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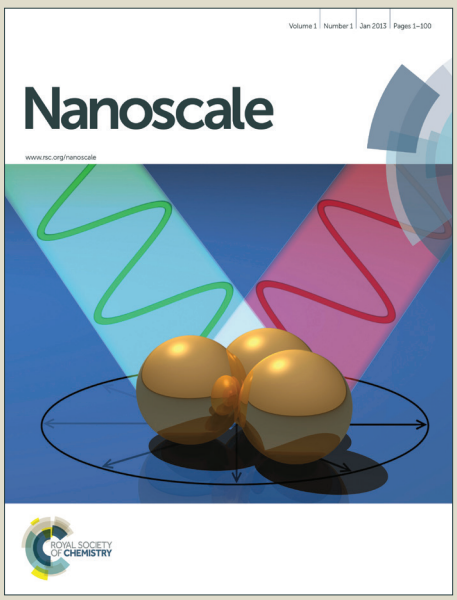





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# One-Step Direct Synthesis of Layered Double Hydroxide Single Layer Nanosheets

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**Layered double hydroxide (LDH) single layer nanosheets were traditionally prepared through multi-step exfoliation process which is very time-consuming and of low efficiency. Herein we report the preparation of LDH single layer nanosheets through a facile direct synthesis method. By introducing a layer growth inhibitor, one can directly synthesize LDH single layer nanosheets instead of LDH layered compounds. The inhibitor weakens the interactions between neighboring layers, thus preventing the interlayer growth. This investigation on blocking interlayer growth by weakening interlayer interactions to obtain inorganic single layer nanosheets opens a new route in the synthesis of 2-dimensional materials.**

Single layer nanosheets have found widespread application in various fields, including electronics,[1] dielectric materials,[2] supercapacitors,[3-5] sensors,[6, 7] nanocomposites,[8] and catalysis.[9-12] Layered double hydroxide (Fig. S1†) (LDH, $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{p-}_{x/p}]\cdot mH_2O$, $M^{2+}$ and $M^{3+}$ represent double and triple charged metal cations, respectively; $A^{p-}$ is interlayer anion), known as hydrotalcite-like anionic clay, consists of brucite-like positively charged layers, counter anions, and interlayer water molecules.[13] LDH single layer nanosheets have been extensively studied and applied in the fields of electronic materials, polymer composites, magnetic materials, nanostructured materials, and catalysis.[14] It is highly desired to obtain a large quantity of LDH single layer nanosheets for the aforementioned applications. Like other layered compounds, the most typical approach to obtain single layer LDH nanosheets is to exfoliate the pre-synthesized LDH layered compounds. The exfoliation of a layered phase typically requires the use of a large intercalant to weaken the interlayer interaction. Extensive processing may be required in order to complete the delamination process. For example, LDHs may be exfoliated by first intercalating to increase the interlayer distance and then violently agitating the product for extended periods of time (usually 24 hours or longer) in a number of solvents, including formamide, butanol, acrylates, and toluene.[14] Li et al. reported the exfoliation of LDH in formamide without the intercalation step, but it required ca. 2.5 days and large excess of formamide (ca. 0.05 g LDH in 100 mL formamide).[15] While the exact exfoliation mechanism of LDH by formamide has not yet been fully clarified, it was proposed that this occurs because the carbonyl groups of formamide molecules can form hydrogen bonds with hydroxyl layers of LDH sheets and solvate the LDH sheet surface, displacing the inherent interlayer water molecules.[16] The amine terminus of formamide forms relatively weak interactions with the interlayer anions, thereby weakening the overall interlayer attraction.[16] Other attempts to prepare thin LDH nanosheets focused on the control of reaction media (micelles) size. This allowed for the synthesis of LDHs with controllable overall dimension and obtained LDHs with only a few layers.[17, 18]

Herein, we report our strategy to inhibit the growth of LDH in the Z-direction by applying a layer growth inhibitor (Fig. 1). Interlayer growth involves the formation of weaker bonds that vary by structure type, such as Van der Waals forces,[19] weak electrostatic interactions,[20] or hydrogen bonds.[21] The layer growth inhibitors weaken overall interlayer attraction, allowing the layers to grow in-plane only, but prevent the layers from stacking (Fig. 1). Such a methodology opens new route to potentially obtain LDH single layer nanosheets, and may result in new valuable materials.

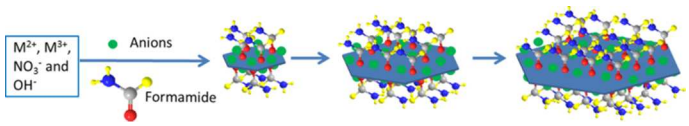


**Fig. 1** Direct growth of single layer nanosheets with the assistance of layer growth inhibitors (not drawn to scale).

We conducted a quick synthesis (10 min) of $Mg^{2+}/Al^{3+}$-LDH (MgAl-LDH) directly in the presence of formamide (23 vol%) (see Supplementary Information for details) with an expectation that formamide molecules can adhere to the LDH sheet surface, thus allowing the sheets to grow laterally while inhibiting interlayer growth (Fig. 1). The energy dispersive X-ray (EDX) spectroscopy analysis (Fig. S2†) detected Mg, Al, and O from the prepared LDH single layer nanosheets (the Cu signal was from the copper sample substrate). The average Mg/Al ratio for the nanosheets was ca. 3.8, which is close to the starting stoichiometry (4.0). The average O/Mg ratio for the nanosheets was ca. 2.1, both of which are consistent with the literature.[15]

MgAl-LDH control sample synthesized in water using the titration method has an interlayer spacing of 7.9 Å,[22] which is observable by X-ray diffraction when the particles are both in powder form (See Fig. S3† insert) and suspended in water (along with a broad peak at ca. 25.8° from Mylar® film[23] used to cover the liquid sample during analysis), as shown in Fig. 2a-I. When MgAl-LDH was synthesized in the presence of formamide and characterized in a dispersion under the same conditions, no diffraction peaks were visible (Fig. 2a-II), indicating the lack of long range ordering. When this dispersion sample was cast and dried onto a silicon wafer, a broad and intense diffraction peak at 11.02° (8.0 Å) was observed (Fig. 2a-III). The diffraction peak is assigned to the interlayer spacing of the re-stacked colloidal MgAl-LDH nanosheets. The slightly increased interlayer distance is attributed to turbostratic disordering and residual water within the interlayer galleries.[24] The virtually transparent MgAl-LDH aqueous dispersion clearly exhibited the Tyndall effect (Fig. 2a inset), which supports the existence of colloidal LDH nanosheets in the dispersion. After centrifuge, a gel like sample was collected, which were loosely and randomly stacked LDH nanosheets. This gel like sample did not show any peak in low-angle regions, but a (*110*) peak at ca. 60° corresponding to LDH in-plane diffraction[25] was observed, indicating the presence of sheet structure in the sample (Fig. S4†). This further supports the formation of LDH nanosheets with virtually no stacking. Analysis of the synthesized MgAl-LDH by transmission electron microscopy (TEM, Fig. 2b) revealed pseudohexagonal nanosheets with a size distribution of ca. 25-50 nm in diameter.

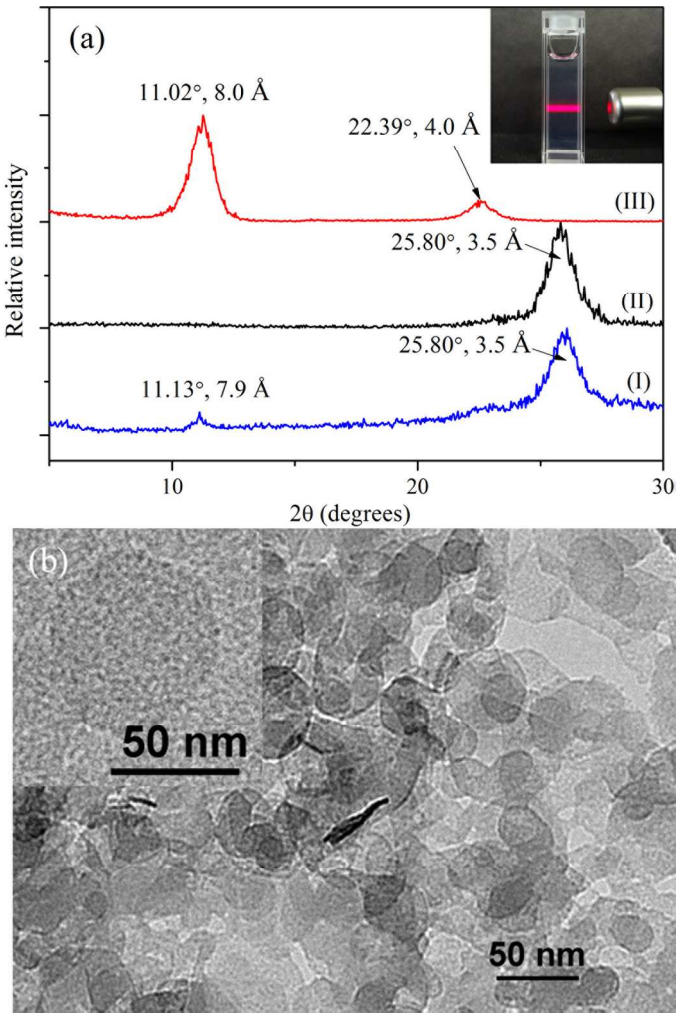


**Fig. 2** (a) XRD patterns of: (I) aqueous dispersion of MgAl-LDH control sample; (II) aqueous dispersion of directly synthesized MgAl-LDH single layer nanosheets in the presence of formamide; and (III) re-stacked MgAl-LDH nanosheets on a silicon wafer after drying. Inset: sample (II) exhibiting Tyndall effect. (b) TEM image of MgAl-LDH single layer nanosheets. Inset: an individual hexagon shaped LDH nanosheet.

To further confirm the formation of single layer MgAl-LDH nanosheets, the synthesized sample was cast on a silicon wafer and characterized by AFM. Fig. 3a and b show representative AFM images of the MgAl-LDH nanosheets. The height of the nanosheets is ca. 0.8 nm. The theoretical thickness of a single layer of metal hydroxide is ca. 0.48 nm.[13, 26, 27] The adsorption of formamide and counter-anions ($NO_3^-$) layer on the sheet surface is expected to be about 0.3 nm.[15, 28] Thus, the thickness from AFM images agrees well with the thickness of a single layer MgAl-LDH nanosheet sandwiched by a layer of formamide and $NO_3^-$ counter-anions, thus supporting that we indeed synthesized MgAl-LDH single layer nanosheets.

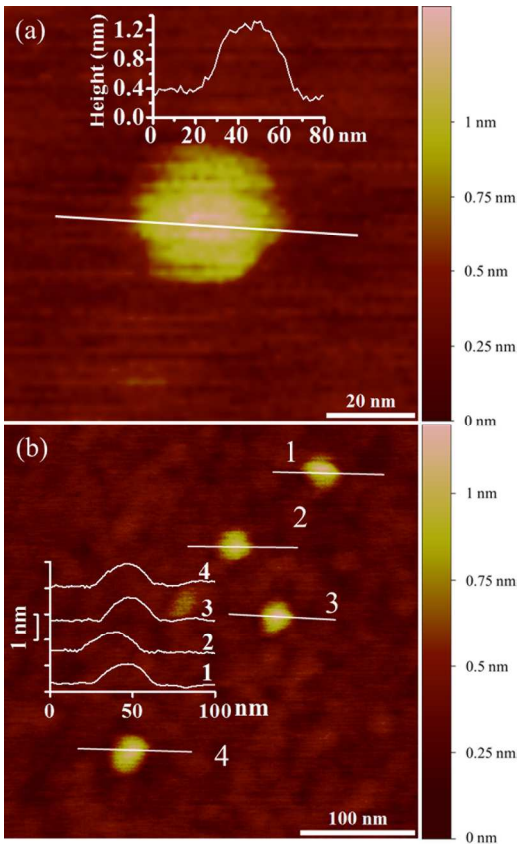


**Fig. 3** (a) AFM image of a pseudohexagonal MgAl-LDH nanosheet; (b) AFM image of multiple neighbouring single layer nanosheets.

In order to verify that the MgAl-LDH single layer nanosheets were not generated through the exfoliation of the conventional multi-layered LDH, the MgAl-LDH control sample (as characterized in Fig. 2a-I and Fig. S5†) was mixed in 23 vol% formamide aqueous solution and stirred vigorously for 10 min (the same duration used for the synthesis of MgAl-LDH in the presence of formamide). XRD analysis of this post-treated sample (Fig. S3†) revealed the presence of the characteristic (*003*) diffraction, which is consistent with the notion that the pre-formed multilayer LDH is stable under this brief treatment (the slightly increased interlayer distance from 7.9 to 8.0 Å is owing to the marginal swelling). To be noted, Fig. S5† shows that the control LDH sample was barely crystalized, which is expected because of the very short reaction time. But their lateral dimension is close to the LDH single layer nanosheets as shown in Fig. 2b.

It is possible that formamide serves multiple functions during the synthesis of single layer nanosheets. In addition to the previously proposed interactions between the carbonyl groups of formamide with the hydroxyl layers on LDH sheet surfaces,[16] it is worth considering the unusually high dielectric constant of formamide ($\varepsilon$ = 111 at 20 °C).[29] Formamide is used to prevent the precipitation of polyions, such as DNA.[30] The presence of formamide weakens the electrostatic interactions between the positively charged sheets and the negatively charged counterions,[31] which in turn lowers layer-layer interactions. Such an ion-ion interaction weakening effect by high dielectric constant solvents have been simulated and modeled. Combining these two mechanisms, we propose that formamide serves as a layer growth inhibitor during the preparation of LDH single nanosheets (shown in Fig.1). The positively charged LDH nanosheets can be electrically balanced by the nitrate anions from the nitrate salts added during the preparation process.

Likewise, $Co^{2+}/Al^{3+}$-LDH (CoAl-LDH) single layer nanosheets have been prepared via the one-step synthesis using formamide as a layer growth inhibitor (See Fig. S6†), and MgAl-LDH single layer nanosheets have also been synthesized using another inhibitor, *N, N*-dimethyl formamide (See Fig. S7†). Based on the general principle of inhibiting as illustrated in Fig. 1, it is believed that these processes can be extended to other layered structures once a suitable inhibitor is identified. In fact, the underlying fundamental mechanism of this methodology is the control of the weak interactions between layers. Since weak interactions, including electrostatic forces and hydrogen bonds, widely exist in liquid system, it is not surprising that this methodology can be applied to a wide range of layered compounds and can serve as a valuable tool to create new materials.

## Conclusions

This methodology provides a facile one-step process offering significant savings in both cost and time. For example, the 10-minute procedure outlined here to synthesize LDH single layer nanosheets should be contrasted with the classical synthesis of LDH layered structures typically requiring multiple hours, followed by an exfoliation process that can take multiple days. As such, this new approach is promising for large scale synthesis of single layer nanosheets for various applications.

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## Notes and references

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Electronic Supplementary Information (ESI) available: Synthesis methods and SEM, EDX, XRD and scheme are included. See DOI: 10.1039/c000000x/

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