One-step synthesis and AFM imaging of hydrophobic LDH monolayers†

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Hydrophobic layered double hydroxide particles with a single layer structure have been successfully synthesised in a reverse microemulsion system; atomic force microscopy has proven a powerful tool for the study of these delicate nanoparticles.

Layered double hydroxides (LDHs) are a family of anionic clays consisting of stacks of positively charged mixed metal hydroxide layers that require the presence of interlayer anions to maintain overall charge neutrality. Due to the unique structural properties of these materials they have been widely studied as host materials in intercalation and de-intercalation reactions.[1]

Structurally analogous layered smectite clays such as montmorillonite have already been widely used as additives to produce some commercial clay–polymer nanocomposites; these materials exhibit improved modulus, tensile strength and thermal stability over the base unmodified polymer.[2a–d] However, these layered clay minerals consist of negatively charged layers and charge-balancing interlayer cations. LDHs are predicted to offer significant benefits and advantages as the inorganic additive in synthesis of inorganic–polymer nanocomposites compared to the existing clay mineral based materials in that the chemical composition can be precisely controlled. For example, colourless, diamagnetic, insulating LDHs can be routinely prepared which should result in transparent polymer composites for electronic applications.[2e,f]

For successful nanocomposite development, it is a pivotal prerequisite to get a stable uniform dispersion of the inorganic phase within the polymer matrix. One approach that can yield miscible clay–polymer dispersions is the direct intercalation of macromolecules between the lamellar structure of the inorganic host. However, a more effective, but more difficult, approach would be the exfoliation of the layers into individual platelets. In this case, inorganic layers with very high aspect ratio become thoroughly separated and dispersed in the polymer.[3] Nanocomposites synthesised in this form will show superior properties. However, exfoliation is very difficult to achieve for LDHs due to the high intralayer charge density, which has severely retarded the successful exploitation of LDH–polymeric nanocomposites.

There are relatively few reports on the exfoliation of LDHs; Forano *et al.* and Hibino *et al.* both used a two-step method to exfoliate pre-synthesised LDHs by intercalation and refluxing.[4a,b] Our group previously reported the delamination of up to 10 wt% $Mg_2Al(OH)_6(C_{12}H_{25}SO_4)$ in a polar acrylate monomers under high shearing forces.[4c] Very recently, Sasaki *et al.* and Norby *et al.* both developed a method to directly delaminate nitrate MgAl-LDH in formamide.[4d,e]‡ Although these results are very promising, it would be more efficient and more widely applicable if stable uniform dispersions of uniform highly exfoliated LDH layers could be synthesised directly and used as additives for the preparation of nanocomposites.

In this paper, we report a facile one-step synthesis of LDH monolayers in a reverse microemulsion. Similar systems have proven to be very effective for the synthesis of unique structures which cannot be obtained by traditional methods.[5] It is worth noting that some unique LDH superstructures have been synthesised in a co-polymer assisted water-in-oil system.[5e] In the present study, the traditional aqueous co-precipitation system ($Mg(NO_3)_2{\cdot}6H_2O + Al(NO_3)_3{\cdot}9H_2O$ at pH $\geqslant$ 10) is introduced into an oil phase of isooctane with sodium dodecyl sulfate as surfactant and 1-butanol as co-surfactant to produce LDH nanoparticles with monolayer structures. The full experimental details may be found in the ESI.†

The aqueous phase which contains the nutrients for the growth of LDH crystals will be dispersed in the oil phase to form droplets surrounded by dodecyl sulfate groups (DDS). These droplets act as nano-reactors which only provide limited space and nutrients for the growth of LDH platelets. The size of the particles can thus be effectively controlled both in diameter and thickness. This system also allows the negatively charged DDS chains to interact with the LDH platelets as charge-balancing anions. A schematic representation of the process is shown in Scheme 1.

To explore the structure of the LDH platelets synthesised in the reverse micelle system, the suspension after reaction was centrifuged to recover a gel-like phase. Elemental analysis shows the dried sample can be formulated as $Mg_2Al(OH)_6(C_{12}H_{25}SO_4){\cdot}nH_2O$. No nitrogen (in the form of NO_3^- as charge-balancing anions) can be detected.§

The XRD patterns of this gel-like material are shown in Fig. 1. Pattern (b) was recorded immediately after centrifugation and two broad reflections are observed at *ca.* $2\theta = 7.5°$ and 20° respectively while all the strong basal plane Bragg reflections, characteristic features for LDHs, are missing. This feature suggests a lack of an organised layered structure in this sample. When the sample was dried in air, remarkable changes appeared (Fig. 1(c) and (d)). The broad reflection at about 7.5° split and another weak reflection grew in intensity at $2\theta = 18°$. Moreover, other reflections at higher angles also grew in intensity.

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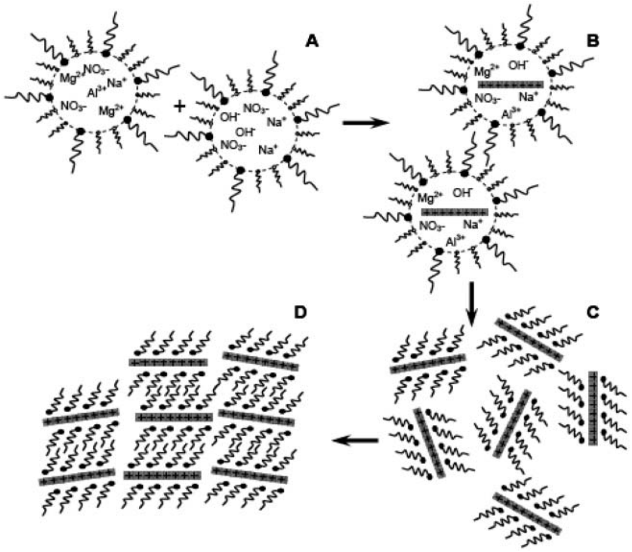
† Electronic supplementary information (ESI) available: Experimental details, TEM, SEM, XRD patterns and models of different DDS-modified LDH structures. See DOI: 10.1039/b514368c



Scheme 1 Schematic representation of the nucleation and growth of LDH platelets.

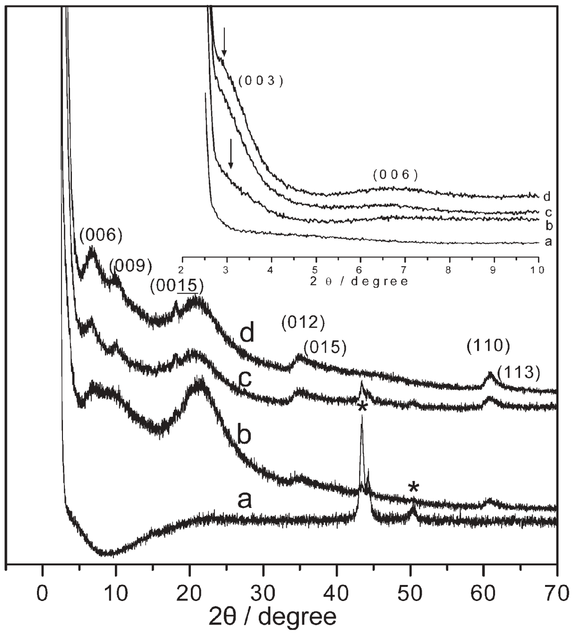


Fig. 1 Powder XRD patterns of (a) empty sample holder; (b) the gel-like product separated by centrifuge; (c) the same product after drying for 30 min; (d) 180 min drying. The 2.5°–10° region is highlighted as inset.

In addition, when compared with the pattern recorded from the empty sample holder (Fig. 1(a)), a weak and broad reflection can be discerned at about $2\theta = 3°$ (indicated by an arrow) for the as-synthesised sample in the inset figure. The patterns also show a gradual growth of a $2\theta = 3°$ Bragg reflection which indicates that the sample gains some structural order upon drying. This process corresponds to the transfer from stage (C) to (D) as shown in Scheme 1. Further drying failed to get clearly resolved reflections at this position but only a shoulder from the background, which reveals the long-range disorder of the corresponding lattice.

All these Bragg reflections can be indexed using a rhombohedral symmetry unit cell with $a = b = 2d_{110} = 3.04$ Å and $c = 3d_{003} = 77.88$ Å (Fig. 1S†). The Bragg reflections indexed on this cell agree with the unit cell dimensions of the intercalated Mg_2Al-LDH samples obtained by ion-exchange method from the pristine nitrate form.[6] This result further indicates that DDS instead of nitrate anions exists as the charge-balancing species in the product.

In previous reports on the exfoliation of LDH layers, the loss of basal plane Bragg reflections provides strong evidence for structural disassembly.[4] It can thus be reasonably concluded in the present study that the absence of well-resolved basal plane reflections, especially the first order 003 Bragg reflection of the as-synthesised sample indicates that highly exfoliated LDH layers formed in the reverse microemulsion system.

Because of its high spatial and vertical resolution, AFM has been previously applied to determine the morphology of nano-sized objects. AFM has also proven very powerful in the study of smectite clay chemistry to determine the size distribution, the morphology of individual sheets, the structure of clay–polymers and even to track the crystallisation process.[7,8] To the best of our knowledge this technique has not been applied to the analysis of LDH monolayers.

Fig. 2(a) shows a typical AFM topology of a HOPG surface with LDH deposits synthesised by the reverse microemulsion method. Isolated oval objects, shown in cross section in Fig. 2(b), can be discerned on the substrate. It is evident that all these particles have a uniform height distribution around 1.5 nm and a diameter distribution centred around 40 nm. This profile corresponds to a flat-lying mode of the LDH platelets on the

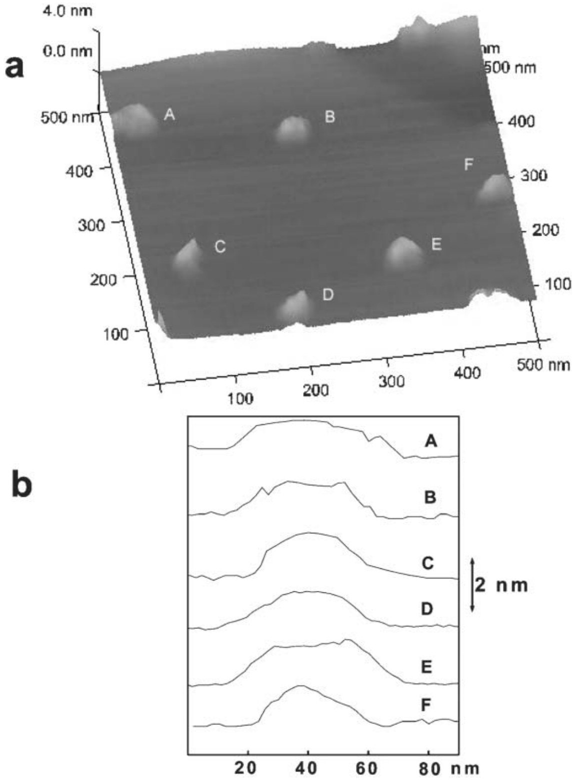


Fig. 2 (a) An AFM image of the particles synthesised by reverse microemulsion method deposited on HOPG surface; (b) a cross-sectional analysis of the labeled particles in (a) showing the dimensional profiles.

HOPG and provides sufficient information to determine the structure in each domain.

Crystallographic studies have already shown that the thickness of a Mg_2Al-LDH monolayer is 0.47 nm.[1a,6a,b,d] Thus the 1.5 nm-thick platelets shown in Fig. 2 can consist of up to 3 monolayers without considering the interlayer spacing expanded by the charge-balancing DDS anions. However, the elemental analysis result indicates that DDS groups are covering the platelets as charge-balancing species, one DDS-modified LDH monolayer should be thicker than 0.47 nm under AFM observation.

According to previous reports on DDS and dodecyl benzyl sulfonate (DBS) intercalated LDHs and other related systems, different arrangements of the interlayer anions have been proposed.[6b,c,9] The bi-layer model proposed by Lagaly implies that the hydrophobic dodecyl chains would align very closely with the hydrophilic LDH layers at an angle of *ca.* 20°,[9a,b] this observation has been questioned by Takagi *et al.* in a study on stearate intercalated LDHs.[9c] They proposed that an interpenetrating anti-parallel arrangement to form a pseudo monolayer DDS structure between two adjacent LDH layers with the angle of DDS chains from the LDH layer increased to about 69° (Fig. 3S) should be more stable.[9d]†

Despite these disputes, it has been recognised that DDS intercalated LDHs have a *ca.* 2.6 nm basal spacing.[4c,6b,c,9d] If the as-synthesised LDH particles consist of only two LDH layers, the height of the particles shown in Fig. 2(b) would be no less than 2.6 nm. It can thus be reasonably concluded that the LDH layers formed in the reverse microemulsion have a monolayer structure with a rigid layer of mixed metal hydroxides at the core (Fig. 3S).† The charge-balancing DDS groups form a flexible shell around the layer which makes the particle thicker than the 0.47 nm layer at the core under AFM observation, which explains the profiles of the oval spots shown in Fig. 2.

Attempts to image this material by TEM and SEM gave images of agglomerates instead of separate nanoparticles due to the severe aggregation of the particles upon drying.† The samples are very electron-beam sensitive due in part to their delicate structural nature and in part to a very rapid amorphisation process under electron beam irradiation.

Naguib and Kelly suggested that amorphisation of ceramics should occur for structures with Pauling ionicities $\leqslant$ 0.47, while Wang *et al.* have reported the process to occur in materials with ionicities of up to 0.68.[10a,b] The ionicity (I) of a structure is defined as $I = 1 - \exp[-0.25(X_A - X_B)^2]$, where X_A and X_B are the electronegativities of atoms A and B forming a bond.[10c] The average bond ionicity of LDH materials with a structure $[Mg_2Al(OH)_6]^-$ is 0.45, and this value put them in the range of materials that should be susceptible to radiation-induced amorphisation, which has actually been proven by our attempts to image the materials with HRTEM. HRTEM imaging of such materials would require delicately designed working conditions as well as sample preparation techniques.[10d] The relevant work is in progress.

Further experiments show that these LDH layers can easily form stable dispersions in acrylate monomers.† This result reveals good compatibility of the LDH particles with the organics and guarantees the development of homogeneous LDH–polymer nanocomposites with good performance.

In conclusion, a reverse microemulsion method has been used to synthesise LDH monolayers in a facile one-step reaction. The DDS surfactant combines with the layers to act as charge-balancing anions and make the layers hydrophobic. This method can deliver bulk quantities of uniform sized LDH monolayers. They currently show promise as additives for the development of high performance LDH–polymer nanocomposites.

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Notes and references

‡ While this paper was under review, two papers (ref. 4*d*,*e*) on the exfoliation of pre-synthesised nitrate LDH were published where AFM was also used to study the structure of the products.

§ An elemental analysis result gives contents of typical elements in percentage as: Mg 10.4%, Al 5.8%, S 7.0% and no nitrogen was detected.

1 (*a*) A. I. Khan and D. O'Hare, *J. Mater. Chem.*, 2002, **12**, 3191; (*b*) A. I. Khan, L. Lei, A. J. Norquist and D. O'Hare, *Chem. Commun.*, 2001, 2342; (*c*) A. M. Fogg, V. M. Green, H. G. Harvey and D. O'Hare, *Adv. Mater.*, 1999, **11**, 1466; (*d*) H. Tagaya, S. Sato, T. Kuwuhara, J. Kadokawa, K. Masa and K. Chiba, *J. Mater. Chem.*, 1994, **4**, 1907.

2 (*a*) T. J. Pinnavaia, *Science*, 1983, **220**, 365; (*b*) A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *J. Mater. Res.*, 1993, **8**, 1179; (*c*) Y. Kojima, T. Matsuoka, H. Takahashi and T. Kurauchi, *J. Mater. Sci. Lett.*, 1993, **12**, 1714; (*d*) B. Chen, *Br. Ceram. Trans.*, 2004, **103**, 241; (*e*) G. Gonzalez, M. A. Santa Ana and E. Benavente, *Electrochim. Acta*, 1998, **43**, 1327; (*f*) J. P. Lemmon and M. M. Lerner, *Chem. Mater.*, 1994, **6**, 207.

3 E. P. Giannelis, *Adv. Mater.*, 1996, **8**, 29; P. B. Messersmith and S. I. Stupp, *Chem. Mater.*, 1995, **7**, 454; L. F. Drummy, H. Koerner, K. Farmer, A. Tan, B. L. Farmer and R. A. Vaia, *J. Phys. Chem. B*, 2005, **109**, 17868.

4 (*a*) M. Adachi-Pagano, C. Forano and J. Besse, *Chem. Commun.*, 2000, 91; (*b*) T. Hibino and W. Jones, *J. Mater. Chem.*, 2001, **11**, 1321; (*c*) S. O'Leary, D. O'Hare and G. Seeley, *Chem. Commun.*, 2002, 1506; (*d*) L. Li, R. Ma, Y. Ebina, N. Iyi and T. Sasaki, *Chem. Mater.*, 2005, **17**, 4386; (*e*) Q. Wu, A. Olafsen, Ø. B. Vistad, J. Roots and P. Norby, *J. Mater. Chem.*, 2005, **15**, 4695.

5 (*a*) M. Li, H. Schnablegger and S. Mann, *Nature*, 1999, **402**, 393; (*b*) M. P. Pileni, *Langmuir*, 1997, **13**, 3266; (*c*) Y. Lalatonne, J. Richardi and M. P. Pileni, *Nat. Mater.*, 2004, **3**, 121; (*d*) M. P. Pileni, *Nat. Mater.*, 2003, **2**, 145; (*e*) G. Hu and D. O'Hare, *J. Am. Chem. Soc.*, DOI: 10.1021/ja0549392.

6 (*a*) Z. P. Xu and H. C. Zeng, *J. Phys. Chem. B*, 2001, **105**, 1743; (*b*) Z. P. Xu and P. S. Braterman, *J. Mater. Chem.*, 2003, **13**, 268; (*c*) E. L. Crepaldi, P. C. Pavan and J. B. Valim, *J. Mater. Chem.*, 2000, **10**, 1337; (*d*) S. P. Newman and W. Jones, *New J. Chem.*, 1998, 105; (*e*) F. Leroux and J.-P. Besse, *Chem. Mater.*, 2001, **13**, 3507.

7 (*a*) A. Cadene, S. Durand-Vidal, P. Turq and J. Brendle, *J. Colloid Interface Sci.*, 2005, **285**, 719; (*b*) R. D. Piner, T. T. Xu, F. T. Fisher, Y. Qiao and R. S. Ruoff, *Langmuir*, 2003, **19**, 7995; (*c*) D. L. Ho, R. M. Briber and C. J. Glinka, *Chem. Mater.*, 2001, **13**, 1923; (*d*) M. M. Malwitz, A. Dundigalla, V. Ferreiro, P. Butler, M. C. Henk and G. Schmidt, *Phys. Chem. Chem. Phys.*, 2004, **6**, 2977; (*e*) K. A. Carrado, G. W. Zajac, K. Song and J. R. Brenner, *Langmuir*, 1997, **13**, 2895.

8 (*a*) J. X. He, S. Yamashita, W. Jones and A. Yamagishi, *Langmuir*, 2002, **18**, 1580; (*b*) J. H. Lee, S. W. Rhee and D.-Y. Jung, *Chem. Commun.*, 2003, 2740.

9 (*a*) S. Carlino, *Solid State Ionics*, 1997, **98**, 73; (*b*) M. Meyn, K. Beneke and G. Lagaly, *Inorg. Chem.*, 1993, **32**, 1209; (*c*) T. Kanoh, T. Shichi and K. Takagi, *Chem. Lett.*, 1999, 117; (*d*) J. P. Hickey, PhD Thesis, Cambridge University, 2003.

10 (*a*) H. M. Naguib and R. Kelly, *Radiat. Eff.*, 1975, **25**, 1; (*b*) S. X. Wang, L. M. Wang and R. C. Ewing, *Nucl. Instrum. Methods. Phys. Res., Sect. B*, 1998, **141**, 509; (*c*) L. Pauling, *The Chemical Bond – A Brief Introduction to Modern Structural Chemistry*, Cornell University Press, Ithaca, NY, 1967, p. 69; (*d*) L. F. Drummy, H. Koerner, K. Farmer, A. Tan, B. L. Farmer and R. A. Vaia, *J. Phys. Chem. B*, 2005, **109**, 17868.