A new synthesis method of ultrathin Zn-Al layered double hydroxide with super adsorption capacity

Qing Nie*, Jiami Ma and Yafan Xie
School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, China

*Corresponding author e-mail: 1311360460@qq.com

Abstract. Layered double hydroxide (LDH) is a kind of stratiform compound with a large specific surface area and strong adsorption capacity, which is widely used in printing and dyeing wastewater treatment. Herein, we synthesized ultrathin Zn-Al LDH (U-Zn-Al LDH) by temperature-assisted intercalation exfoliation strategy using sodium dodecyl benzene sulfonate (SDBS) at 80 °C. The thickness of the obtained U-Zn-Al LDH was about 4.5 nm and it featured higher specific surface area (49.5 m²/g) as compared to the pristine sample (26.6 m²/g). As a result, U-Zn-Al LDH exhibited higher adsorption activity of methyl orange (MO) dye. Furthermore, the possibly existed defects during the ultrathinning process changed the adsorption mode of MO, resulting in a vertical and ordered configuration of MO on U-Zn-Al LDH, which was another reason for its higher adsorption capacity.

1. Introduction
Nowadays, people's activities have a great impact on the environment, especially the water environment. Printing and dyeing wastewater is difficult to be treated by conventional treatment methods owing to their complex composition, high concentration and many refractory substances. Adsorption method plays an important role in wastewater treatment because of its selective adsorption of some compounds. Since Andre Geim and Konstantin Novoselov[1] prepared graphene by mechanical stripping in 2004, two-dimensional materials have been widely studied in recent decades.

Layered double hydroxide is a kind of typical two-dimensional material including hydrotalcite and hydrotalcite-like compounds. A variety of functional materials can be prepared by the adjustable structure and the exchangeable ions between layers of the hydrotalcite, which has great potential application in sewage treatment. There are many methods to synthesize hydrotalcite, such as hydrothermal method, coprecipitation method, ion exchange method and microwave method. Zhao et al. [2] have synthesized Mg-Al LDH with uniform grain size by using nucleation crystallization isolation method and the crystallization of the product was slightly better than that of traditional coprecipitation method. G.Fetter et al. [3] showed that the particles synthesized by microwave irradiation method were significantly smaller than those synthesized by traditional methods and longer irradiation time could reduce the amount of aluminum ion. P. Benito et al. [4] have synthesized Ni-Al LDH and Zn-Al LDH by microwave-hydrothermal method with urea as precipitant. Alexandra Inayat et al. [5] introduced the nitrate into the Zn-Al LDH by urea synthesis, which broadened the application of Zn-Al LDH in catalysis, ion exchange and stripping intercalation.
The number of active sites and specific surface area can be increased by reducing the atomic thickness [6]. Therefore, the catalytic and adsorption properties of LDH may be greatly enhanced by synthesizing thinner LDH. Liu et al. [7] have synthesized ultrathin Ni-Al LDH with outstanding electrochemical performance by introducing urea. Miao et al. [8] developed a method for preparing ultrathin MnO$_2$ by intercalation exfoliation strategy by introducing CTAB. The obtained ultrathin MnO$_2$ exhibited higher H$_2$ production compared to the pristine MnO$_2$.

There are many methods to synthesize ultra-thin hydrotalcite, such as ultrasonic method and coprecipitation method. However, no study has reported the careful control of the ultrathin Zn-Al LDH. Herein, we have adopted a new method for synthesizing thinner Zn-Al LDH by temperature-assisted intercalation exfoliation strategy. The thickness of the U-Zn-Al LDH was thinner than original Zn–Al LDH. MO was regarded as the target pollutant, U-Zn-Al LDH showed better adsorption effect than that of pristine Zn–Al LDH. This method provides new ideas for the synthesis of other ultrathin hydrotalcite compounds.

2. Experimental section

2.1. Materials synthesis

2.1.1. Preparation of pristine. Zn–Al LDH. ZnCl$_2$·H$_2$O (0.14mol/L) and AlCl$_3$·6H$_2$O (0.07mol/L) were dissolved in 70mL deionized water and stirred on a thermostatic magnetic stirrer for 30 minutes. Then the pH value of the mixture was adjusted to 9.5 by adding NaOH solution and the mixture was transferred to a hydrothermal reactor (100mL) into an oven. The temperature was kept at 140 ℃ for 24 hours. After the reaction, the outcome was centrifuged and washed with deionized water for 5 times. Then the sediment was dried in an oven at 60 ℃ for 10 hours. Finally, the sample was acquired after being grinded.

2.1.2. Preparation of U-Zn–Al LDH. 0.5 g of the above-prepared pristine Zn-Al LDH and 0.05 g of SDBS were dissolved in 70 mL deionized water. Then, the mixture was stirred on a thermostatic magnetic stirrer for 30 minutes and after that the mixture was transferred to a stainless steel reaction vessel of polytetrafluoroethylene (100mL). The stainless steel reaction vessel was put into an oven and the hydrothermal condition was kept at 80 ℃ for 6 hours. After the reaction, the outcome was centrifuged and washed for 5 times with deionized water. Finally, the sediment was dried in an oven at 60 ℃ for 10 hours.

2.2. Characterization methods

X-ray diffraction (XRD) analysis were conducted on a X-ray diffractometer (Rigaku, Japan). Brunauer–Emmett–Teller (BET) analysis were conducted on a fully automatic specific surface area and porosity analyzer (ASAP 2020M, USA). Field emission scanning electron microscopy (FE-SEM) analysis were conducted on a field emission scanning electron microscope (Zeiss Ultra Plus, German). Field emission transmission electron microscopy (FE-TEM) analysis were carried out on a transmission electron microscope (JEM-2100F, Japan). Atomic force microscopy (AFM) images of samples were operated at an atomic force microscope (SPM9700, Japan). X–ray photoelectron spectroscopy (XPS) analysis were conducted on a X-ray photoelectron spectrometer (Thermo Fisher, USA).

2.3. The evaluation of activity

20 mg of the two kinds of samples were respectively dispersed in 100 mL of 30 mg/L MO aqueous solution. The mixture was continuously stirring on a thermostatic magnetic stirrer. 6 ml of the MO solution was taken out and centrifuged every 30 minutes. The absorbance of the MO solution was measured at 464 nm on an ultraviolet-visible spectrophotometer. The degradation effect of the MO solution was analyzed according to the change of absorbance.
3. Results and discussion

3.1. Material synthesis and characterizations

As illustrated in Figure 1, U-Zn–Al LDH were synthesized by hydrothermal method by introducing SDBS. The thermal velocity of the H₂O between the layers increased owing to the high temperature of 80 °C, which weakening the Van der Waals force. Therefore, more H₂O can enter and expand the space of layers. Then the SDBS molecular gradually infiltrate into the interlayers and exchange with the Cl⁻. The expansion and subsequent spalling of Zn–Al LDH were triggered due to the large size of SDBS ions.

![Figure 1. The schematic of the synthesized process.](image)

The XRD patterns are presented in Figure 2 (a), the peaks located around 10.8 °, 22.4 ° and 31.3 ° are the characteristic 2θ diffraction peaks of layered compound. They agreed well with the (003), (006) and (009) planes [9]. The diffraction peak at 10.8°, which is more sharp than other planes, indicating that the (003) plane was the main plane with a long range of arrangement. Furthermore, the diffraction peaks didn't change after the ultrathin process, indicating that the hydrothermal synthesis did not cause any damage to the structure of Zn–Al LDH. Figure 2 (b) displays N₂–desorption and sorption isotherm of samples. The BET surface area of U–Zn–Al LDH is 49.5 m²/g, which is higher than that of pristine Zn–Al LDH (26.6 m²/g). The result proved that it is feasible to obtain U–Zn–Al LDH by intercalation exfoliation strategy.

![Figure 2. (a) XRD patterns of samples. (b) N₂–desorption and sorption isotherm.](image)

The FE-SEM images and FE-TEM images of samples are presented in Figure 3 (a) and Figure 3 (b) respectively. As shown in Figure 3 (a), both original Zn–Al LDH and U-Zn–Al LDH all exhibit an irregular mixture of sheets and rods. As shown in Figure 3 (b), both pristine Zn–Al LDH and U-Zn–Al LDH all exhibit dark contrast indicating that they consist of several stacked layers. The layers of U-Zn–
Al LDH less than pristine Zn–Al LDH, it may be caused by the introduction of SDBS which promoted the peeling of the layers.

![Figure 3](image1.png)

**Figure 3.** (a) FE-SEM images of samples. (a) FE-TEM images of samples.

AFM images of the two kinds of samples are showed in Figure 4, the thickness of original Zn–Al LDH was 8 nm. However, the thickness of U-Zn–Al LDH was 4.5 nm. The result further confirmed that the U-Zn–Al LDH was successfully synthesized.

![Figure 4](image2.png)

**Figure 4.** (a) AFM images of pristine Zn–Al LDH. (b) AFM images of U-Zn–Al LDH.

The XPS patterns are presented in Figure 5. As shown in Figure 5 (a), there are peaks corresponding to Zn, Al, O and C for pristine Zn–Al LDH. However, the peak corresponding to element S appears in U-Zn–Al LDH. In addition, as shown in Figure 5 (b), the peak of C for U-Zn–Al LDH increases. The results further indicating that SDBS successfully intercalated the layers. As shown in Figure 5 (c), the binding energy of Zn 2p peak for U-Zn–Al LDH increased to 1022.1 eV, which is much higher than original Zn–Al LDH (1021.2 eV), indicating that defects may appear in U-Zn–Al LDH and changed the adsorption mode of MO. Figure 5 (d) shows the schematic diagram of adsorption. After ultrathin process, more defects appear, resulting in a vertical and ordered configuration of MO on U-Zn-Al LDH, which was another reason for its higher adsorption capacity.
Figure 5. (a) XPS survey spectra of samples. (b) C 1s XPS of samples. (c) Zn 2p XPS of samples. (d) The schematic diagram of adsorption of samples.

3.2. Adsorption activity

In order to evaluate the adsorption property, the absorbance of MO at different time was tested. As shown in Figure 6, the absorbance decreased when pristine Zn–Al LDH or U-Zn–Al LDH was added into the MO solution. After stirring for 6 hours, the adsorption capacities of pristine Zn–Al LDH was 17%. As for U-Zn–Al LDH, MO was absorbed 86% in 30 minutes, indicating that the ultrathin structure improves the adsorption property of the Zn–Al LDH.

Figure 6. MO degradation efficiency by samples.
4. Conclusion
We successfully prepared ultrathin Zn–Al LDH and studied its adsorption performance by employing MO as the target pollutant. The thickness of U-Zn–Al LDH is 4.5 nm, which is thinner than that of pristine Zn–Al LDH. The experimental results showed that the adsorption performance of U-Zn–Al LDH was much higher than pristine Zn–Al LDH under the same condition.

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References
[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, Science, 306 (2004) 666-669.
[2] Yun Zhao, Feng Li, Rui Zhang, David G. Evans and Xue Duan, Preparation of layered double-hydroxide nanomaterials with a uniform crystallite size using a new method involving separate nucleation and aging steps, Chem. Mater., 14 (2002) 4286-4291.
[3] G. Fetter, F. Hernández, A.M. Maubert, V.H. Lara and P. Bosch, Microwave irradiation effect on hydrotalcite synthesis, Journal of Porous Materials, 4 (1997) 27-30.
[4] P. Benito, M. Herrero, C. Barriga, F. M. Labajos and V. Rives, Microwave-assisted homogeneous precipitation of hydrotalcites by urea hydrolysis, Inorg. Chem., 47 (2008) 5453-5463.
[5] Alexandra Inayat, Michael Klumpp and Wilhelm Schwieger, The urea method for the direct synthesis of Zn-Al layered double hydroxides with nitrate as the interlayer anion, Applied Clay Science, 51 (2011) 452-459.
[6] Y.F. Sun, S. Gao, F.C. Lei and Y. Xie, Atomically-thin two-dimensional sheets for understanding active sites in catalysis, Chem. Soc. Rev., 44 (2015) 623-636.
[7] Huili Liu, Tingting Yu, Dongqin Su, Zehua Tang, Junhao Zhang, Yuanjun Liu, Aihua Yuan and Qinghong Kong, Ultrathin Ni-Al layered double hydroxide nanosheets with enhanced supercapacitor performance, Ceramics International, 43 (2017) 14395-14400.
[8] Lei Miao, Qing Nie, Jinlong Wang, Gaoke Zhang and Pengyi Zhang, Ultrathin MnO2 nanosheets for optimized hydrogen evolution via formaldehyde reforming in water at room temperature, Applied Catalysis B: Environmental, 248 (2019) 466-476.
[9] B. Wan, Y. Yan, R. Huang, D.B. Abdala, F. Liu, Y. Tang, W. Tan, X. Feng, Formation of Zn–Al layered double hydroxides (LDH) during the interaction of ZnO nanoparticles (NPs) with γ-Al2O3, Sci. Total Environ., 650 (2019) 1980-1987.
[10] Yasi Li, Hydrotalcite-like hydrothermal synthesis, structure characterization and phosphate adsorption capacity research, Fuzhou, Fuzhou University, 2014.
[11] L. Ju, W. Zhang, X. Wang, J. Hu, Y. Zhang, Aggregation kinetics of SDBS-dispersed carbon nanotubes in different aqueous suspensions, Colloids Surf. A Physicochem. Eng. Asp., 409 (2012) 159-166.