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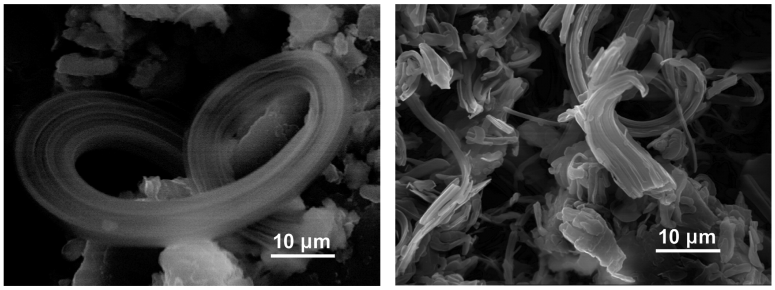

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Unique Layered Double Hydroxide Morphologies Using Reverse Microemulsion Synthesis

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Abstract: We report the first controlled synthesis of a layered double hydroxide (LDH) in a water-in-oil reverse microemulsion system. This synthesis of Mg_2Al-LDHs was carried out in the reverse microemulsion of NaDDS (sodium dodecyl sulfate)−water−isooctane with water/surfactant molar ratio = 24. This enables us to obtain nanometer sized LDH platelets typically with a 40−50 nm diameter and 10 nm thickness. Further modification of the reverse microemulsion using triblock copolymers during crystallization allowed us to express different growth orientations of the LDH structure. These data show that the aspect ratio of LDHs can be flexibly adjusted over a wide range.

Introduction

Layered double hydroxides (LDHs) are a large family of materials with a generally formulated composition of $[M^{z+}_{1-x}M'^{3+}_{x}(OH)_2]^{p+}(X^{n-})_{p/n}\cdot mH_2O$. They consist of positively charged layers of mixed metal hydroxides that require the presence of interlayer anions to maintain overall charge neutrality. Traditionally, coprecipitation methods are used to synthesize these materials in bulk aqueous solutions. LDHs have been widely investigated by intercalation chemistry to develop potential applications in fields of catalysis, absorption/separation, and medicine.[1a,b] In addition, these materials were also tried as inorganic additives in the development of new nanocomposites.[1c−e] To get high quality nanocomposites, highly exfoliated LDH layers with hydrophobic surface characteristics are required in order to obtain stable homogeneous LDH dispersions in a polymer matrix. However, the high intralayer charge density of LDHs makes it very difficult to achieve these requirements. Considering the versatility of reverse micelles/microemulsions in the study of "crystal tectonics",[2,3] we were interested in investigating merging the traditional coprecipitation methodology of LDH synthesis with a reverse micelle/microemulsion system, which might generate LDHs with new structural properties and morphology for potential applications in new fields of materials research. To the best of our knowledge, no other previous work was reported in detail on the synthesis of LDHs in a water-in-oil system except a recent publication using a Tween85−water system to synthesize cobalt LDHs as precursors to Co_3O_4 nanocrystals.[2f]

Surfactants dissolved in organic solvents form spheroidal reverse micelles with the hydrophobic chains pointing out into the solvents. When water is added, the reverse micelles swell with water droplets entrapped at the polar core formed by the hydrophilic heads of the surfactants. The water/surfactant molar ratio ($w = [H_2O]/[S]$) is defined to describe the properties of such dispersions.

A wide range of studies has been carried out either on the physical/chemical nature or on the application of such systems (when containing aqueous solution of reactants instead of pure water) to produce well-defined inorganic structures. In some space-confined reactions, reverse micelles/microemulsions are used to disperse reactants and act as microreactors providing only limited space and nutrients for the proceeding reactions. Nanocrystal particles with uniform size distributions are therefore obtained.[2] Such systems also provide ideal approaches to "crystal tectonics" or the controlled synthesis of macroscopic structures consisting of higher-order surfactant-inorganic-crystalline assemblies.[3]

Reverse micelle/microemulsion systems are fluid, and the micellar aggregates are subject to Brownian motion. Collisions between the aggregates cause continuous coalescence and decoalescence of the aggregates and consequently the exchange of water content from one "water pool" to another. Besides the fluid systems, there are also some reports on bicontinuous microemulsions structured as compartmentalized liquids with highly branched and interconnected networks in the solidified oily phase at low temperature. Three-dimensional porous inorganic frameworks with promising chemical and biological

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(1) (a) See: Khan, A. I.; O'Hare, D. *J. Mater. Chem.* **2002**, *12*, 3191 and the references therein. (b) Braterman, P. S.; Xu, Z. P.; Yarberry, F. Layered double hydroxides (LDHs). In *Handbook of Layered Materials*; Marcel Dekker Inc.: New York, 2004; pp 373−474. (c) O'Leary, S.; O'Hare, D.; Seeley, G. *Chem. Commun.* **2002**, 1506. (d) Adachi-Pagano, M.; Forano, C.; Besse, J. *Chem. Commun.* **2000**, 91; (e) Hibino, T.; Jones, W. *J. Mater. Chem.* **2001**, *11*, 1321.

(2) (a) Meyer, M.; Walberg, C.; Kurchara, K.; Fendler, J. H. *J. Chem. Soc., Commun.* **1984**, *90*, 90. (b) Petit, C.; Pileni, M. P. *J. Phys. Chem.* **1988**, *92*, 2282. (c) Pileni, M. P. *Langmuir* **1997**, *13*, 3266. (d) Teng, F.; Xu, J.; Tian, Z.; Wang, J.; Xu, Y.; Xu, Z.; Xiong, G.; Lin, L. *Chem. Commun.* **2004**, 1858. (e) Chen, Z.; Li, S.; Yan, Y. *Chem. Mater.* **2005**, *17*, 2262. (f) Xu, R.; Zeng, H. C. *Langmuir* **2004**, *20*, 9780. (g) Pileni, M.-P. *Nat. Mater.* **2003**, *2*, 145.

(3) (a)Lisiecki, I.; Albouy, P.-A.; Pileni, M.-P. *J. Phys. Chem B* **2004**, *108*, 20050. (b) Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393. (c) Patil, A. J.; Muthusamy, E.; Seddon, A. M.; Mann, S. *Adv. Mater.* **2003**, *15*, 1816. (d)Pileni, M. P.; Lalatonne, Y.; Ingert, D.; Lisiecki, I.; Courty, A. *Faraday Discuss.* **2004**, *125*, 251.

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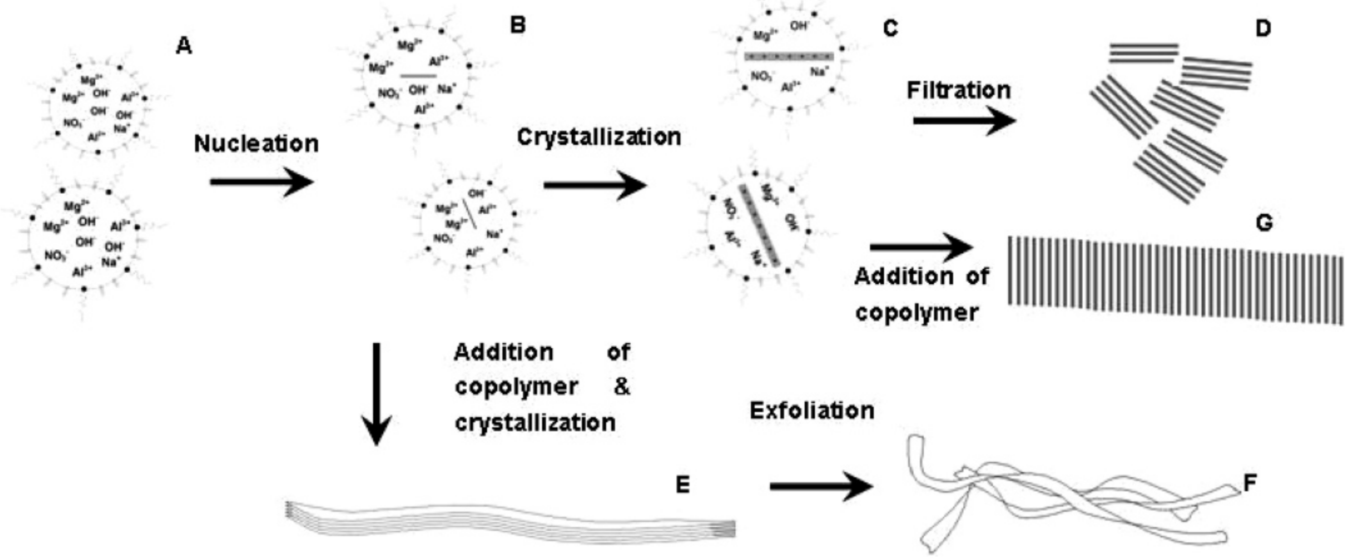
Scheme 1. Schematic Illustration of the Proposed Stages of LDHs Growth in a Reverse Microemulsions System[a]



[a] Normal microemulsion only produce highly separated platelets (A−D), while new structures (G and E) induced from different oriented growth modes can be obtained with specific unique morphologies.

applications have been obtained using this system while only individual particles can be obtained in a normal fluid system with the same recipe.[4a,b] Such immobilized microemulsion-based systems can also be prepared by solubilization of gelatin, a hydrophilic protein in an AOT−water−isooctane mixture for promising photochemical applications as well as the synthesis of nanoparticles.[4c,d]

Results and Discussion

We have studied the synthesis of Mg_2Al-LDHs in reverse microemulsion of NaDDS (sodium dodecyl sulfate)−water−isooctane with $w = 24$.[5] In the first step, LDH nanoplatelets were formed in the reverse microemulsion by dispersing aqueous solution of the reactants in NaDDS/isooctane reverse micelles (containing 1-butanol as cosurfactant) at room temperature (Scheme 1A). The system soon became cloudy, which indicates the formation of crystal nuclei within the microemulsion (Scheme 1B). With further heating at 75 °C for 24 h, the whole system became milky and the as-synthesized sample (denoted as **LDH-RM**) was later recovered from the microemulsion by filtration, as illustrated in Scheme 1C,D.

Elemental analysis gives molar ratios of $M_{\mathrm{Mg/Al}} \approx 2$ and $M_{\mathrm{S/Al}} \approx 1$ and no detectable content of nitrogen (in form of nitrates from reactants of $Mg(NO_3)_2$, $Al(NO_3)_3$, and $NaNO_3$). This result indicates an intralayer chemical composition of $[Mg_2Al(OH)_6]^+$ with an equal amount of DDS groups ($C_{12}H_{25}SO_4^-$) instead of nitrate anions for charge-balancing in the interlayer gallery. The IR spectrum of this sample shows strong absorbances in the region 2800−2940 cm^{-1} (antisymmetric and symmetric ν_{CH} from the dodecyl groups) and 1215−1235 cm^{-1} (S═O stretching mode in the sulfate groups) while the characteristic IR adsorption at 1369 cm^{-1} from the NO_3^- in a typical nitrate LDH sample is not visible.[6] These data (Supporting Information, Figure 1S) are consistent with elemental analysis results and confirm the chemical composition of **LDH-RM**.

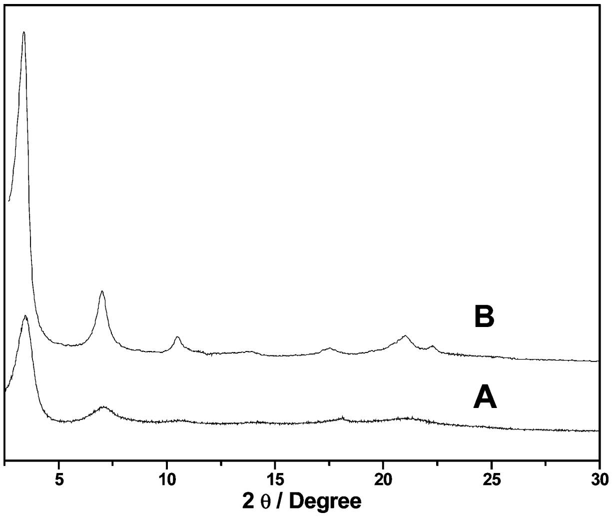


Figure 1. (A) XRD data for sample **LDH-RM** synthesized in reverse microemulsions. (B) XRD data for a standard DDS intercalated LDHs sample by ion-exchange method.

The XRD pattern of this sample is shown in Figure 1A. The observed Bragg reflections agree with the pattern in Figure 1B which is from a standard DDS-intercalated LDH sample by ion-exchange method from a nitrate LDH precursor host synthesized by the traditional coprecipitation method (see Experimental Section for details). It has been generally acknowledged that the *d*-spacing (d_{003}) of a DDS-intercalated LDH sample is about 26 Å (2.6 nm). The host framework, which contains stacking of $[Mg_2Al(OH)_6]^+$ layers, has a rhombohedral structure with an $a = b$ and $c = 3d_{003}$ unit cell. The structure in Figure 1A

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(4) (a) Walsh, D.; Hopwood, J. D.; Mann, S. *Science* **1994**, *264*, 1576. (b) Sims, S. D.; Walsh, D.; Mann, S. *Adv. Mater.* **1998**, *10*, 151. (c) Quellet, C.; Eicke, H. F. *Chimia* **1986**, *90*, 5892. (d) Lisiecki, I.; Billoudet, F.; Pileni, M. P. *J. Mol. Liq.* **1997**, *72*, 251.

(5) (a) Pileni, M. P. *J. Phys. Chem.* **1993**, *97*, 6961. Although there is no clear-cut parameter for classification, generally the aggregates with $w < 10−15$ are taken as reverse micelles while systems with the value above are denoted as reverse microemulsions. Also see refs 2 and 3 for examples. (b) With *w* value and experimental procedures changed, monolayer LDH particles with completely exfoliated structure can be synthesized. This work has been submitted by Hu, G.; Wang, N.; O'Hare, D.; Davis, J.

(6) (a) Xu, Z. P.; Zeng, H. C. *J. Phys. Chem. B* **2001**, *105*, 1743. (b) Xu, Z. P.; Braterman, P. S. *J. Mater. Chem.* **2003**, *13*, 268.

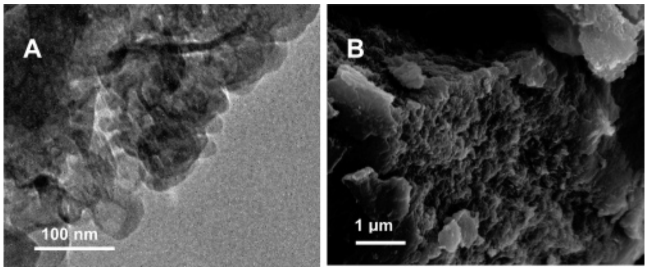

Figure 2. (A) TEM image of the platelets in sample **LDH-RM** synthesized in a reverse microemulsion. (B) SEM image of a large block by random stacking of the platelets shown in part A.

can thus be indexed using $a = b = 2d_{110} = 3.04$ Å and $c = 3d_{003} = 78$ Å for a rhombohedral symmetry unit cell.[6a,7]

The fwhm (full width at half-maximum) value for **LDH-RM** is about 1.2° for the 003 reflection in Figure 1A which gives an estimated crystallite coherence size to be ca. 100 Å (10 nm) along the *c* direction by the Scherrer equation, indicating a stacking of 3−4 monolayers. All other basal plane reflections also become broader and weaker, indicating a poorly crystalline structure, i.e., fewer stacking layers in this direction. TEM observations show that the sample is composed of platelet crystallites of basal planes with a 20−50 nm diameter distribution (Figure 2A). These platelets will stack into large blocks of various sizes without specific morphology (Figure 2B). No edge-on image of the platelets was seen which suggests that very thin platelets of a couple of layers were obtained in the reverse microemulsions.

Previous studies have shown that for a given reverse micelle/microemulsion system, the size of the water pools is only determined by *w* value[2c,5] despite the fact that the small reverse micellar aggregates collide continuously with one another due to Brownian motion in the system. During this dynamic process, a small fraction of droplets exist as short-lived dimers with exchange of the content in the water pools and split again. Such a spontaneous coalescence and decoalescence sequence makes the reverse microemulsion serve as hosts to the solute reactants, shielding the platelet products from stacking or growing too big (Scheme 1C), and modifying the platelets with charge-balancing DDS groups. The reverse microemulsion is thus acting as soft secondary templates for the formation of separated LDHs platelets. Therefore, it is reasonable to propose that other LDH products with unique structural and morphological properties may be obtained if suitable modifications are made in order to adjust the structure of the micellar aggregates in this reverse microemulsion system.

We have studied previous reports on the behavior of microemulsion-based gels.[8] For example, the protein, gelatin,[9] is solubilized in an AOT−water−isooctane reverse microemulsion to produce a modified stable gel. Although the mechanism of the gelation and the structure ensuing from this phase change are still rather obscure, it can be reasonably assumed that gelatin is pivotal to congregate the water pools into branching networks due to the interactions between the hydrophilic strands and the microemulsion, which have been unexceptionally recognized in different structural models proposed on this system.[3c,8c,1010]

Triblock copolymers have a general composition formula as $HO(C_2H_4O)_n(C_3H_6O)_m(C_2H_4O)_nH$ (Aldrich, $M_{average.}$ ca. 1900 with 40 wt % of C_2H_4O content used for the present study and denoted simply as P1940 hereafter). While the whole molecule presents as hydrophilic, the two PEO moieties at the ends are more hydrophilic and structurally flexible than the PPO strand in the middle. Due to this structural resemblance, such molecules are expected to result in identical phase evolution as gelatin molecules.

During the study, we found that this addition of copolymer molecules into the reverse microemulsion at different stages could produce different structures.

When the copolymer was added to the reverse microemulsion before the crystallization process proceeded (parts B−E in Scheme 1), new structures with belt like morphology can be easily discerned from some blocks with random shapes, which (denoted as **LDH-N**) are completely different from the morphology of **LDH-RM**.

A typical SEM image of the new structure is shown in Figure 3A. The belt has a length of a few hundred micrometers along the long axis and the cross-sectional dimension of the belt is about 10 μm × 3 μm. By SEM observations, we also found some other structures with similar beltlike shape but different cross-sectional dimensions in the sample (Supporting Information, Figure 2S). It is also discernible from the morphology of the belt in Figure 3A that some parallel linear patterns appear on the structure along the long axis, indicating a stacking of layers in the same direction. This structure can be confirmed by a TEM study. A picture shown in Figure 3B reveals the lamellar structure on the edge of a long belt (highlighted in a white rectangle) with the inset high-resolution image presenting a ca. 3 nm *d*-spacing. EDX analysis on this belt is shown in Figure 3C, no nitrogen was detected in this structure, which excludes the existence of nitrates in this structure. A brief estimation of $M_{Mg/Al}$ and $M_{S/Al}$ gives consistent values with those values of **LDH-RM** when considering the accuracy in the quantitative elemental analysis by EDX. A notable characteristic with this structure is that these long belts are easily destroyed by ultrasonic irradiation. Images of the exfoliated layers from the belts can be observed under EM scopes and presented in Figure 3D,E. Both of the two images show a cluster of entangled thin layers instead of the original beltlike morphologies. An SAED (selective area electron diffraction) pattern of the layers is shown in Figure 3F. The reflections can be indexed by a hexagonal unit cell with unit cell parameters of approximately $a = b = 0.32$ nm, which within the errors of the ED experiment is in agreement with the values ($a = b = 0.304$ nm) determined by XRD for Mg_2Al LDH.[6a,7] These results give corroborative evidence that the long beltlike structures in **LDH-N** are actually LDHs with oriented growth in the *ab* plane.

When the copolymer (P1940) was added to a reverse microemulsion system which had already undergone a 24-h crystallization process at 75 °C and had been heated further

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(7) JCPDS, PDF-No. 890460. The charge-balancing anions are nitrates and dodecyl sulfates in the present study instead of carbonates in the cited index. However, the replacements of carbonates only change the interlayer distance (*d*-spacing) and thus the *c* parameter for the unit cell. It is thus reliable to index the samples of the present study according to JCPDS, PDF-No. 890460.

(8) (a) Petit, C.; Zemb, Th.; Pileni, M. P. *Langmuir* **1991**, *7*, 223. (b) Haering, G.; Luisi, P. L. *J. Phys. Chem.* **1986**, *90*, 5892. (c) Capitani, D.; Segre, A. L.; Haering, G.; Luisi, P. L. *J. Phys. Chem.* **1988**, *92*, 3500.

(9) For a detailed knowledge about the molecular structure of gelatin, see: Lehninger, A. L.; Nelson, D. L.; Cox, M. M. *Lehninger Principles of Biochemistry*, 4th ed.; W. H. Freeman & Co.: New York, 2004; Chapter 4, pp 127−128.

(10) Atkinson, P. J.; Grimson, M. J.; Heenan, R. K.; Howe, A. M.; Robinson, B. H. *J. Chem. Soc., Chem. Commun.* **1989**, 1807.

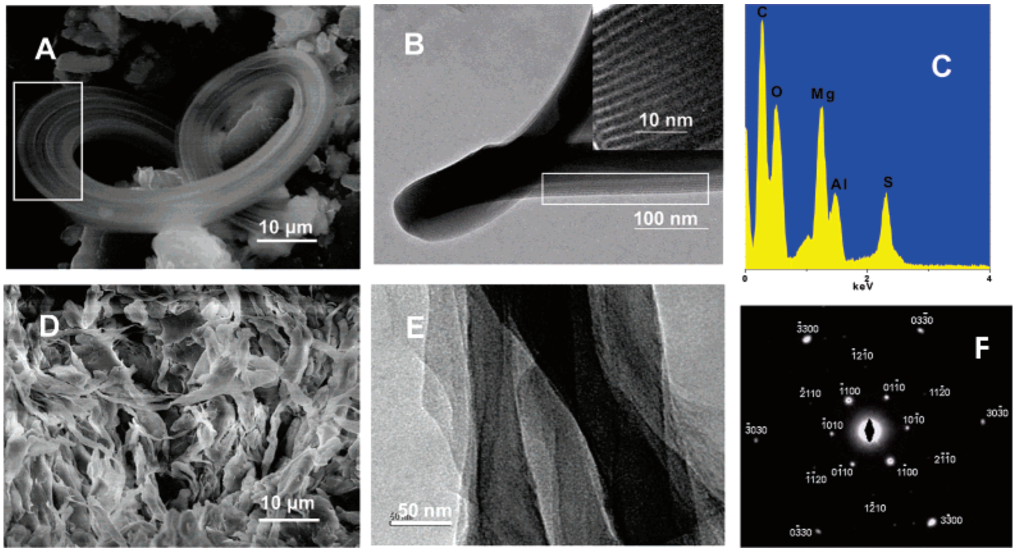


Figure 3. (A) SEM picture of a beltlike structure in **LDH-N** with the parallel linear pattern highlighted in the white rectangle. (B) TEM image of one belt reveals the lamellar structure with a HR image of this structure shown in the inset picture, and the chemical compositions are analyzed by EDX with the spectrum in part C. The belts are easily exfoliated to give structures shown by an SEM picture in part D and a TEM image shown in part E. The corresponding selective area electron diffraction pattern is indexed in part F.

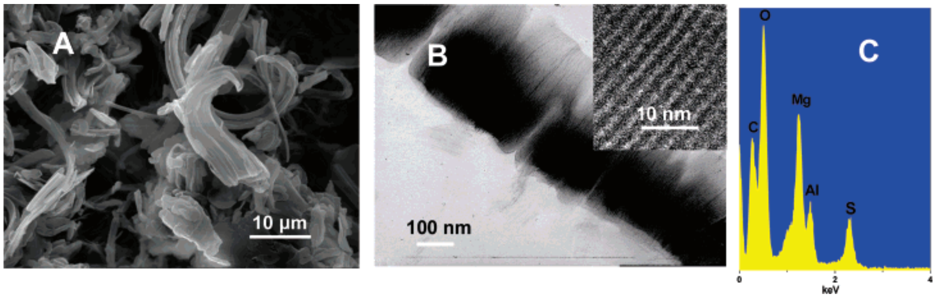


Figure 4. (A) SEM picture showing the rodlike structure in **LDH-C**. (B) TEM image of one rod reveals the lamellar structure by the stacking of platelets along the long axis. The inset picture shows the HRTEM image of this structure. The chemical compositions are analyzed by EDX with the spectrum in part C.

(B–G in Scheme 1), a considerable amount of rodlike structures a few tens of micrometers in length could be observed by SEM (Figure 4A) (denoted as **LDH-C**). A TEM image of one rod is shown in Figure 4B, and the image clearly shows that these rod structures are a few hundred nanometers in the dimension perpendicular to the long axis. The linear patterns resolved on this image indicate that the rod may have a layered structure which is constructed by stacking of platelets. The inset HRTEM image confirms this model (Scheme 1G) and shows that this structure has an interlayer spacing of approximately 3 nm, which is consistent with the value for **LDH-N**. The chemical composition of this structure was also probed by EDX analysis. The spectrum in Figure 4C shows the existence of Mg, Al, and S and excludes nitrogen content in the rodlike structure. An EDX-based estimation on $M_{\mathrm{Mg/Al}}$ and $M_{\mathrm{S/Al}}$ values of **LDH-C** (Figure 4C) gives similar results to those of **LDH-N**.

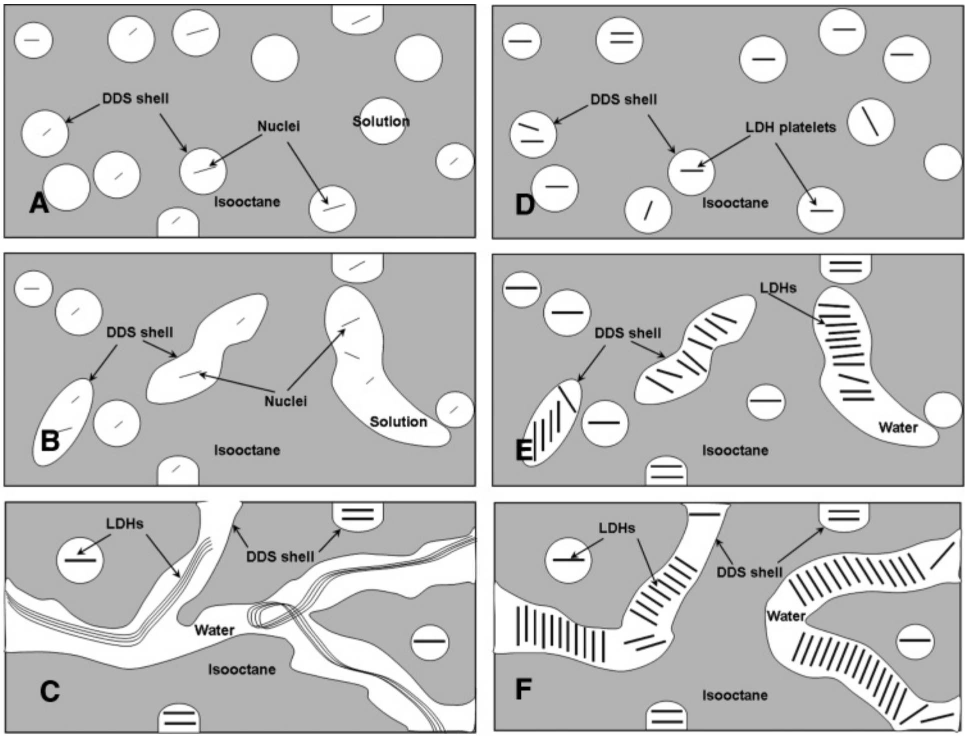
During these investigations, we noticed that the randomly shaped blocks of the same composition as the LDHs platelets always coexisted with the new rodlike structures. We have tried to investigate conditions on which the percentage of these structures could be significantly increased by adjusting some reaction parameters but with little effect. We will discuss these observations later in connection with the proposed mechanism of this reaction.

It can now be concluded that the addition of P1940 copolymer in the DDS–water–isooctane reverse microemulsion system significantly modifies the interior environment and thus the structure of the micellar aggregates. As a result, some new structures can be synthesized, which have completely different morphological properties from the platelets obtained without the addition of copolymer molecules. A further analysis on the copolymer-modified environment in the reverse microemulsion would be more helpful to get better knowledge on the two oriented LDH structures.

On a similar system reported previously, detailed studies have been performed in order to describe the microscopic structure. This microemulsion-based gel system was modified from an AOT–water–isooctane reverse microemulsion system with the solubilization of gelatin. Since the first work done by Haering[8b] and Quellet,[4c] at least three structural models have been proposed on the basis of the different techniques used to characterize systems falling in different regions of the phase diagram. However, all the different models describing the structure share a common recognition that the hydrophilic protein chains undergo a solubilization process and thus connect the initially separated water droplets which exist in the form of a reverse microemulsion.[4c,5,8c,10] The substitutions of AOT to DDS and gelatin to copolymer P1940 make the reverse microemulsion system in the present study very similar to the gel system reported before.

Previous researchers pointed out that there is a competition in such a system between the branching network induced by

Scheme 2. Schematic Illustrations of the Microscopic Structure Transformation Resulting from Copolymer-Induced Polar Media Percolation Phenomenon in the DDS−Water−Isooctane System and Two Modes of LDH Growth in the Modified System



the long hydrophilic strands and the spontaneous compartmentalization induced by the surfactant.[8] Therefore, the P1940-modified reverse microemulsion system actually provides two types of water pools for LDH growth: the smaller spheroidal ones spontaneously formed by DDS and the larger branching reservoirs that originated from the former ones and are induced by long hydrophilic P1940 chains.

On the basis of this analysis, the mechanism of the reactions taking place in the present study can be schematically illustrated by Scheme 2. The normal DDS−water−isooctane system only provides separated spheroidal microemulsions as microreactors for the nucleation and crystallization of LDHs (Scheme 2A,D). Different microemulsions might temporarily coalesce due to Brownian motion but decoalesce again to keep the whole system in a dynamic equilibrium. Only highly dispersed particles rather than large aggregates can be obtained in such a system, which has been verified by the characterization of sample **LDH-RM**. However, when long-chain hydrophilic molecules are added, part of the microemulsion will aggregate as branching aqueous compartments to cater to the hydrophilic nature of the long chains. A new dynamic equilibrium will occur between the larger compartments and the spontaneously formed spheroidal microemulsion. This process is also known as polar media percolation, and such a process was clearly explained by a study on a similar system.[11]

If P1940 copolymer is added before LDH crystallization, there are sufficient nutrients in the aqueous compartments. Further growth occurs upon heating, and LDH crystals develop from the limited number of nuclei in the branching compartments. These larger "water pools" also act as soft templates to induce an oriented growth of the LDHs in the *ab* plane by a limited nutrient-supply mode both spatially and quantitatively different from the environment in the traditional coprecipitation method. This route results in the growth of **LDH-N** and can be illustrated with model in Scheme 2A−C.

However, if the normal reverse microemulsion system is heated for a fully developed crystallization process before the addition of copolymers, the nutrients in the microemulsion are highly consumed. The P1940-assisted compartments will still occur when the copolymers are added, but further growth of the LDH platelets is unlikely to occur due to the shortage of the nutrient supply. What happens in this environment is more likely a stacking of the preformed LDH platelets into the structure with a preferred orientation along the *c* axis for **LDH-C**. This process is illustrated in Scheme 2 D−F.

It should be noted that the polar media percolation caused by the introduction of long hydrophilic chains into the normal reverse microemulsion system only breaks the original dynamic equilibrium between the coalescence/decoalescence evolution of the spontaneously formed microemulsion and creates new equilibrium between the microemulsion and the P1940-induced larger branching compartments. This means it is unlikely to form a sample containing uniform structures of either **LDH-C** or **LDH-N**, but instead a mixture with **LDH-RM**, though the relative content of different structures can be changed to an extent by shifting the equilibrium with certain adjustments on the temperature and the recipe.

Conclusions

In conclusion, the present study first reports the synthesis of LDHs in a water-in-oil reverse microemulsion system to obtain nanometer sized LDH platelets typically with a 40−50 nm diameter and 10 nm thickness. With a further modification of the reverse microemulsion, LDH structures of different growth orientations can be induced by a soft-template effect. This result

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(11) Erike, H. F.; Quellet, C.; Xu, G. *J. Surf. Sci. Technol.* **1988**, *4*, 2.

shows that the aspect ratio of LDHs can be flexibly adjusted over a wide range, which might endow LDHs with some novel physical and chemical properties for the development of applications.

Experimental Section

Synthesis. Reagents were used as received without further purification. A brief description of the optimized synthetic procedures is as follows: 18.43 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 9.00 g of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 30 mL of deionized water to make solution A. A 6.97 g portion of $NaNO_3$ and 4.8 g of NaOH were dissolved in 30 mL of deionized water to make solution B. All the mixing and reaction processes were carried out with continuous magnetic stirring.

Synthesis of LDH-RM. (LDH-RM refers to an LDH sample synthesized in the DDS−water−isooctane reverse microemulsions.) A 1.44 g portion of sodium dodecyl sulfate and 1.51 g of 1-butanol (as cosurfactant) were dissolved in 100 mL of isooctane. To this mixture was added 1.73 g of solution A dropwise. The whole system became clearly transparent. Then, 1.25 g of solution B was dropped into the reaction mixture and a 4 M NaOH solution (about 0.47 g) was later added into the mixture to adjust the pH value (usually ≥10). This mixture was stirred for ca. 1 h after which time it became slightly cloudy, and the flask was then sealed and heated at 75 °C in an oil bath for 24 h. The solid product obtained at 24 h was collected by filtration.

Synthesis of LDH-N. (LDH-N refers to the LDH sample synthesized with the addition of copolymer at the nucleation stage.) A 1.44 g portion of sodium dodecyl sulfate and 1.51 g of 1-butanol (as cosurfactant) were dissolved in 100 mL of isooctane. To this mixture was added 1.73 g of solution A dropwise. The whole system became clearly transparent. Then, 1.25 g of solution B was dropped into the reaction mixture, and 4 M NaOH solution (about 0.47 g) was later added into the mixture to adjust the pH value (usually ≥10). Then, 1.90 g of the nonionic triblock copolymer surfactant $H(OC_2H_4)_{11}(OC_3H_6)_{16}(OC_2H_4)_{11}$-OH (denoted as P1940 hereafter, $\bar{M} = 1900$) was added. This mixture was stirred for ca. 1 h after which time it became slightly cloudy, and the flask was then sealed and heated at 75 °C in an oil bath for 24 h. The solid product obtained at 24 h was collected by filtration.

Synthesis of LDH-C. (LDH-C refers to the LDH sample synthesized with the addition of copolymer at the crystallization stage.) A 1.44 g portion of sodium dodecyl sulfate and 1.51 g of 1-butanol (as cosurfactant) were dissolved in 100 mL of isooctane. To this mixture was added 1.73 g of solution A dropwise. The whole system became clearly transparent. Then, 1.25 g of solution B was dropped into the reaction mixture, and 4 M NaOH solution (about 0.47 g) was later added into the mixture to adjust the pH value (usually ≥10). This mixture was stirred for ca. 1 h after which time it became slightly cloudy, and the flask was then sealed and heated at 75 °C in an oil bath for 24 h. Then, 1.90 g of P1940 was added, and an additional heating cycle at 75 °C for 72 h was carried out. After heating, the solid product was collected by filtration.

Synthesis of LDH-NO_3 and LDH-DDS. For comparison, pristine nitrate Mg_2Al-LDH was also synthesized using the same recipe through a coprecipitation method. The as-synthesized nitrate LDHs were mixed with NaDDS (1:3 in weight) in water and heated at 75 °C with stirring for 72 h to get DDS-intercalated Mg_2Al-LDH.

Characterization. The products were characterized by X-ray diffraction (Philips X'pert Pro diffractometer with Cu Kα radiation, $\lambda = 1.5406$ Å, 40 kV, 40 mA), electron microscopy (JSM 840F at 25 kV, samples coated with Pt/Pd before test; JEOL 4000EX at 400 kV for TEM imaging and SAED; JEOL 2000FX at 200 kV for EDX analysis. Samples were dispersed in ethanol and loaded onto copper grids supporting Formvar film), and Fourier transform infrared spectroscopy (Bruker Tensor 27 FT-IR, spectra recorded within the range of 500−4000 cm^{-1} with 30 scans at 4 cm^{-1} resolution).

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Supporting Information Available: IR spectra and SEM pictures of different LDH samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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