# Hollow nanoshell of layered double hydroxide†

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**Hollow nanoshells of layered double hydroxide (LDH) have been fabricated using exfoliated LDH nanosheets as a shell building block and polystyrene beads as a sacrificial template.**

Layered double hydroxides (LDHs), consisting of stacked brucite-type octahedral layers with anions and water molecules occupying the interlayer space, are currently attracting intense research interest due to their potential applications in catalysis, drug storage/release, selective separation, chromatography and chemical or biosensors.[1–3] It is generally recognized that their performance is highly dependent on their morphologies. However, little attention has been paid to the control over the shape, particle size, surface area and pore architecture of LDH materials. To date, only a few works have addressed this topic.[4]

Hollow nanoshells have emerged as an intriguing nanostructure for a range of applications in recent years.[5] Among them, inorganic hollow spheres with well-defined architecture are particularly interesting because of their low density, high surface area, stability, and surface permeability.[6] One of the general approaches adopts a sacrificial template, on which shell materials are deposited layer-by-layer through a self-assembly technique.[5] We have demonstrated that unilamellar exfoliated nanosheets of $Ti_{1-\delta}O_2$ and $MnO_2$ are very useful as shell building materials.[7] They are flexible enough to replicate a spherical core and their lateral dimension of submicrometer scale helps to confer high mechanical strength to the shell. In addition, the layer-by-layer deposition procedure allows the control of the shell thickness in a step of 1 nm.

The delamination of LDHs has attracted considerable attention in the past years. The previously reported procedures involve the intercalation of fatty acids or amino acids followed by the treatment with organic solvents.[8–10] Recently we have succeeded in total delamination of LDH crystals in nitrate form upon treatment with formamide.[11,12] The resulting nanosheets are much better-defined in terms of crystallinity and lateral size in comparison with those from conventional LDH precursors in gel-like form. The LDH nanosheets in high quality should be suitable as shell building blocks.

The synthesis of the nanoshells with LDH nanosheets involves an additional challenge thanks to a peculiar property of LDH materials, that is, the layer memory effect. The LDH structure collapses upon heat treatment above 500 °C to yield mixed oxides of constituent elements, which undergo restoration of the LDH structure in the presence of water and anions.[13] This so-called memory effect property of LDHs has been employed as an effective synthetic route for inserting various inorganic and organic anions into LDHs.[14,15] We can expect that hollow LDH nanoshells will be formed through reconstruction of thermally decomposed core–shell composites. LDHs having such a unique morphology should be useful in a variety of applications such as drug delivery.

In this paper, we report the synthesis and characterization of LDH hollow shells through layer-by-layer assembly of the nanosheets and reconstruction of LDH structure.

Mg–Al LDH powder (mole ratio Mg : Al = 3 : 1) in carbonate form was obtained from Kyowa Chemical Industry Co., Ltd. Mg–Al LDH was anion-exchanged to a nitrate form in a typical salt-acid treatment and subsequently delaminated in formamide.[11,12] Polystyrene beads (PS, $\Phi$ = 1.3 μm) were purchased from Fluka and poly(sodium 4-styrene sulfonate) (PSS, $M_w \approx 70000$) was purchased from Aldrich. A typical synthetic procedure of hollow nanoshells is as follows. PS beads (0.5 g) were dispersed in 100 cm$^3$ of the formamide suspension containing 0.05 g of LDH nanosheets and then ultrasonically agitated for 20 min to promote the adsorption of LDH nanosheets onto the PS surface. The sample was recovered by centrifugation (6000 rpm, 30 min) and washed with ultrapure water. In the next step, the sample was redispersed in an aqueous solution of PSS (100 cm$^3$, 2 g dm$^{-3}$, pH = 4.5). The product was recovered by centrifugation. Core–shell composites coated with multilayer shells of $(PSS/LDH)_{20}$ were synthesized by repeating the above procedures 20 times. The obtained sample was heated to 480 °C at a ramp rate of 20 °C h$^{-1}$ and kept at this temperature for 4 h to remove the PS core and PSS. Finally the calcined material was exposed to humid air (relative humidity of 95%) to recover the LDH structure.

Fig. 1 depicts X-ray diffraction (XRD) data for the sample at various stages of the fabrication of hollow LDH nanoshells. A characteristic halo from the PS core that occurred in an angular range of 10–30° was largely suppressed upon coating with 20 layer pairs of LDH nanosheets/PSS. The two major peaks at a $2\theta$ value of 4.4 and 10.0°, indicated by arrows, can be ascribed to a repeating nanostructure of LDH/PSS with a periodicity of *ca.* 2.0 nm.[16] A similar value has been obtained for multilayer LDH/PSS films on a flat substrate.[11,12] Two additional peaks at 34.8 and 60.5° are assignable to intrasheet reflections of 10 and 11 bands from a two-dimensional hexagonal cell ($a$ = 0.31 nm), confirming that the LDH nanosheet architecture remained intact in the process.

Fig. 2(a) shows a scanning electron microscopy (SEM) image of the obtained core–shell composite. The homogeneous curvature of the spherical PS beads was preserved after the deposition of the

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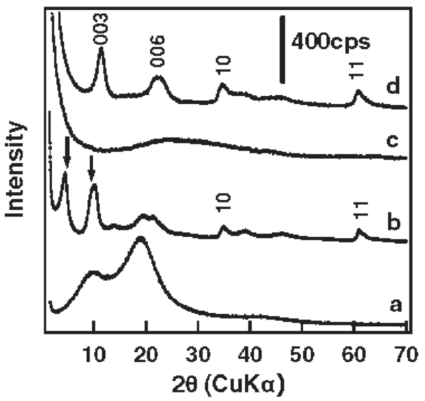

**Fig. 1** XRD patterns of PS core (a); after deposition of 20 LDH/PSS layer pairs (b); after calcination at 480 °C for 4 h (c); and after treatment in air of 95% humidity (d). Arrows indicate basal reflections giving *d* spacing of ~2.0 nm.

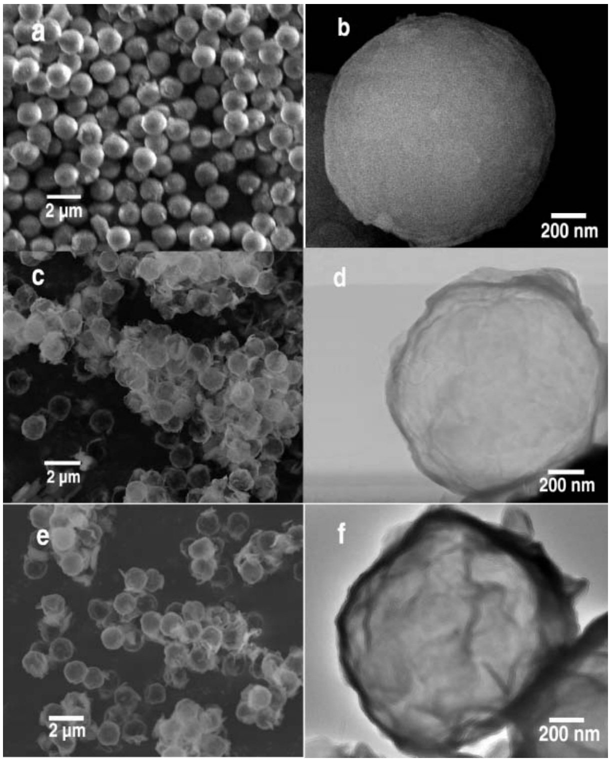

**Fig. 2** Low (a) and high (b) magnification SEM images of core–shell composites coated with 20 bilayers of LDH/PSS; SEM (c) and TEM (d) images of oxide shells after calcination; SEM (e) and TEM (f) images of LDH hollow shells after treatment in air of 95% humidity.

LDH/PSS shell. The only noticeable difference for the spheres with or without shells was the surface roughness. The LDH nanosheets were scarcely perceived even in a high-magnification image (Fig. 2(b)).

When calcined to 480 °C, the core–shell sample lost 91% of its weight in two steps (Fig. 3). These weight losses were accompanied by huge exotherms, suggesting the combustion of the template PS core and PSS layer. A slow heating rate of <1 °C min$^{-1}$ was essential to retain the shell structure. Rapid heating of the sample could disrupt hollow shells due to violent gas evolution of water and carbon dioxide.

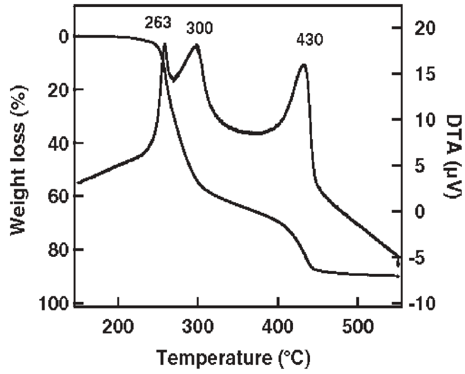

**Fig. 3** TG-DTA diagram of core–shell composite.

The calcination destroyed the original LDH structure. The XRD pattern (Fig. 1(c)) did not have any peak, suggesting the transformation to amorphous metal oxides such as MgO and $Al_2O_3$. The spherical morphology was preserved except for a small amount of broken shells as shown in the SEM image (Fig. 2(c)). The transmission electron microscopy (TEM) image (Fig. 2(d)) clearly displayed the hollow and homogeneous nature. The diameter of the spheres was comparable to that of the core–shell composite.

When the amorphous shells of metal oxides were exposed to humid air for 12 h, the sample turned crystalline again (Fig. 1(d)). The two major peaks that emerged at 2$\theta$ value of 11.3 and 23.1° can be ascribed to a basal diffraction series giving an interplanar spacing of 0.78 nm. The additional two peaks at 35.4 and 60.5° can be identified as two-dimensional diffraction bands of 10 and 11 for a hexagonal cell with $a$ = 0.31 nm. The XRD data strongly suggest the reconstruction of the LDH structure due to the layer memory effect and the basal spacing of 0.78 nm is characteristic of LDHs in carbonate form.

FT-IR data shown in Fig. 4 support the chemical and structural modifications of the sample described above. The as-prepared core–shell composite showed sharp absorption bands attributable to PS and PSS. Assignments for some of strong bands are given in ESI.† In addition to these peaks, there were strong absorption bands at 3700–3000 and at 1620 cm$^{-1}$, which are attributable to

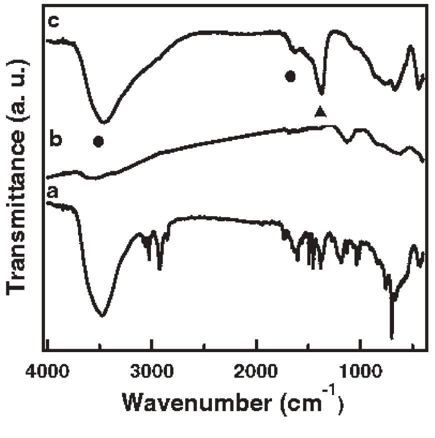

**Fig. 4** FT-IR spectra of as-prepared core–shell composites (a), after calcination at 480 °C for 4 h (b), after reconstruction in air with humidity of 95% for 12 h (c).

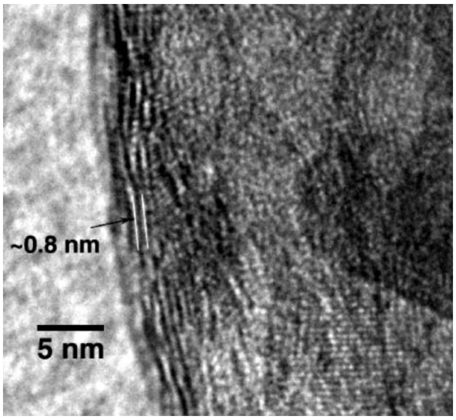

**Fig. 5** HRTEM image of the wall of LDH hollow shell.

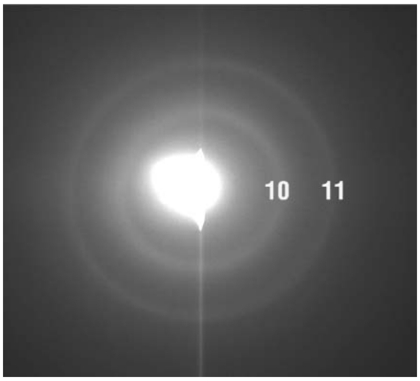

**Fig. 6** Selected area electron diffraction pattern of LDH hollow shell.

the stretching and bending vibrations of water molecules. This suggests that the LDH/PSS shell was hydrated. On the other hand, the spectrum of the calcined sample was rather featureless as a consequence of the removal of organic components and the collapse of LDH layers. Upon exposure to humid air, absorption bands indicating the reconstruction of the LDH structure clearly appeared again as labeled by circles. Furthermore, a strong peak at 1368 $cm^{-1}$ (indicated by a triangle) evolved. This band can be ascribed to a vibration mode of carbonate ions, again indicating the formation of LDH in carbonate form.

After the shell structure changed from the amorphous metal oxides to the LDH structure, the spherical and hollow morphology was obvious (Fig. 2(e) and (f)). Compared with the sample before reconstruction, the shell thickness became somewhat larger and the surface became rougher. The high-resolution TEM (HRTEM) image showed a lamellar structure with a repeating fringe of ~0.8 nm (Fig. 5), being consistent with XRD results. The selected area electron diffraction measurement detected two faint rings for the 10 and 11 intra-layer periodicity of LDH (Fig. 6). All these data are compatible with the formation of the carbonate LDH shells.

The average diameter and thickness of the obtained hollow shells were 1.4 μm and 20 nm, respectively, indicating a high proportion of inside voids of 91.5%. The thickness is close to the value of 16 nm expected for 20 stacked LDH layers (= 0.78 × 20). This new morphology for anionic clays may be taken as a counterpart of silica vesicles or hollow aluminosilicates, which have been investigated extensively.[17] Most recently, Géraud *et al.* have reported an interesting morphology of 'inverse opals' for LDH material.[4a] The obtained macroporous structure has some similarity to the material in the present study ; it may be taken as an ordered arrangement of the hollow nanoshell. Furthermore, its synthetic procedure is also similar in that it is involved by the templating with PS and reconstruction of LDH structure.

In conclusion, LDH hollow nanoshells have been fabricated through a synthetic route involving layer-by-layer assembly of LDH nanosheets, thermal decomposition of organic moieties and reconstruction of LDH structure. Various characterizations clearly indicated the formation of hollow LDH nanoshells.

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## Notes and references

1 B. Sels, D. De Vos, M. Buntinx, F. Pierard, A. K. Mesmaeker and P. Jacobs, *Nature*, 1999, **400**, 855.
2 J.-H. Choy, J.-M. Oh, M. Park, K.-M. Sohn and J.-W. Kim, *Adv. Mater.*, 2004, **16**, 1181.
3 M. Darder, M. López-Blanco, P. Aranda, F. Leroux and E. Ruiz-Hitzky, *Chem. Mater.*, 2005, **17**, 1969.
4 (*a*) E. Géraud, V. Prévot, J. Ghanbaja and F. Leroux, *Chem. Mater.*, 2006, **18**, 238; (*b*) G. Hu and D. O'Hare, *J. Am. Chem. Soc.*, 2005, **127**, 17808; (*c*) Z. P. Xu, G. S. Stevenson, C.-Q. Lu, G. Q. M. Lu, P. F. Bartlett and P. P. Gray, *J. Am. Chem. Soc.*, 2006, **128**, 36.
5 F. Caruso, *Adv. Mater.*, 2001, **13**, 11.
6 (*a*) H. Huang, E. E. Remsen, T. Kowalewski and K. L. Wooley, *J. Am. Chem. Soc.*, 1999, **121**, 3805; (*b*) P. Jiang, J. F. Bertone and V. L. Colvin, *Science*, 2001, **291**, 453.
7 (*a*) L. Z. Wang, T. Sasaki, Y. Ebina, K. Kurashima and M. Watanabe, *Chem. Mater.*, 2002, **14**, 4827; (*b*) L. Z. Wang, Y. Ebina, K. Takada and T. Sasaki, *Chem. Commun.*, 2004, 1074.
8 M. Adachi-Pagano, C. Forano and J. P. Besse, *Chem. Commun.*, 2000, 91.
9 T. Hibino and W. Jones, *J. Mater. Chem.*, 2001, **11**, 1321.
10 T. Hibino, *Chem. Mater.*, 2004, **16**, 5482.
11 L. Li, R. Ma, Y. Ebina, N. Iyi and T. Sasaki, *Chem. Mater.*, 2005, **17**, 4386.
12 Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2006, **128**, 4872.
13 S. Miyata, *Clays Clay Miner.*, 1980, **28**, 50.
14 T. Hibino and A. Tsunashima, *Chem. Mater.*, 1998, **10**, 4055.
15 M. del Arco, D. Carriazo, S. Gutiérrez, C. Martín and V. Rives, *Inorg. Chem.*, 2004, **43**, 375.
16 The second-order basal peak was not located in a perfect position expected from the first peak at 4.4° in $2\theta$. This may be due to the interference of the halo from the PS core or some mixed-layer effects. Note that the second peak showed a broad profile.
17 S. S. Kim, W. Z. Zhang and T. J. Pinnavaia, *Science*, 1998, **282**, 1302.