as compared to those films discussed above. When the SDS/P123 and SDS/F127 complexes are used as the templates, the XRD pattern of such films shows a set of evenly spaced weak peaks with the same d spacings ($d(100) = 37.4$ Å) as those shown in Figure 1b.[42] At the same time, traces of lamellar phase are found in TEM images in addition to a large number of featureless domains (more than 95%) in such films. This phenomenon can thus only be explained by the fact that a small amount of spherical micelles (<5%) bound to a copolymer are dissociated into SDS−Ni²⁺ bilayers on the electrode surface, where the electrode surface force can prevail over the polymer−surfactant binding. In the case of the SDS/PEG complex as the template, a mixture of single lamellar (major phase) and two-dimensional hexagonal (minor phase) mesostructures with the same $d(100) = 37.4$ Å is obtained. Pure PEO chains probably produce greater surface excess concentration of SDS due to the stronger interaction between PEO segment and SDS, which gives rise to the appearance of hexagonal mesophase. In addition, it should be pointed out that spherical micelle geometry is not a structure-directing factor at all in the synthesis of mesoporous materials.[3] Hence, this control experiment shows that the electrodeposition of the hexagonal mesoporous nickel hydroxide films is temperature sensitive.

Nickel hydroxide films are also deposited from aqueous solution and dilute aqueous solutions of ethylene glycol (<20 wt %) in the presence of SDS (1.5 wt %)/cosurfactant (0.4 wt %). The XRD pattern of the as-deposited mesoporous films is the same as that obtained with only SDS as the template in aqueous solution (see Supporting Information Figure IV). TEM analysis provides further evidence of the mere existence of lamellar mesophase. Despite the introduction of poly(alkylene oxide) polymers, it can be seen that the template configuration is still SDS bilayers when doped with low levels of ethylene glycol (<20 wt %). Obviously, a large amount of ethylene glycol (≥20 wt %) changes the microenvironment for organic array. Ethylene glycol gradually enlarges the spherical micelle volume of SDS as an "expender" by increasing its doping level. As a consequence, when the concentration of ethylene glycol equals to or exceeds 20 wt % with respect to water content, the sphere-to-rod micelle transformation takes place. Hence, the cylinder SDS−Ni²⁺ interfaces are formed on the electrode surface. In terms of charge density matching, the lower curvature of SDS cylinder micelles provides the high possible surfactant density to balance Ni²⁺ cations on the electrode surface. When the concentration of ethylene glycol is above the minimum value required for the formation of hexagonal mesophase, such SDS−Ni²⁺ interface is not affected any more.

Conclusion

We systematically studied the electrochemical synthesis of mesostructured Ni(OH)₂ films in dilute surfactant solutions. The

(42) To compare the XRD intensity among different samples, the composite Ni(OH)₂ films were electrodeposited with approximately the same cell current density (<±10% deviation).

formation of mesoporous structures essentially originates from the self-assembly of inorganic Ni^{2+} and SDS at the electrode surface through the S^-I^+ pathway. First, lamellar biphases (d_{001} = 37.4 Å and d_{001*} = 28.5 Å) are deposited from aqueous solution with anionic surfactant SDS as the template. A couple of different orientations of SDS−Ni^{2+} bilayer render the microphase separation. Bilayers are often the favorable packing of anionic surfactants on the electrode surface during the in situ inorganic condensation because the maximum charge density is provided on a zero-curvature surface to balance the inorganic cations adsorbed on the cathode surface. Of course, the favorable van der Waals interactions between the surfactant hydrophobic tails are always the other factor in the determination of organic profile. The deposition medium is another significant factor that affects the mesostructure of the deposits. A transformation from lamellar biphase (d_{001} = 37.4 Å and d_{001*} = 28.5 Å) to single lamellar mesophase (d_{001} = 37.4 Å) occurs by increasing the concentration of an aqueous solution of ethylene glycol to above 20 wt %. In both cases, the formation of lamellar phases does not rely on the concentration of SDS and deposition potential.

Unlike preformed arrays of the extensively applied liquid crystals in the electrodeposition of mesoporous materials, the two-dimensional hexagonal mesophase (d_{001} = 37.4 Å) is templated through the cooperative organization of the inorganic cations and the complex templates comprised of SDS and cosurfactants, such as poly(alkylene oxide) triblock copolymers P123, F127, and poly(ethylene glycol). The hexagonal me- sophase is directly templated by SDS cylinder micelles, which are induced by the secondary template poly(alkylene oxide) polymers. At the same time, the formation of the hexagonal mesostructure not only is sensitive to the ratio of SDS to cosurfactants but also is temperature and solvent dependent. The deposition bath temperature (ca. 70 °C) and composition ($\geq$20 wt % aqueous solutions of ethylene glycol) are also decisive in the preparation of the hexagonal mesoporous $Ni(OH)_2$ film. However, for all of the electrodepositions described in this context, albeit the mesostructures do not change within the potential window for yielding $Ni(OH)_2$, the deposition potential has impacted heavily on the surface morphology of composite $Ni(OH)_2$ films. What the potential changes is just the rate of inorganic wall polymerization rather than the geometry of the organic arrays. Electrodeposition from dilute surfactant solutions is a versatile approach to mesostructured inorganic−organic composite films.

Supporting Information Available: Additional SEM image, current density curves, FTIR spectra of as-deposited and as-treated $Ni(OH)_2$ films, and low-angle XRD pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

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