Electronic supplementary information

Self-sacrificial templating synthesis of self-assembly 3D layered double hydroxide nanosheets using nano-SiO_2 under facile conditions

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Experimental

Materials:

$Mg(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$, Na_2CO_3, $NaNO_3$ and NaOH were used to synthesize LDH and supplied by Shantou Xilong Chemical Factory, Guangdong, PRC. Nano-SiO_2 with size distribution of 20-40 nm was supplied by Baisen Yanling Nano Technology Co. Ltd, Shanghai, PRC. Micro-sized SiO_2 with size distribution of 0.5-2 μm was purchased from Guangzhou chemical reagent factory, Guangzhou, PRC. Paraffin liquid and hydrochloric acid were supplied by Shantou Xilong Chemical Factory, Guangdong, PRC. All of the chemicals are analytical reagents.

Synthesis of LDHs:

SiO_2-MgAl-LDH The mixed metal nitrate Solution A was prepared by dissolving 7.69 g $Mg(NO_3)_2·6H_2O$ and 3.75 g $Al(NO_3)_3·9H_2O$ in 100 ml deionized water. 4.00 g NaOH was dissolved in 100 ml deionized water to make Solution B. 4.24 g Na_2CO_3 and 0.60 g nano-SiO_2 were added to 100 ml deionized water, and then ultrasonically treated in an ultrasonic bath for 30 min to disperse the nano-SiO_2 to make the Base solution. Solution A and Solution B were added drop-wise into the Base solution, while maintaining the pH at 10±0.2, with vigorous stirring. The obtained white slurry was aged in the mother liquid at 338K for 15 h. Finally, the resulting product was collected by centrifugation at 4000 rpm, washed 5 times with deionized water and dried at 353 K in a vacuum oven for 24 h. It is denoted as SiO_2-

MgAl-LDH. The upper by-product was also collected and dried at 353 K in a vacuum oven for 24 h for further use.

Na_2SiO_3-MgAl-LDH With reference to the above experiment, the nano-SiO_2 was replaced by sodium silicate with the same molar ratio of silica to synthesize the LDH, the product is presented by Na_2SiO_3-MgAl-LDH.

M-SiO_2-MgAl-LDH With reference to the synthesis of SiO_2-MgAl-LDH, the nano-SiO_2 was replaced by micron-sized SiO_2 with the same molar ratio of silica to synthesize the LDH, the product is presented by M-SiO_2-MgAl-LDH.

SiO_2-MgAl-LDH-H Following the procedure for the synthesis of SiO_2-MgAl-LDH, after Solution A and Solution B were added drop-wise into the Base solution, the mixture was transferred into an autoclave pressure vessel and maintained at 413 K for 15 h to synthesize SiO_2-MgAl-LDH-H.

MgAl-LDH Solution A and solution B were prepared as above. Solution A and solution B were added drop-wise into water, while maintaining the pH at 10±0.2, with vigorous stirring. The obtained white slurry was aged in the mother liquid at 338K for 15 h. This is the same as the synthesis of SiO_2-MgAl -LDH with no additional additives.

SiO_2-MgAl-LDHs at different pHs

With reference to the synthesis of SiO_2-MgAl-LDH at pH=10, SiO_2-MgAl-LDHs at different pHs (pH=9, pH=12 and pH=13, Solution A and Solution B were added drop-wise into the Base solution, while maintaining the pH as noted, with vigorous stirring) were obtained.

SiO_2-MgAl-LDHs at different initial concentrations of nano-SiO_2

With reference to the synthesis of SiO_2-MgAl-LDH at the nano-SiO_2 initial concentration of 0.1 mol/L, the SiO_2-MgAl-LDHs at different initial concentrations of nano-SiO_2 (0.04 mol/L, 0.08 mol/L, 0.2

mol/L) were prepared.

Preparation of Pickering emulsions

0.19 g SiO_2-MgAl-LDH was dispersed into 4.5 mL deionized water by stirring for 15 min. Six repeated experiments were carried out to make dispersions. The pHs of dispersions were adjusted to 3, 5, 7, 9, 11, 13 by using HCl and NaOH, respectively. Then 5 mL paraffin liquid was added into the dispersions, followed by homogenizing with an Ultra Turrax at 8500 r/min for 8 min, respectively. The Stability of the emulsions was tested by centrifugation (Xiangyi Centrifuge TDZ5-WS, Changsha, PRC) at 4000 r/min for 5 min.

Characterization

X-ray diffraction (XRD) analysis was performed on a PANalytical PRO powder diffractometer equipped with a Cu Kα radiation source (λ=0.15405 nm) at 40 kV and 40 mA. X-ray photoelectron spectroscopy was measured on an ESCALAB 250Xi. Fourier transform infrared spectroscopy (FTIR) was performed with a Thermo Nexus 470 infrared spectrometer. The specimens were oven dried and stored in a desiccator. The sample was finely ground, combined with oven dried spectroscopic grade KBr before measurement in the FTIR spectrometer. Scanning electron microscopy (SEM; S-4800) and transmission electron microscopy（TEM; JEM-2100F）were used to characterize the microstructure of the samples. For SEM characterization, the specimen was dispersed in ethanol and treated ultrasonically for 15 min. Then one drop of the dispersion was placed on a conductive adhesive and the solvent was allowed to evaporate. Finally, the specimen was coated with gold before the test. For TEM characterization, the specimen was dispersed in ethanol and treated ultrasonically for 15 min. Then one drop of the dispersion was placed on a holey carbon film supported by a copper grid and the solvent was allowed to evaporate before observation. The specific surface areas and pore size distribution were detected by micromeritics tristar II 3020. Before the BET measurements, the specimens were oven dried, and then degassed at 373K for 12 h.

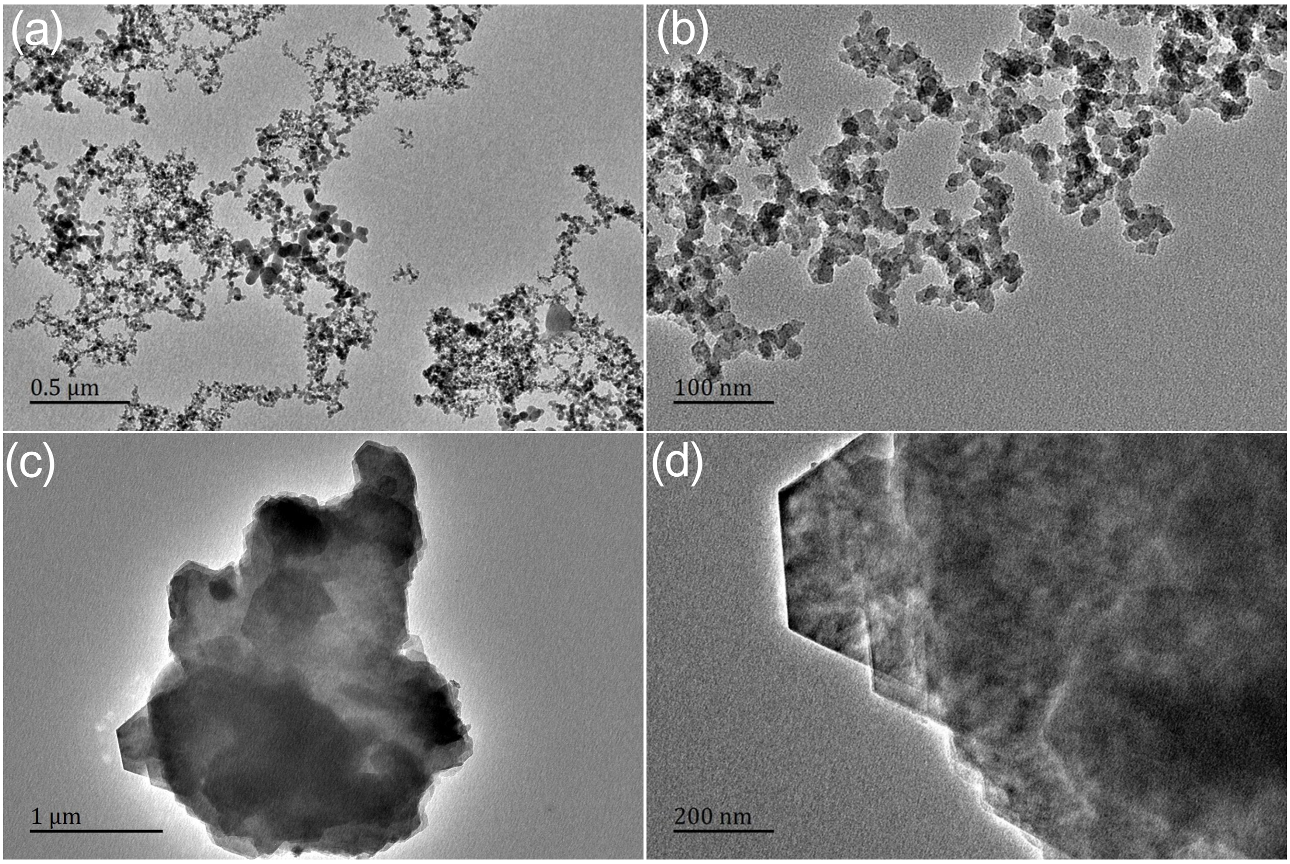

Fig. S1 TEM images of (a, b)nano-SiO_2 and (c, d)micron-sized SiO_2.

The size of nano-SiO_2 distributed in 20-40 nm, while the size of micron-SiO_2 distributed in 0.5-2.0 μm.

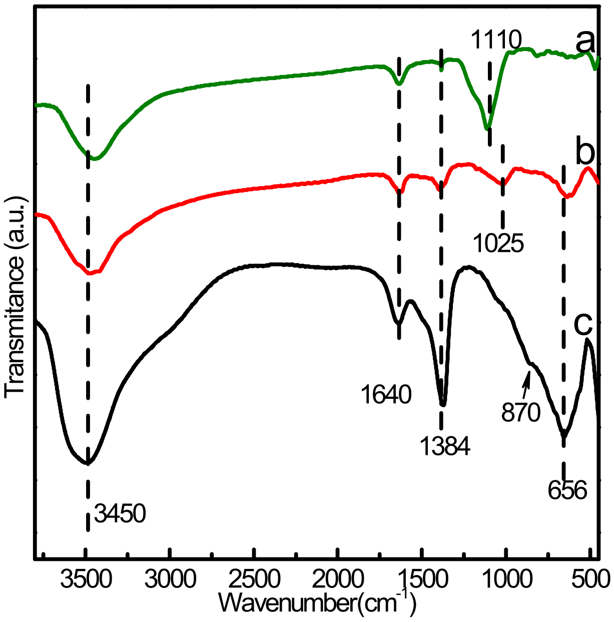

Fig. S2 FTIR spectra of the (a)SiO_2, (b)SiO_2-MgAl-LDH and (c)MgAl-LDH.

In the infrared spectrum of the MgAl-LDH (Fig. S2c), the v_2 mode of carbonates is observed at 870 cm^{-1}. The band around 3000 cm^{-1} is attributed to CO_3^{2-}-H_2O bridging mode of carbonate and water in the interlayer.[1] The layer O-H stretching vibrations can be identified around 3450 cm^{-1},[2] and bending vibrations of adsorbed water in the interlayer can be seen near 1640 cm^{-1}. In the infrared spectrum of the SiO_2-MgAl-LDH (Fig. S2b), the band at 1025 cm^{-1} is related to Si–O stretching vibrations, while the original Si-O-Si band in nano-SiO_2 (shown in Fig. S2a) is detected at 1100 cm^{-1}, which provides evidence for the transformation of the nano-SiO_2. Compared to lattice vibrations of pristine MgAl-LDH at 656 cm^{-1}, the lattice vibrations of the SiO_2-MgAl-LDH are shifted, from which one can infer that converted product from nano-SiO_2 causes the reduction in the brucite-like octahedral layers. This may be ascribed to the nascent [SiO_4] tetrahedrons on the broken bonds of the brucite-like layers.[3]

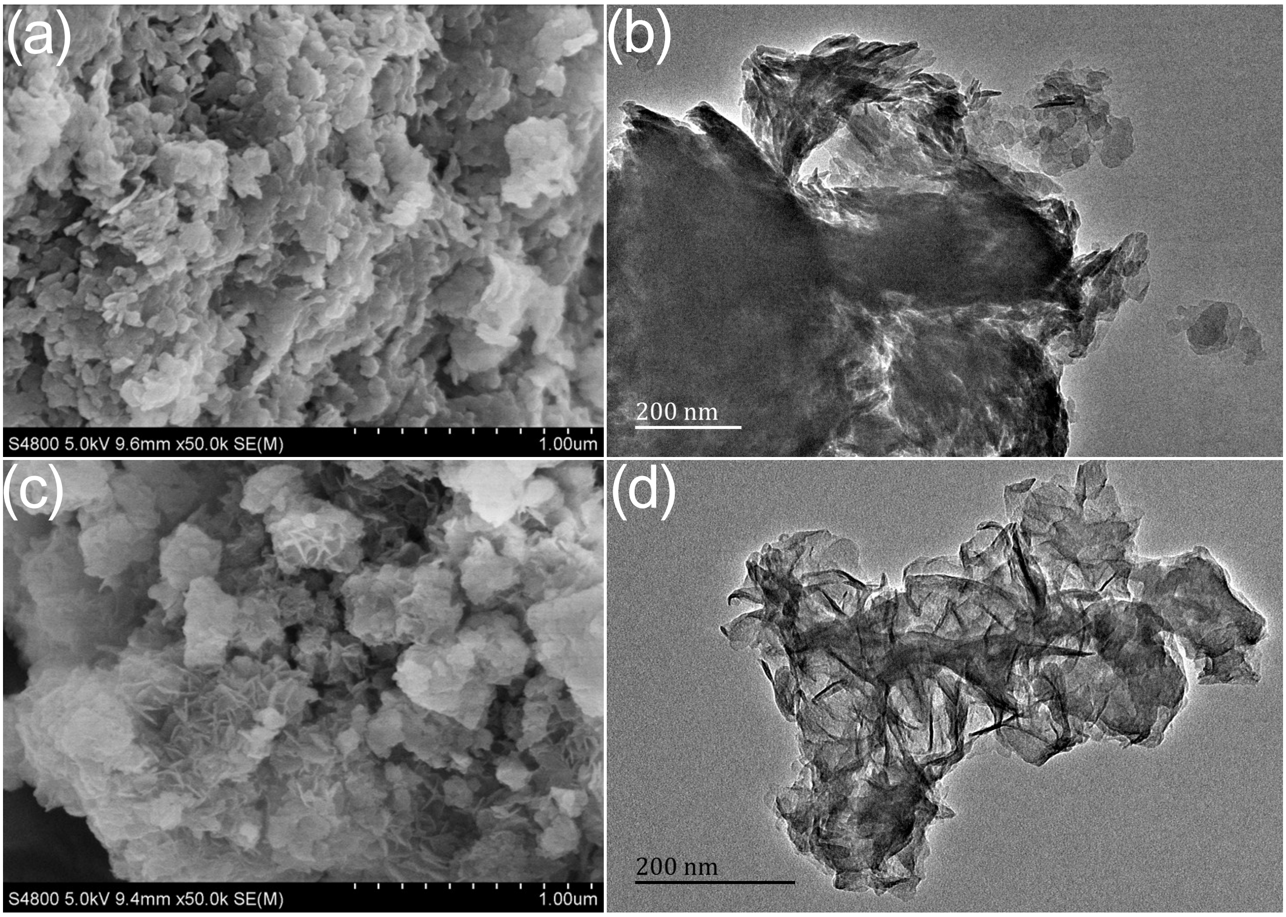

Fig. S3 SEM and TEM images of (a-b)MgAl-LDH and (c-d)Na_2SiO_3-MgAl-LDH.

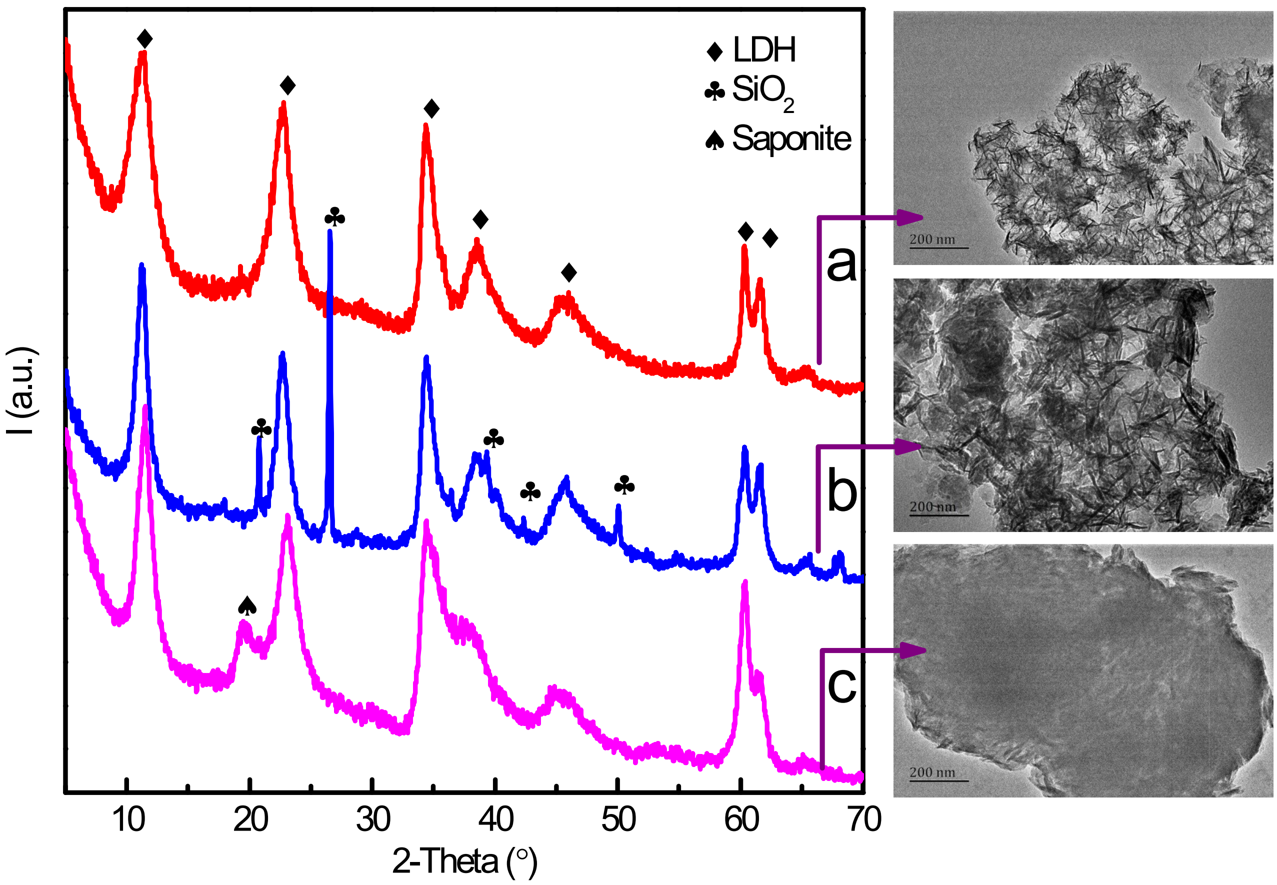

Fig. S4 XRD patterns and TEM images of (a)SiO_2-MgAl-LDH, (b)M-SiO_2-MgAl-LDH and (c)SiO_2-MgAl-LDH-H.

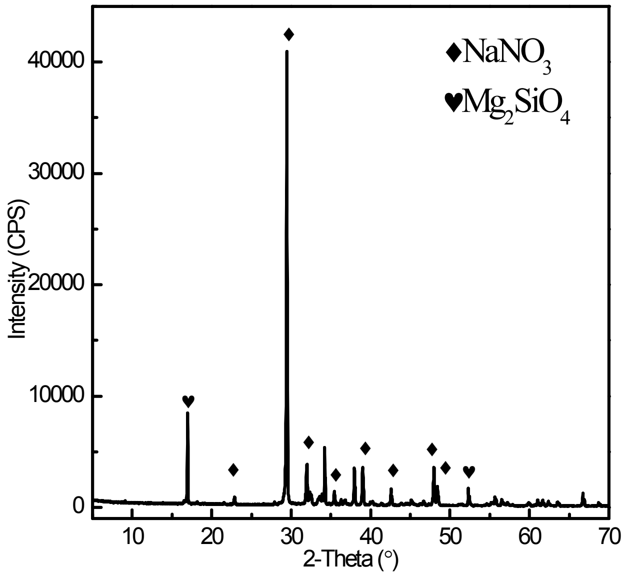

Fig. S5 XRD pattern of the upper by-product in the synthesis of SiO_2-MgAl-LDH

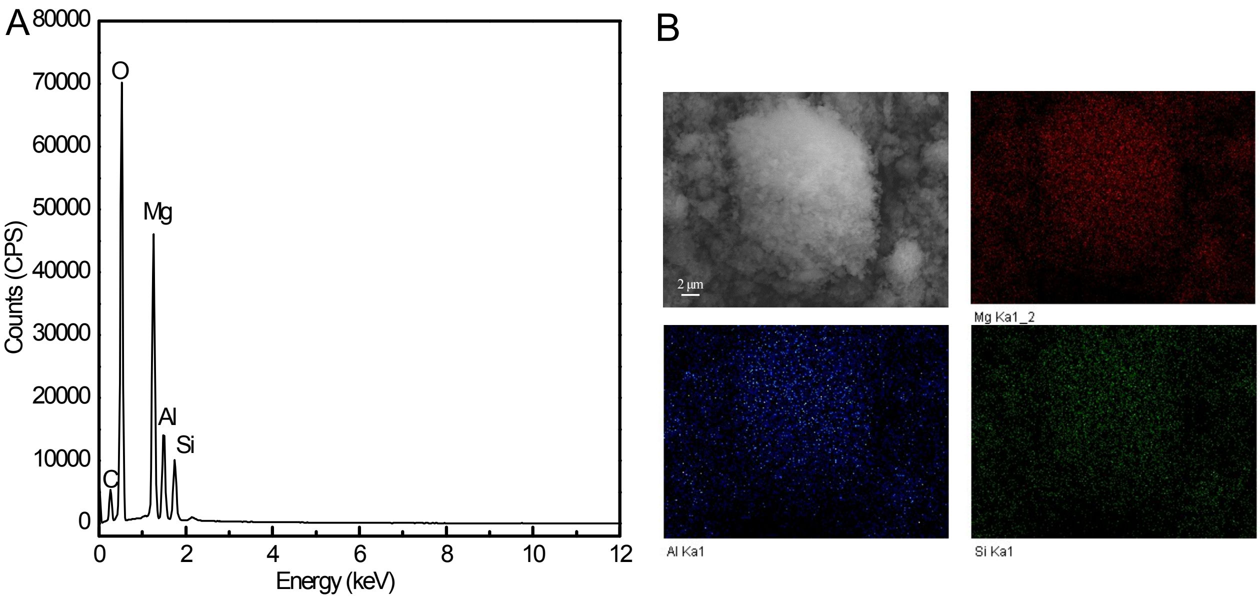

Fig. S6 EDS spectrum of SiO_2-MgAl-LDH and mapping images of Mg, Al and Si

EDS spectrum of SiO_2-MgAl-LDH and mapping images of Mg, Al and Si are given in Fig. S6. The weight content of Mg, Al, Si, C and O is 18.56%, 6.35%, 5.79%, 9.8%, 59.5%, respectively. The high content of C is ascribed to the organic carbon pollution on EDS probe. Mg, Al and Si mapping images clearly reveal chemical composition and distribution, which indicates that the components of the LDH nanosheets containing magnesia, alumina and silicon.

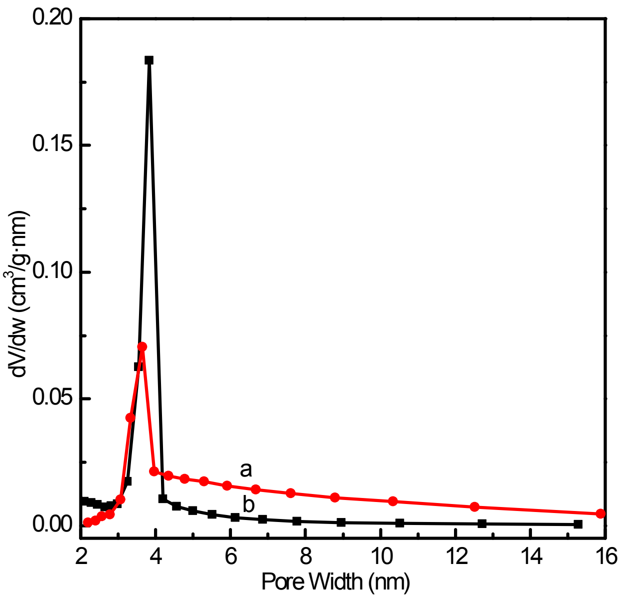

Fig. S7 Pore size distribution of (a)MgAl-LDH and (b)SiO_2-MgAl-LDH.

The pore size of SiO_2-MgAl-LDH distributed in 3-4 nm with the average pore size of 3.77 nm, while the pore size of MgAl-LDH distributed in a wide range with the average pore size of 5.99 nm.

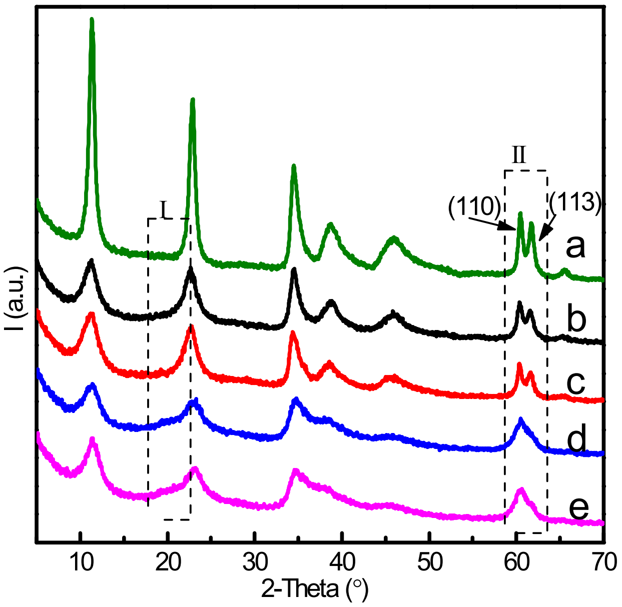

Fig. S8 XRD patterns of (a)MgAl-LDH, (b)SiO_2-MgAl-LDH (pH=9), (c)SiO_2-MgAl-LDH (pH=10), (d)SiO_2-MgAl-LDH (pH=12) and (e)SiO_2-MgAl-LDH (pH=13).

The main phase of LDH could be prepared at different pH values. However, as the pH increases from 9 to 13, the crystallinity of LDH decreases, as evidenced by the intensity of main reflections and superposition of (110) and (113) (Box II). The small intensity increase at 2-theta values around 20° may be the trace of saponite (Box I), indicating that more [SiO_4] tetrahedrons may yield with pH increased.

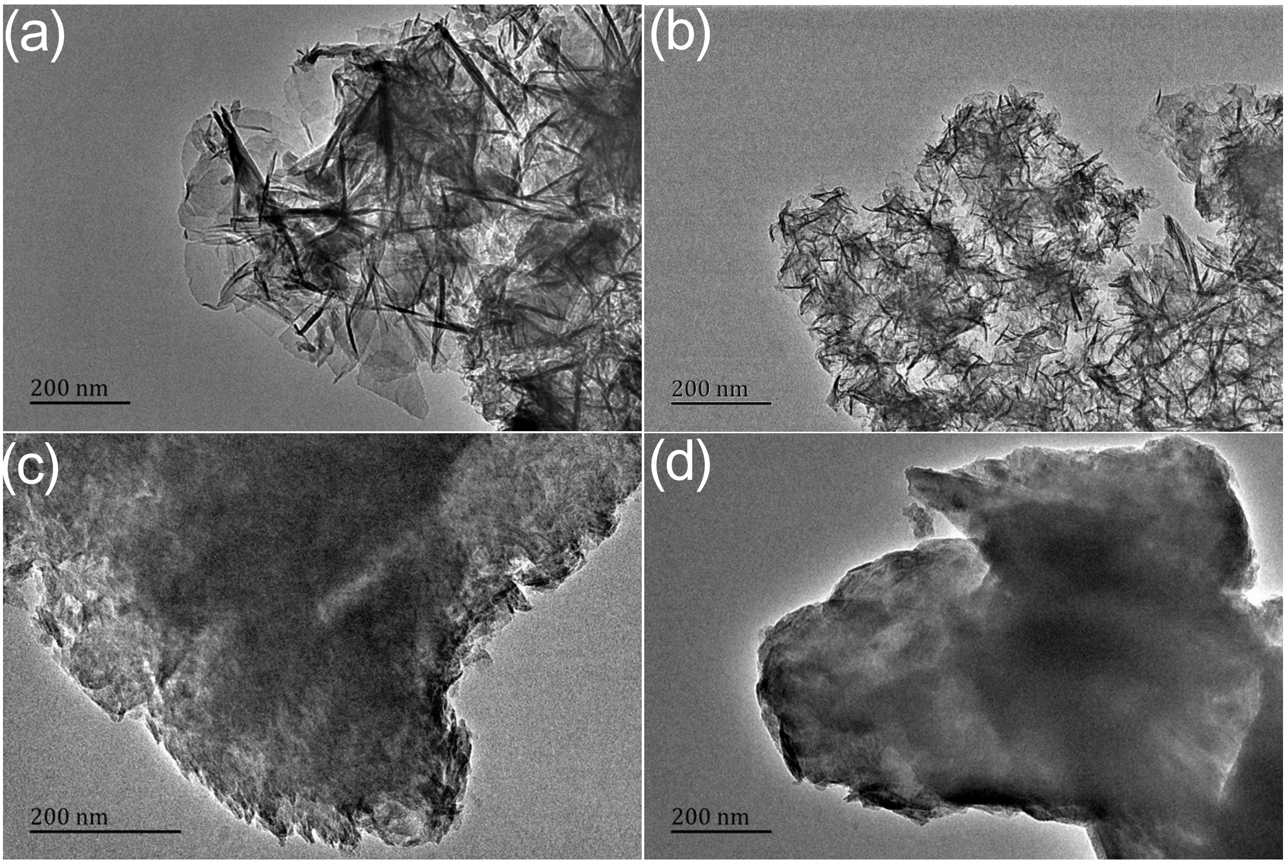

Fig. S9 TEM images of SiO_2-MgAl-LDHs at different pH values: (a)SiO_2-MgAl-LDH (pH=9), (b)SiO_2-MgAl-LDH (pH=10), (c)SiO_2-MgAl-LDH (pH=12) and (d)SiO_2-MgAl-LDH (pH=13).

Self-assembly 3D LDH nanosheets could be obtained at the pH around 10. The thickness and the size of LDH became thicker and larger as the pH increases from 9 to 13.

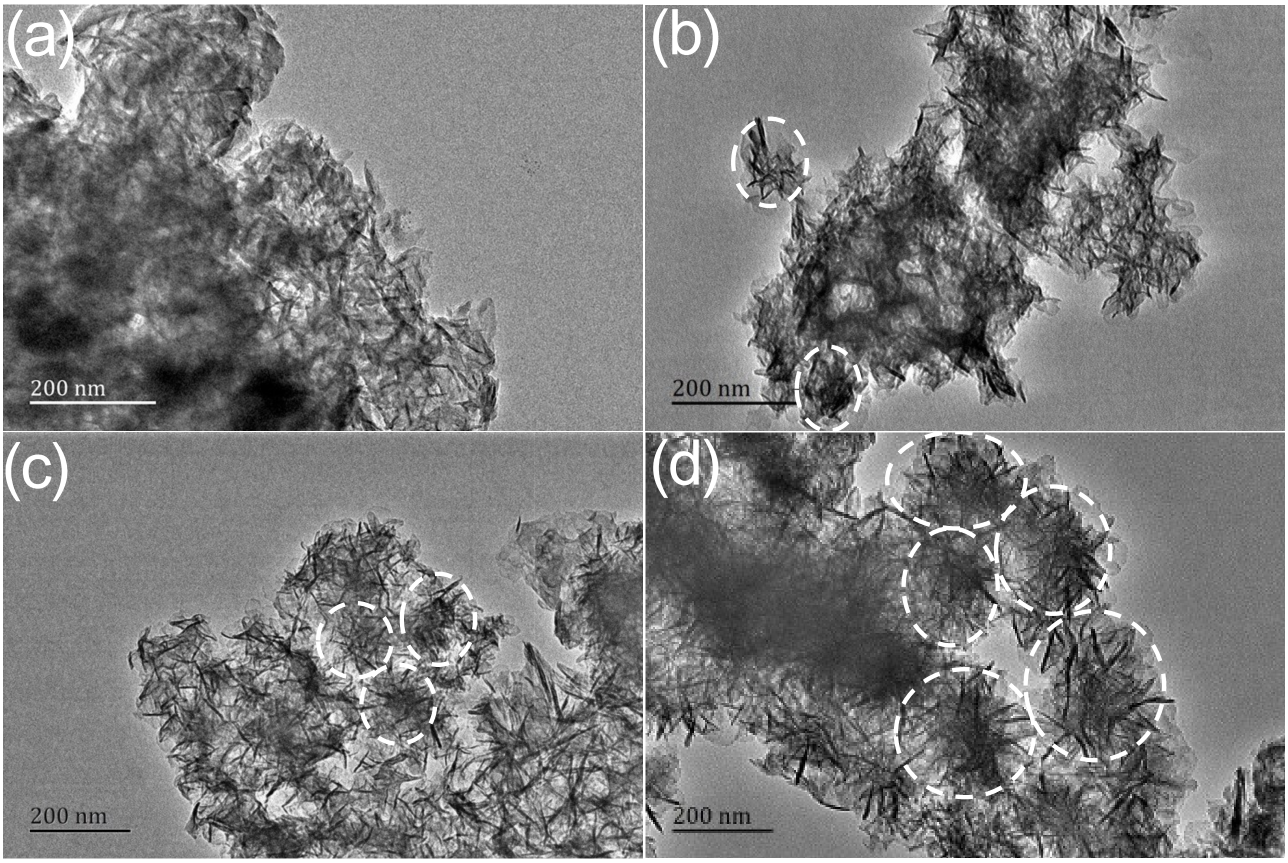

Fig. S10 TEM images of SiO_2-MgAl-LDHs at different initial concentrations of nano-SiO_2: (a)SiO_2-MgAl-LDH (0.04 mol/L), (b)SiO_2-MgAl-LDH (0.08 mol/L), (c)SiO_2-MgAl-LDH (0.1 mol/L) and (d)SiO_2-MgAl-LDH (0.2 mol/L).

When the amount of nano-SiO_2 increased to 0.2 mol/L, individual 3D LDH nanosheets clusters can be clearly observed, as shown in the dashed circles.

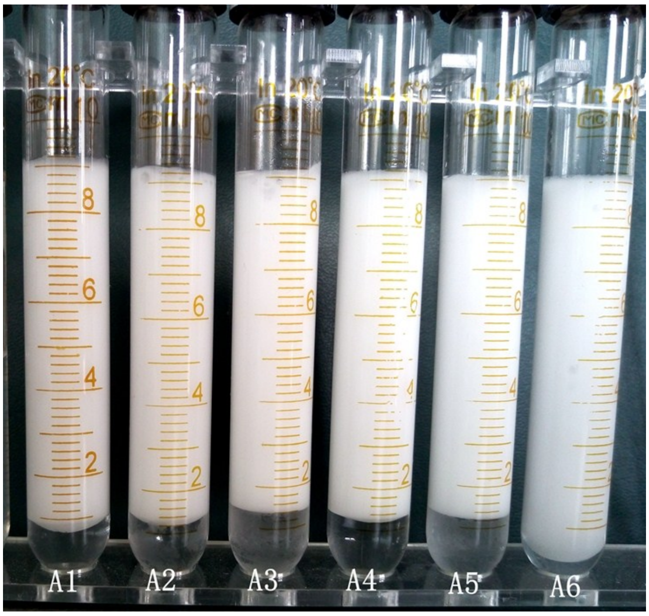

Fig. S11 Picture of emulsions stabilized by SiO_2-MgAl-LDH at different pHs: A1(pH=3), A2(pH=5), A3(pH=7), A4(pH=9), A5(pH=11), A6(pH=13).

References

1 J. T. Kloprogge and R. L. Frost, *J. Solid State Chem.*, 1999, **146**, 506-515.

2 W. Tongamp, Q. Zhang and F. Saito, *J. Mater. Sci.*, 2007, **42**, 9210-9215.

3 M. Del Arco, S. Gutierrez, C. Martin, V. Rives and J. Rocha, *J. Solid State Chem.*, 2000, **151**, 272-280.