We demonstrated that analyzing the formed gels containing exfoliated nitrate or glycine intercalated LDH nanosheets in formamide using X-ray diffraction is a simple and reliable method for determining the delamination degree of LDHs in formamide, which shows many advantages compared to the common characterization technologies.

Layered double hydroxides (LDHs) are ionic lamellar compounds that consist of positively charged hydroxide sheets and interlayers filled with anions and water. Due to their unique structure and properties, LDHs have been widely studied for a range of applications such as anion exchangers, catalyst supports, nanocomposites, electroactive materials, gas adsorbents, etc. However, the inaccessibility to the inner surfaces of the LDH layers largely restricts their applications. The delamination of LDHs into single layers may be the most effective solution to this problem. The delaminated nanosheets have an exceedingly high two-dimensionality with a molecular thickness and a higher degree of freedom than the stacked sheets, which are expected to be used as building blocks for the construction of various functional nanostructures and nanocomposites.

In recent years, there has been increasing research interest in the study of delamination and application of LDH nanosheets. For instance, Wang and O’Hare have reviewed that LDHs can be delaminated in various solvents including butanol, acrylates, CCl₄ and toluene, N,N-dimethylformamide–ethanol mixture, water, formamide, and so on. With the rapid research progress in delamination of LDHs, much concern has been paid to the characterization of the obtained LDH single nanosheets. As it is well known that the thickness of one LDH single layer is only ca. 0.46 nm, it is very difficult to separate such single layers from the delamination solution.

In addition, during the drying step, delaminated LDH single layers will combine together and reconstruct into layered materials. Consequently, most of the characterization was performed with the obtained colloidal solutions using technologies including X-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM), etc. And they were often assisted with the analyses of Tyndall light scattering and transparency as well.

In order to examine the delamination degree of LDHs, dispersing one or several drops of delaminated LDH solution onto a glass slide, followed by XRD analysis was often used. However, this method has some limitations and is not suitable when the concentration of the delaminated LDH dispersion is high. It is believed that the LDH single layers might reconstruct immediately when they became dry. Another effective technology is AFM, which can provide the three-dimensional structural information. However, since the delaminated nanosheets are usually in lateral size, and often in an aggregated form of heavily buckled fine crystallites, they also have some limitations. In addition, the multistep process during AFM analysis was complicate and time consuming as well. TEM can only provide partial information since the thickness of the particle cannot be determined. Although the delaminated LDH colloidal solution can definitely show the Tyndall light scattering phenomenon, we cannot judge whether the LDH particles were delaminated or not from it. Because any stable colloidal solution containing small particles can show the Tyndall effect. Transparency was often mentioned for a good delamination of LDHs, however we demonstrated here that not all delaminated LDH dispersions were transparent. When the lateral size of the delaminated single layers is big, a milky colloidal solution will be obtained even with a complete LDH delamination. Thus, a simple and reliable method that can determine the delamination degree of LDHs in solutions is highly desired.

In our recent work, we found that the delaminated LDH dispersion in formamide could transform into gels after standing for certain time. And the time needed is highly dependent on the concentration of LDH single nanosheets in the formamide solution. Furthermore, we demonstrated that analyzing the XRD patterns of such gels is a simple and highly reliable technology for determining the delamination degree of LDHs in formamide.
The nitrate and glycine intercalated LDHs (Mg–Al–NO₃ and Mg–Al–Gly) were produced using the hydrothermal synthesis method. Powder XRD data confirmed that the synthesized Mg–Al–NO₃ and Mg–Al–Gly LDHs were phase pure, which only showed the characteristic peaks of LDHs (see Fig. 2(a)). Then LDHs were exfoliated by adding the dried Mg–Al–NO₃ and Mg–Al–Gly LDHs into formamide, followed by magnetic stirring for several hours. Gradually, no sediment could be observed and the solution became transparent or translucent depending on the concentration of LDHs. It is considered that the delamination of LDHs in formamide follows a two-step process:22 (1) a certain volume of formamide replaces the water molecules and produces a highly swollen phase, and (2) the magnetic stirring leads to complete exfoliation. Similarly, in order to demonstrate the successful delamination of LDHs, we first checked the Tyndall effect of the LDH suspension (Fig. 2(b)). With the increase in the concentration of dispersed LDHs in formamide, the Tyndall effect became more significant (see Fig. 2(c)). However, as we mentioned in the introduction the Tyndall effect could not prove the delamination of LDHs. Any dispersion which has small particles could lead to the Tyndall effect. In order to prove it, another experiment was carried out. We synthesized a kind of nano-sized spherical Mg–Al–CO₃ LDH which has been reported by our group.23 By deliberately controlling the pH of the synthesis mixture at 12, nanospherical LDHs with an average size of ca. 20 nm were synthesized. In order to obtain a stable LDH suspension in water, the concentration of Mg(NO₃)₂ and Al(NO₃)₃ was controlled to be very low (0.075 and 0.0375 M, respectively). After aging, the LDH suspension was filtered as well, from which a stable LDH colloidal solution was made. This LDH suspension did not sediment even after long-time standing.23 Although they are nano-sized particles, they were not delaminated into single layers. However, we can also see the Tyndall effect with this solution (see Fig. 2(d)). Therefore, it is a good example to demonstrate that the Tyndall effect is not sufficient evidence for the successful delamination of LDHs.

However, we found that the LDH dispersions in formamide transformed into stable gels after standing for a few days (Fig. 2(e)). The higher the concentration of LDHs was, the shorter the time needed for gel formation. The gel-like state was characterized by the tube inversion test, as shown in Fig. 2(f). All gels were stable upon long-term standing, even when the concentration of LDHs was low (10 g L⁻¹). It has been reported by Wu et al.25 that the delaminated LDH dispersion with the concentrations of 5, 10, 20 and 40 g L⁻¹ formed gels after several days to weeks. While Naik et al.24 exfoliated the LDHs in toluene and found that the dispersions formed stable gels. They considered that cohesive dispersive interactions between surfactant chains anchored on opposing inorganic layers are modified by inclusion of nonpolar solvent molecules, leading to the delamination and gel formation. Gels are defined as a substantially dilute cross-linked system, which exhibits no flow when in the steady-state.25 By weight, gels are mostly liquid, yet they behave like solids due to a three-dimensional cross-linked network within the liquid. It is the cross linking within the fluid that gives a gel its structure and contributes to the adhesiveness. Because of the nature of the gels, we found that XRD is a good method to analyze the gel to determine the delamination of LDHs.

Fig. 3(a and b) and Fig. S1 (ESI†) show the XRD patterns of the formed gels containing exfoliated Mg–Al–NO₃ and Mg–Al–Gly LDH nanosheets in formamide. When the LDH concentration was below 100 g L⁻¹, the typical diffractions of LDH structures cannot be observed for all samples. There was only the halo at 2θ = 20–30° produced by formamide.26 And the faint reflection at 2θ = 62° indicated that the 2D crystallinity of the LDH layer was preserved. The absence of 00l diffractions suggested that the host sheets were not in parallel to induce interference of the X-rays.25 Therefore, these data clearly demonstrated that the LDHs have been completely delaminated into individual nanosheets. A similar broad hump has been observed for the exfoliated Mg–Al LDH or MnO₂ nanosheets.27 Li et al.17 have demonstrated that colloidal materials centrifuged from suspensions of exfoliated layered hosts, such as H₀.₇/Ti₁₋₀.₆₂₅/C₂₀.₇₅O₄·₄H₂O (☐: vacancy), H₀.₇MnO₂·0.₇H₂O and HCa₃Nb₂O₈·1.₅H₂O, exhibited a broad diffraction pattern, losing sharp reflections attributable to the corresponding layered structure. Sasaki et al.28 have concluded that the profile is characteristic of the exfoliated layered
material, representing close similarities to the square of the structure factor of the host layer. A similar profile has been taken as compelling evidence for total exfoliation, which arises from the scattering of the individual sheets.11

However, in order to further prove that LDHs have been delaminated, TEM analysis was performed as well. Fig. 3(c) clearly shows that the delaminated LDH nanosheets have a translucent plate-like morphology, which was different from the flower-like morphology of their original LDH particles (Fig. 3(d)).17 For both Mg–Al–NO$_3$ and Mg–Al–Gly LDHs, the highest delaminated concentration was 100 g L$^{-1}$. When the LDH concentration was 120 g L$^{-1}$, the typical LDH peaks started to appear, which indicated that some samples were still in layered structures. In other words, the LDHs cannot be completely delaminated if the concentration of LDHs in formamide is too high.

In addition, it has often been mentioned that the delaminated LDH at last became transparent solution. However, in this communication, we demonstrated that there is no correlation between the delamination degree and the transparency of the solution. After the successful delamination of LDHs, the turbidity of all LDH dispersions in formamide at different concentrations from 10 to 100 g L$^{-1}$ was measured before gel formation. Table 1 shows that the turbidity of the solutions increased with the increase in LDH concentration. When the LDH concentration was low (10 g L$^{-1}$), the turbidity for Mg–Al–NO$_3$ and Mg–Al–Gly was 87 and 100 NTU, respectively. However, when the LDH concentration was 80 g L$^{-1}$, their turbidity reached 388 and 543 NTU, respectively. In the whole concentration range, the turbidity of delaminated Mg–Al–NO$_3$ solution was lower than those for Mg–Al–Gly. One reason is that the lateral size of Mg–Al–Gly is bigger than that of Mg–Al–NO$_3$, LDH. When the concentration of Mg–Al–Gly is 100 g L$^{-1}$, the turbidity exceeded the detection limit of the equipment. However, the XRD analysis suggested that all samples were completely delaminated although the turbidity was very high. In all, we have demonstrated here that the delamination of LDHs cannot be judged from their transparency. The solution with turbidity does not mean that it has not been completely exfoliated.

In conclusion, we reported a simple and reliable method for determining the delamination degree of LDHs in formamide by analyzing the formed LDH dispersion gels using XRD. In addition, we also demonstrated that the Tyndall effect and the transparency of the delaminated solution cannot be used alone for judging the delamination of LDHs.

This work was supported by the Fundamental Research Funds for the Central Universities (TD-JC-2013-3), the Program for New Century Excellent Talents in University (NCET-12-0787), the Beijing Nova Programme (Z131109000413013), and the National Natural Science Foundation of China (51308045).

Notes and references