

# Hybrid Assembly of Layered Double Hydroxide Nanocrystals with Inorganic, Polymeric and Biomaterials from Micro- to Nanometer Scales

Jong Hyeon Lee,<sup>[a]</sup> Hye Jin Nam,<sup>[a]</sup> Seog Woo Rhee,<sup>[b]</sup> and Duk-Young Jung\*<sup>[a]</sup>

**Keywords:** Layered double hydroxide / Hybrid assembly / Inorganic particles / Polymer beads / Ferritin

Monolayer assemblies of zeolite microcrystals, polymer nanobeads and caged proteins were successfully applied to a highly ordered MgAl-LDH monolayer by using the electrostatic attractions between the negatively charged particles and positively charged MgAl-LDH without chemical modifications. Ultrasonication leads to the monolayer assembly of ZSM-5 microcrystals with a maximum preferred contact over the MgAl-LDH monolayer, where the ZSM-5 microcrystals are oriented in the (0k0) crystallographic direction. PMMA and ferritin were also adsorbed on the monolayer LDH nanocrystal surface through self-assembly in solution. Homogeneous PMMA colloids-LDH composite layers on Si were successfully prepared, thanks to the improved interfacial compatibility between the immobilized LDH and polymer surface

charges. Thermal treatment at 150 °C resulted in the formation of continuous polymer coatings over the LDH/Si monolayer. The mixing of colloidal solutions of LDH and PMMA led to the formation of bulk-type polymer-LDH composites after the melting of the polymer phase, where the polymer was homogeneously coated over the LDH crystals without the phase segregation of the LDH nanocrystals. The charged hydroxide layers of the LDH nanocrystals provided the multifunctional interface characteristics required to assemble the functional particles, resulting in the binary hybrid structures of inorganic-inorganic, polymer-inorganic or bio-inorganic composites.

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## Introduction

Layered double hydroxides (LDHs), also known as anionic or hydrotalcite-like clays, are able to intercalate neutral guest molecules or to exchange interlayer inorganic/organic anions. LDHs are layered compounds that consist of positively charged metal hydroxides and interlayer anions along with water molecules to compensate the net positive charge. The compositions of LDHs are expressed by the general formula  $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]A^{n-}_{x/n} \cdot mH_2O$ , wherein  $M^{2+}$  and  $M^{3+}$  can be any divalent and trivalent metal ions, respectively, capable of occupying the octahedral holes of a brucite-like layer and  $A^{n-}$  is virtually any hydrated exchangeable anion positioned in the gallery between the layers.<sup>[1]</sup>

Over the last two decades, interest has been growing in the availability for intercalation of various anions, ranging from halides to polymeric macromolecules having a flexible or rigid molecular framework, into the LDH structures both from the scientific and industrial viewpoints.<sup>[2]</sup> Because of the reactive hydroxide surfaces and positively

charged host layers, LDHs have also received considerable attention as catalysts, separation and stable immobilizers of biomaterials.<sup>[3]</sup> To date, the adsorption of various anions onto the surfaces of LDHs has been strongly governed by either ionic or hydrogen bonding between the incoming guests and LDH hosts.

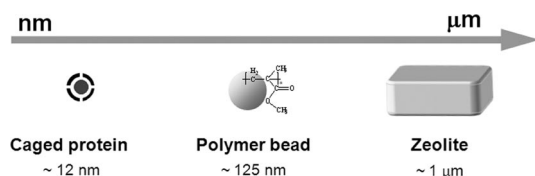
Recently, we reported that electrostatic attraction leads to the effective attachment of the positively charged LDH crystals onto the negatively charged solid substrates in the form of monolayers, which is also accelerated by ultrasound-induced vibration in colloid solutions.<sup>[4]</sup> In this context, Coulombic repulsion prevents the further adsorption of the LDH crystals onto the pre-deposited LDH monolayers. Our research has also been focused on the self-assembly of surface-modified LDH nanocrystals, which can generate the opposite surface charge in comparison with the pristine ones, in layer-by-layer multilayer LDH materials.<sup>[4d]</sup> The use of electrostatic interactions for the self-assembly of LDH nanocrystals enables us to extend their application to various charged particles with sizes ranging from the micro to nanometer scales.

We utilized zeolite microcrystals, polymer nanobeads and caged-proteins as model systems, as described in Scheme 1, to investigate the self-assembly of representative inorganic, polymeric and bio-materials on the charged LDH monolayers, where the electrostatic interaction<sup>[5]</sup> is the major factor and the LDH crystals act as an inorganic immobilizer of these materials. In particular, these selected materials

[a] Department of Chemistry-BK21 and Sungkyunkwan Advanced Institute of Nanotechnology, Institute of Basic Sciences, Sungkyunkwan University, Suwon 440-746, Korea  
Fax: +82-31-290-7076  
E-mail: dyjung@skku.edu

[b] Department of Chemistry, School of Natural Sciences, Kongju National University, Chungnam 314-701, Korea

were able to be produced in uniform sizes and shapes prior to their use in this research, and their monolayers on LDH monolayers can be employed in practical applications such as molecular sieves membranes,<sup>[6]</sup> catalyst supports,<sup>[7]</sup> polymer-inorganic composite films<sup>[8]</sup> and catalytic thin film precursors for the growth of carbon nanotubes.<sup>[9]</sup> The self-assembly of nanostructures with different origins into complex ordered materials is greatly influenced by the size, shape, composition and surface properties of the component phases.<sup>[10]</sup> Among the materials used in this study, the poly-methyl methacrylate (PMMA) nanobeads are the most interesting building blocks for binary hybrid assembly, along with the pallet-shaped LDH nanocrystals, to form a well-organized structure. This LDH-PMMA nanocomposite is based on the heterocoagulation of charged particles, which is ascribed to the improved interfacial stability that depends on the surface potential, shape and size of the desired components. These polymer-LDH nanocomposites with nanoscale homogeneity are evaluated for applications such as mechanical strengtheners, gas permeable membranes, or polymer electrolytes.<sup>[11]</sup>



Scheme 1.

Herein, we describe the particle self-assembly for multifunctional materials to fabricate thin films and bulk-type composite materials as inorganic-inorganic, polymer-inorganic and bio-inorganic hybrid systems. To the best of our knowledge, this is first example in which the LDH monolayers act as 2D inorganic substrates to immobilize functional crystalline materials, such as ZSM-5 microcrystals, PMMA nanobeads and ferritin, in the form of monolayers without chemical modifications.

## Results and Discussion

### Bilayer of ZSM-5/LDH Crystals

The diameter of the carbonate form of LDH crystals,  $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]\text{CO}_3 \cdot n\text{H}_2\text{O}$ , denoted as MgAl-LDH, ranged from 100 nm to 500 nm, and their thickness was about 70 nm determined by scanning electron microscope (SEM), as typically shown in Figure 1 (a). The monolayer assembly of MgAl-LDH crystals on Si (Figure 1, b) was successfully obtained without chemical linkers, and additional ultrasonic treatment in clean solvents for 30 minutes produced no distinguishable changes in the assembly. Consistent with the SEM image, the X-ray diffraction (XRD) pattern of the monolayer of MgAl-LDH crystals showed only the (00 $l$ ) reflections, as shown in Figure 2, indicating their highly ordered orientation along the  $c$  axis.

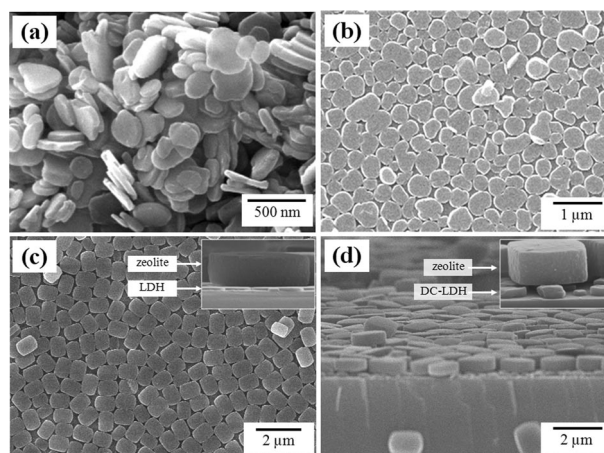


Figure 1. Typical SEM images of the pristine MgAl-LDH powder sample (a), the monolayer assembly of MgAl-LDH crystals on Si prepared in 1-butanol (b), the bilayer assembly of ZSM-5 and MgAl-LDH crystals on Si (c) and the bilayer of ZSM-5 and MgAl-LDH exchanged with 1,10-decanedicarboxylate (d). The insets in (c) and (d) show bilayers of ZSM-5/MgAl-LDH and ZSM-5/DC-LDH on Si, respectively.

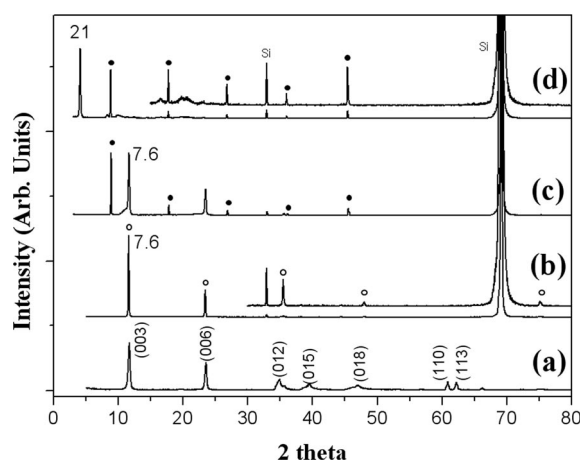


Figure 2. XRD spectra and basal spacings (Å) of the MgAl-LDH powder sample (a) and the monolayer assembly of MgAl-LDH crystals on Si prepared in 1-butanol (b), the bilayer assembly of ZSM-5 and MgAl-LDH crystals on Si (c) and the bilayer of ZSM-5 and MgAl-LDH exchanged with 1,10-decanedicarboxylate (d). The hollow circles correspond to the (00 $l$ ) harmonics of the MgAl-LDH monolayer, and the full circles to the (0 $k$ 0) harmonics of the ZSM-5 monolayer.

The negatively charged ZSM-5 microcrystals adhered on the MgAl-LDH monolayer with a maximum face-to-face contact. Excess aggregates over the monolayer of ZSM-5 were readily removed in 1-butanol. The adsorbed ZSM-5 crystals have a large surface coverage (87%) and a high lateral packing, which is close to the previous results for the adsorption of zeolite on glass using chemical linkers.<sup>[12]</sup> In the present study, the zeolites were assembled on non-flat, discontinuous inorganic particulate layers, implying the strong binding between the ZSM-5 and monolayer LDH crystals. The XRD pattern showed only the (0 $k$ 0) reflections of ZSM-5, meaning that the ZSM-5 microcrystals on

LDH consistently assembled with preferred orientation along their *b*-crystalline axes.<sup>[13]</sup>

The anion-exchange of 1,10-decanedicarboxylate into the LDH crystals was successfully carried out, denoted as DC-LDH, resulting in a dramatic layer expansion perpendicular to the substrate. The enlarged image indicates that the height of the DC-LDH crystals expanded to  $2.7 \pm 0.3$  times that of MgAl-LDH, corresponding to the ratio of the basal spacing values,  $2.7 (\pm 0.1)$ , based on the XRD spectra in Figure 2. The SEM image further shows the sharp edges of DC-MgAl-LDH, indicating that reactions in organic solvents have little influence on the crystallinity of the LDH layers.<sup>[4]</sup> Interestingly, the ZSM-5 microcrystals assembled on the LDH monolayer kept their lateral positions after the anion-exchange reactions of the LDH layer or the thermal treatment at 300 °C, demonstrating the strong binding properties between the ZSM-5 and LDH crystals. We also note that the expansion of the LDH layers spectacularly pushed up the ZSM-5 monolayer through the intercalation of the organic anions, where the DC-MgAl-LDH has identical basal spacings compared to the previous results<sup>[4a,4b]</sup> even though the LDH crystals were compressed by the ZSM-5 monolayer, approximately  $1.70\text{--}1.92 \times 10^{-5}$  Pa per single ZSM-5 microcrystal based on the average size and crystallographic data.

### LDH and PMMA Composites

The attraction between the PMMA nanobeads (zeta potential of  $-50$  mV at pH 6.7) and the LDH crystals ( $+98$  mV, at pH 9.3) drives the direct incorporation of the monodisperse PMMA beads into the monolayer LDH on Si, as shown in the SEM image of Figure 3. When the adsorbed PMMA nanobeads were melted at 150 °C, conformal polymer films were formed over all the faces and edges of the LDH monolayers.

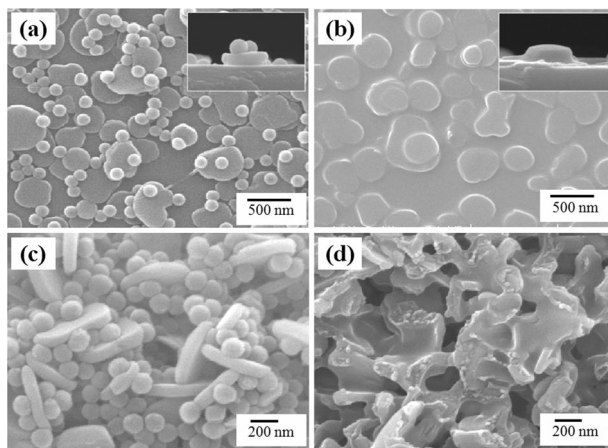


Figure 3. Typical SEM images for the PMMA beads adsorbed on the monolayer of MgAl-LDH/Si at 60 °C (a) and after thermal treatment at 150 °C (b). (c) shows the composites of MgAl-LDH and PMMA beads prepared by ultrasonication in deionized water and after thermal treatment at 150 °C (d). The insets in (a,b) show the cross-sectional views of the as-prepared film samples.

We extended the two-dimensional binary assembly of PMMA and LDH on Si to bulk powder samples of the polymer-LDH nanocomposites, since the PMMA nanobeads cause the LDHs to assemble into well-organized polymer-LDH composites. Generally, the simple mixing of clay materials into a polymer matrix leads to the inevitable phase segregation of the inorganic parts, owing to the immiscibility of the two phases,<sup>[14]</sup> as illustrated in Figure 4. In the direct intercalation<sup>[15]</sup> of high molecular weight macromolecules or the in-situ polymerization<sup>[16]</sup> of an intercalated monomer, the polymer guests are filled in the interlayer space or the LDH layers are partially exfoliated.<sup>[17]</sup> However, the synthesis of fully dispersed LDH-polymer nanocomposites is difficult to achieve, owing to the high charge density of the layers<sup>[1,2]</sup> and strong interparticle interaction.<sup>[18]</sup> Recently, an exfoliated polystyrene (PS)-clay nanocomposite was prepared using ion-exchange, where the modified PS nanobeads were electrostatically incorporated into Na-clay.<sup>[19]</sup> However, the PS nanobeads were sparsely adsorbed onto the clay platelets, which may cause uncovered regions to remain after the thermal treatment.

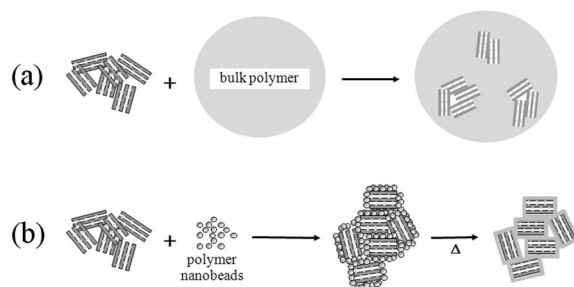


Figure 4. Schematic illustrations of the polymer-LDH composites prepared by the conventional mixing of the bulk polymer solution and LDH particles (a), and by the hybrid assembly of the polymer nanobeads and LDH particles.

In order to realize the benefits of the polymer-LDH nanocomposites to increase the compatibility between the polymer matrix and LDHs, we suggested the hybrid assembly of PMMA nanobeads and pallet-shaped LDH nanocrystals to develop homogeneous nanocomposites. The negatively charged PMMA nanobeads were effectively embedded on the positively charged LDH surfaces, which is practically impossible in polymer solutions, owing to the strong interparticle attraction of LDHs with house of cards forms.<sup>[17]</sup> In the present case, the PMMA nanobeads were adsorbed on the LDH surfaces in the form of a monolayer, which remained after solvent drying. The PMMA nanobeads, once adsorbed onto the LDH surface, were confined between the LDH particles, thereby preventing them from coagulating.

A continuous and thin polymer coating was successfully achieved on the outer surface of the LDH particles through the assembly of the PMMA nanobeads and LDH nanocrystals. The XRD spectra in Figure 5 confirmed that the pristine LDH structure remained even after the thermal treatment, implying that the polymer is not involved in the



intercalation into the interlayer of LDH. This result may be the first example of homogeneous polymer coatings onto individual LDH particles through the hybrid assembly of charged polymer nanobeads. Our synthetic protocol does not include chemical modifications for the purpose of making a stable interface of LDH materials. We believe that the use of charged polymer nanobeads will enable the mass production of polymer-layered silicates or layered hydroxides nanocomposites for the purpose of improving the properties of the polymer and developing multifunctional materials.

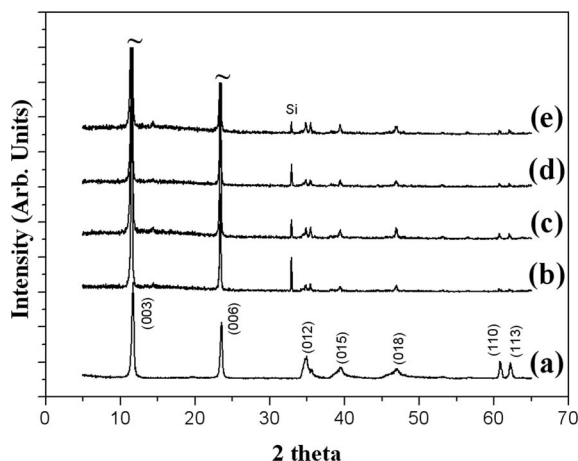


Figure 5. XRD spectra of the pristine MgAl-LDH powder sample (a), the composites of MgAl-LDH crystals and PMMA beads (b), and after thermal treatment at 105 °C (c), 130 °C (d) and 150 °C (e). The XRD spectra of (b – e) were obtained from the composites on Si substrates.

### Ferritin Assembly on LDH Surface

The electrostatic interaction enables the assembly of charged biomolecules such as horse spleen ferritin in solution. Ferritin consists of a spherical protein shell (apoferritin) consisting of 24 subunits with a diameter of 12 nm, and a central ferric oxyhydroxide crystal with a diameter of 7–8 nm.<sup>[20]</sup> The immobilization of the ferritin onto the surface of the LDH crystals, which are originally very smooth as shown in Figure 6, was attempted in a manner similar to that carried out for the PMMA beads. The immersion of the monolayer LDH film in the colloidal ferritin solution resulted in the immobilization of the negatively charged ferritin (zeta potential of –32 mV at pH 7.0)<sup>[21]</sup> on the LDH crystals. In contrast to the case of the PMMA beads, the ferritins were adsorbed over the whole surface of the LDH crystals, presumably due to their smaller size. Based on this observation, we infer that the atomic force microscopy (AFM) images show a single layer of ferritin with an average height of around 7 nm. The smaller height of the ferritin monolayer than their actual size definitely comes from electrostatic attraction and hydrogen bonding. The SEM images further reveal the rare adsorption of ferritin on the bare silicon surface. This experimental strategy sug-

gests that the active hydroxide surface of the LDH crystal can be used as an adhesive substrate for immobilizing ferritin and other similar biomaterials.

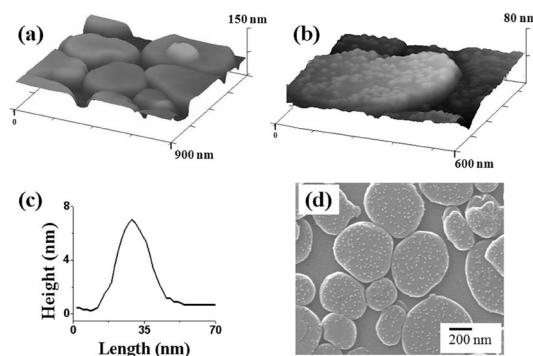


Figure 6. AFM data of the monolayer assembly of MgAl-LDH on Si (a), the ferritin adsorbed onto the MgAl-LDH monolayer (b), the height profile of selected ferritin/LDH/Si samples (c), and the typical SEM image of the ferritin/LDH/Si samples (d).

### Conclusions

We demonstrated a novel method of assembling electrostatically charged particles on a monolayer of LDH nanocrystals that act as a stable inorganic particulate interface, due to their plate-like particle shape and surface charges. In the case of the zeolite/LDH bilayer system, the zeolite microcrystals were tightly attached onto the LDH monolayer, where the zeolite monolayer has a preferred orientation. Most significantly, this assembly strategy provided the necessary compatibility between the hydrophobic polymers and hydrophilic LDHs, resulting in the formation of homogeneous PMMA-LDH nanocomposites with a structure consisting of PMMA nanobeads uniformly embedded into the LDH nanocrystals, thanks to their nanometer-sizes and charged surfaces. We anticipate that conformal polymer films induced by thermal treatment can act as active membranes in controlling the release properties of the interlayer anions. The present technique is of great interest in the development of well-defined polymer-LDH nanocomposites possessing the specific requirements for a given application, combined with the advantage of LDHs, such as a large variety of compositions, tunable layer charge density and high compatibility with biomaterials.

### Experimental Section

**Materials:** The carbonate form of MgAl-LDH was prepared by the coprecipitation method.<sup>[1]</sup> The resulting precipitate was collected by centrifugation and washed with deionized water three times. Hydrothermal treatment was carried out in deionized water at 180 °C to increase the crystal size and improve the crystallinity of the MgAl-LDH crystals, followed by drying at 120 °C in a convection oven.<sup>[22]</sup> ZSM-5 crystals with an average size of 1.6 μm × 1.2 μm × 0.6 μm were synthesized according to the literature procedure.<sup>[23]</sup> The ZSM-5 micro-crystals were thoroughly washed with copious amounts of water and dried at 120 °C for 3

hours prior to use. PMMA beads with an average diameter of 125 nm were prepared by modified-emulgator free-emulsion polymerization according to the literature method.<sup>[24]</sup> Solvents and remaining monomer were separated by evaporating them at 90 °C under a flow of air. To eliminate any ionic impurities, the beads were separated by centrifugation and redispersed in deionized water prior to use. Horse spleen ferritin purchased from Sigma was purified by size exclusion chromatography to remove free iron ions using a Sephadex G-25 column.<sup>[25]</sup>

**Particle Self-Assembly:** In order to immobilize the MgAl-LDH nanocrystals as a monolayer, the cleaned Si substrates were dipped in a colloidal suspension of MgAl-LDH in 1-butanol and treated by ultrasound for 2 minutes. The MgAl-LDH-coated substrates were placed in the solvents without MgAl-LDH, followed by sonication for 1 minute to rinse them off and then dried at 70 °C in air. The immobilization of the ZSM-5 microcrystals on the monolayer MgAl-LDH film was accomplished by the application of ultrasound for 5 minutes in a 1-butanol/toluene (2%, v/v) mixture, followed by shaking the substrate in 1-butanol to remove excess ZSM-5 crystals from the substrate, and then drying at 70 °C in air. The anion-exchange reaction of the underlying MgAl-LDH monolayer with 1,10-decanedicarboxylic acid was performed by solvothermal treatment in a 1-propanol/toluene (5%, v/v) mixture at 120 °C for 24 hours, and the product was denoted as DC-MgAl-LDH. The incorporation of PMMA beads into the dispersed MgAl-LDH was performed by ultrasonic treatment in a colloidal suspension of MgAl-LDH (10 mg in 10 mL of deionized water) and PMMA beads (10 wt.-%). The adsorption of PMMA beads on the monolayer MgAl-LDH film was carried out by dipping the substrate in 10 wt% of the PMMA colloidal solution at 60 °C for 3 hrs, followed by washing with water and drying with a nitrogen flow. To obtain the ferritin monolayer on the LDH monolayer, the LDH-coated substrate was immersed in a ferritin solution (1 mg/mL) for 3 hours at room temperature, then washed with water and dried with a nitrogen flow.

**Characterization:** The XRD patterns were measured with a Rigaku X-ray diffractometer, D/MAX-2000 Ultima, in  $\theta$ - $2\theta$  scanning mode. The measurements were performed at 40 kV and 30 mA using Cu- $K_\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). All of the XRD spectra were calibrated using the Si (200) peak from the substrates ( $2\theta = 32.9^\circ$ ,  $d = 2.74 \text{ \AA}$ ). The SEM measurements were made using a Philips XL-30-ESEM-FEG instrument operating at 15 kV. Before imaging, the samples on carbon were coated by sputtering with Pt to a thickness of about 3 nm. The AFM images were obtained in air using a Nanoscope IV multimode instrument (Digital Instruments Co.); the images were obtained in tapping mode using a 10 nm Mikro-Masch silicon cantilever tip and "E" scanner with a scan limit of 10  $\mu\text{m}$ . The particle size measurements in colloidal suspensions were performed with a Malvern Instruments laser-beam particle size analyzer, model 1000HSA. The zeta potentials were measured using a DT-300 instrument, Dispersion Technology, Inc., at 25 °C.

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