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Cosynthesis, Coexistence, and Self-Organization of α- and β-Cobalt Hydroxide Based on Diffusion and Reaction in Organic Gels

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We report the cosynthesis of highly stable laminated single crystal α- and β-$Co(OH)_2$ using the reaction and diffusion of a hydroxide solution into a gel containing Co(II). The obtained α-$Co(OH)_2$, which is known to be thermodynamically unstable and transforms in a short period of time to the β form, has been stabilized in the gel medium for weeks. The system also exhibits Liesegang banding where complicated spatial dynamics during the formation of the two polymorphs are shown to take place.

Cobalt hydroxide crystallizes into two polymorphs having hexagonal layered structures and are denoted as α- and β-$Co(OH)_2$.[1,2] The pink colored β-$Co(OH)_2$ has a brucite-like structure where the divalent cobalt and hydroxide ions, coordinated in octahedral sites, form charge-neutral layers stacked one over the other. The crystallographic study of this polymorph revealed the absence of intercalated species between these layers. The interlayer spacing was found to be 4.6 Å.[3] On the other hand, the blue-green α-$Co(OH)_2$ was found to exhibit a hydrotalcite-like structure consisting of positively charged layers separated by charge-balancing anions (e.g., NO_3^-, CO_3^{2-}, Cl^-, etc.) and water molecules. The α-cobalt hydroxide acquires a positive charge by partial protonation of the hydroxyl ions.[4] The intercalation of the anions results in a substantial increase in the interlayer spacing, which is usually greater than 7 Å depending on the intercalated anion species.[5]

Cobalt hydroxide is shown to be of great interest in various fields of science and technology. By coupling this hydroxide to ultrastable Y-type zeolite, $Co(OH)_2$/Y zeolite nanocomposites are obtained; these proved to have the properties of supercapacitors with high energy density.[6] The cobalt hydroxide was also used as an additive to $Ni(OH)_2$ electrodes in alkaline secondary batteries to improve electrochemical performance.[7] In such applications, the α-$Co(OH)_2$ was found to be of a greater interest than the β-polymorph due to the existence of an interesting interlayer chemistry.[2] The combination of $Co(OH)_2$ with some organic pillars led to porous layered materials whose thermal stability and magnetic behavior could be tailored via the choice of the pillaring agents.[8] The β-$Co(OH)_2$ platelets were also used as templates in the fabrication of textured cobaltite ceramics with enhanced thermoelectric properties.[9]

Both polymorphs can be prepared using various methods such as the homogeneous precipitation[10] and the electrochemical synthesis.[11] However, one major drawback in the synthesis of α-$Co(OH)_2$ showing some liquid crystalline properties[12] lies in its thermodynamic instability; it was found that it is metastable and transforms rapidly to the stable β-form especially in alkaline media.[13] Furthermore, it was found that in most syntheses, the α-$Co(OH)_2$ exhibits a poor crystalline and disordered structure.[12] Recently, Sasaki and co-workers have reported a novel synthetic method which yielded excellent crystalline α and β-$Co(OH)_2$.[12]

Herein we report a new method to cosynthesize stable α- and β-$Co(OH)_2$. This method is based on the Liesegang banding phenomenon of precipitates in gels.

Liesegang banding is a periodic precipitation pattern that manifests itself when soluble ions interdiffuse into a gel to react and form sparingly soluble salts.[14] The resulting spatial distribution of the precipitate is often inhomogeneous and leads to the appearance of bands parallel to the diffusion front and separated by distinct spacings.[15] The presence of a gel is essential to prevent sedimentation and convection and to slow down nucleation and growth phenomena. If there is an initial concentration difference between the interdiffusing electrolytes, a reaction wave is initiated at the interface between the two solutions and propagates leaving the banded structure. The morphology of the pattern depends, among many other parameters, on the nature of the gel, the initial degree of supersaturation and the initial concentration difference of the diffusing electrolytes. These latter parameters affect the rate of nucleation of the salt particles, which are dissolved colloidal clusters, their rate of growth from colloids to form the precipitates, and at a later stage the rate of coarsening of the precipitates. Theoretically, the Ostwald cycle based on supersaturation, precipitation, and depletion coupled to the competition of growing particles of different sizes has been used to explain many features of the Liesegang phenomenon.[16]

In this work, we study the formation of the two polymorphs, α- and β-$Co(OH)_2$, which are of different sizes, within the context of the aforementioned Liesegang paradigm where hydroxide ions are diffused into a cobalt-doped gel. A sodium hydroxide solution was added to the upper part of a glass tube containing an organic gel (agar or gelatin) that was prepared in the presence of a cobalt (II) chloride solution. The solid−liquid interface was indicated prior to the addition of the base solution. The tube was left for a certain period of time and photos were taken with a digital camera.

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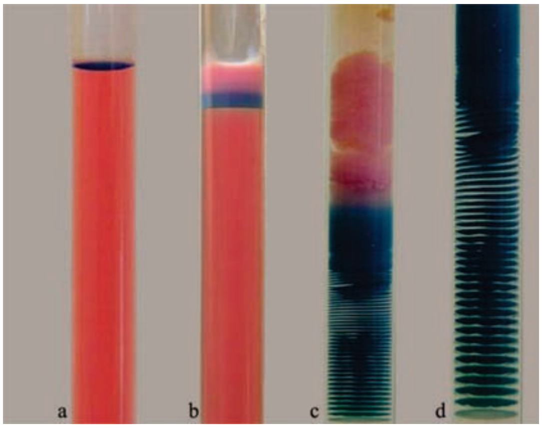

Figure 1. (a) The formation of a blue band of α-$Co(OH)_2$ near the boundary directly after the addition of the hydroxide solution. (b) The formation after few minutes of the pink β-$Co(OH)_2$ above the blue band, which propagated downward. (c) The tube after two weeks. (d) A blowup of the Liesegang bands of α-$Co(OH)_2$ in 1c.

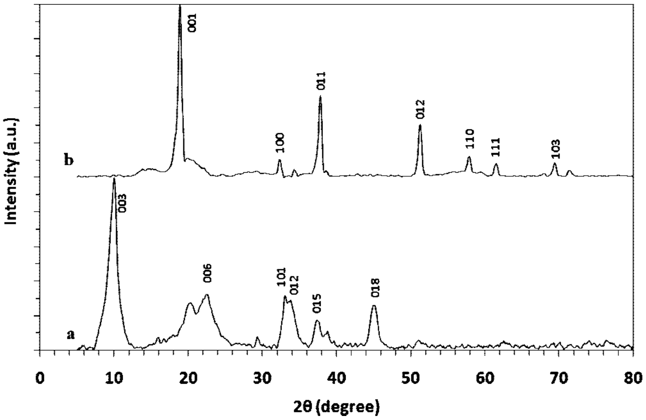

Figure 2. Powder X-ray diffraction of (a) blue and (b) pink compounds.

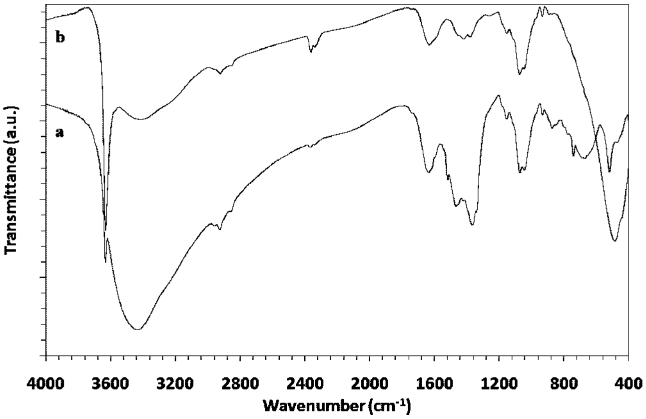

Figure 3. FTIR spectra of (a) α-$Co(OH)_2$ and (b) β-$Co(OH)_2$.

In the first few seconds of the experiment, a blue precipitate was formed at the liquid−solid interface indicating a spontaneous reaction between the diffusing ions and those existing in the pores of the gel (Figure 1a). After a while, another pink-colored precipitate was noticed in the tube, which appeared on the top of the blue precipitate, that in turn started moving slowly down the tube (Figure 1b). The evolution of these different precipitates was monitored for three weeks and yielded a Liesegang pattern of clearly separated bands of a blue precipitate (Figure 1c,d). The blue precipitate was stable for additional two weeks without conversion to the pink precipitate and vice versa. It was noticed that the formation time of the bands depended on the initial concentration difference and the initial degree of supersaturation of cobalt (II) ions and hydroxide solutions: the system having the smallest cobalt chloride concentration or the smallest degree of supersaturation showed the slowest appearance of the colored precipitates. It is worth to note that no Liesegang band pattern was observed for the pink compound.

The colored products were collected and separated after the removal of the organic network. They were characterized by powder X-Ray diffraction (XRD) using a diffractometer with a Cu Kα target tube ($\lambda = 1.5418$ Å) and Fourier transform infrared (FT-IR) spectroscopy using the KBr pellet technique. The structural characterization was able to identify with no doubt the chemical nature of the colored compounds.

The XRD patterns (Figure 2) showed the existence of two different crystalline structures. The diffractograms clearly suggest that the pink compound showing sharp *hkl* reflection peaks has a higher crystalline nature than the blue product giving an XRD spectra signal/noise ratio relatively high. The low crystallinity and small crystallite sizes of the α-polymorph revealed by a considerable broadening of the peaks in the diffraction pattern could be due to some disorder of the layers oriented along the *c*-axis leading to a small number of parallel planes available for the diffraction.

The positions and intensities of the diffraction peaks, coupled to the chemical nature of the expected products revealed the existence of cobalt hydroxide crystals in two different structures. These hydroxides, having a very low solubility ($K_{sp} = 1.6 \times 10^{-15}$), are obtained after the diffusion of the outer electrolyte (OH^-) inside the gel and its reaction with the inner electrolyte (Co^{2+}).

The XRD diffraction peaks of the pink crystal indicate clearly its nature as being the brucite-like β-$Co(OH)_2$ having a hexagonal cell. The blue crystal is shown to be the hydrotalcite α-$Co(OH)_2$ with a rhombohedral symmetry.[17] The plane-spacing calculation according to Bragg's equation allowed us to deduce the lattice parameters of the α- and β-unit cells, respectively. The α-$Co(OH)_2$ parameters were found to be 3.14 Å (*a*) and 24.00 Å (*c*), while those of the β-polymorph were 3.17 Å (*a*) and 4.61 Å (*c*).

The FTIR spectra of the two colored compounds are shown in Figure 3. These spectra exhibit bands centered around 3450 cm^{-1} corresponding to the O−H stretching vibrations of the interlayer water molecules and hydrogen atoms bound to OH groups. The bands appearing around 1634 cm^{-1} correspond to the water molecules deformation vibration. Peaks around 1466 and 1072 cm^{-1} are assigned to carbonate ions, and their existence could be due to the dissolution of carbon dioxide molecules in water. The sharp peak appearing at 3631 cm^{-1} is easily attributed to O−H stretching mode of the free Co−OH groups. The spectra showed clearly that this peak is by far more intense in the β-$Co(OH)_2$ than in the α-$Co(OH)_2$. This difference in the peaks' intensities could be due to the existence of a larger number of non-hydrogen bonded OH in the charge-neutral cobalt hydroxide layers than in the positively charged layers in the α-polymorph, where the OH group vibrations are expected to be lowered due to the existence of hydrogen bonding between the hydrogen atoms and the intercalated anions within the layers. The broad peak appearing at low frequency (486 cm^{-1}) is assigned to the bending vibration mode of the free Co−OH groups in the brucite-like structure, while in the α-compound these vibrations are not well expressed due to limitations caused by the hydrogen bonding.

By making use of the Liesegang phenomenon and the theory of competitive particle growth, and the fact that crystals of different sizes will competitively grow in a gel, we were able to cosynthesize α- and β-$Co(OH)_2$.

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Supporting Information Available: Experimental details of preparing the Liesegang patterns in the organic gel. This material is available free of charge via the Internet at http://pubs.acs.org.

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