SUPPORTING INFORMATION

Direct assembly of Mg-Al LDH nanosheets and Mn(II) salen complex into sandwich-structured materials and their enhanced catalytic properties

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1. Experimental Details and Characterising Data

Scheme S1. The image of exfoliated LDH suspension in formamide with different LDH concerntrations-10g/L, 20g/L, 30g/L and 40g/L (a) after ultrasonic treatment; (b) rested for several days to months.

Figure S1. (a) Image of delaminated LDH-BA suspension (10g/L). (b) TEM image. (c)& (d) Zeta potential and DLS curves of LDH-BA nanosheets sol. (c) AFM image of delaminated LDH-BA deposited on a mica substrate and its height profile.

Table S1. Element analysis of Cat.1, Cat.2 and their homogeneous analogue.

Figure S2 XRD pattern of complex prepared by adding salen complex solution dropwised into LDH-BA nanosheets suspension

Figure S3 FTIR spectra of LDH-BA, Cat.1 and Cat2.

Figure1 (a) XRD patterns of LDH-BA, Cat.1 and Cat.2. SEM images of (b) LDH-BA, (c) Cat.1 and (d) Cat.2

Figure 2 ESR spectra of Cat.2 and Cat.2'(after 6 recycles); EPR spectra: 9.85 GHz, room temperature, 102mW microwave power.

1.1 The synthesis of samples

Synthesis of LDH-BA: LDH-BA was synthesized according to Kooli's method. As an illustration, 12.82g (50mmol) $Mg(NO_3)_2 \cdot 6H_2O$ and 9.38g (25mmol) $Al(NO_3)_3 \cdot 6H_2O$ were dissolved in 100mL deionized and decarbonated water. The solution was added dropwise into 100mL Sodium benzoate solution (0.5mol/L) at 55℃. The pH of the solution was held constant at 10 by the addition of 2M sodium hydroxide solution. The suspension was aged at 55℃ for 18h and washed with DD water until pH close 7. Then the slurries were dried in vacuum at 50℃ for 4h.

Synthesis of Na_2[Mn(II)(Salen)]·$2H_2O$:To an aqueous solution (20 ml) of the ligand (1.75 g) was added dropwise an aqueous solution (30ml) of $Mn(Ac)_2 \cdot 4H_2O$(1.97 g) at

room temperature under N_2 protection. The solution was maintained stirring for 12h and green solid was separated and filtered and washed with cold water, then dried in vacuum.

Synthesis of Cat.1: 0.1g $Na_2[Mn(II)(Salen)]\cdot 2H_2O$ was dissolved in 200mL DD water. 0.5g LDH-BA was added into the solution and stirred at room temperature for 10h. The green solid was filtered and washed thoroughly and dried in vaccum at 50℃ for 4h.

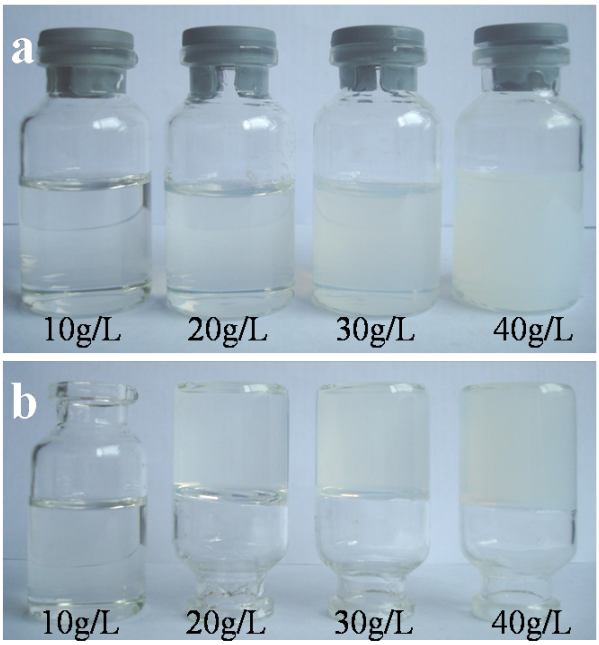
Synthesis of Cat.2: A 50mL suspension of delaminated LDH-BA nanosheets (10g/L) was added dropwise into 100mL $Na_2[Mn(II)(Salen)]\cdot 2H_2O$ solution (1g/L) at fast stirring speed. Then, the solution was stirred at speed of 20r/min for another 30min. The suspension was maintained for 1d and separated by centrifuge. The solid was washed with DD water and dried in vaccum.

1.2 The catalytic experiment

All reactions were carried out using 10mmol 4-picoline and 20 mg catalyst in 20 mL DD water with 0.68g (30mmol) H_2O_2 or molecular oxygen at room temperature. The reaction process was detected by TLC.

1.3 Characterization of samples

The XRD patterns were detected by using Ni-filtered Cu Kα radiations with a Rigaku diffractometer. The accelerating voltage was set at 40 kV with 40 mA current (λ = 1.542A°) at 10°/min from 0.5° to 70° with a slit size of 1/4 degree. The chemical compositions of the presented samples were analysed by CHNS element analysis (Vario Macro) and ICP-AES (Iris intrepid II XSP). Thermal decomposition study of LDH-BA, Cata2 and cata3 was carried out in a simultaneous TGA–DA (SDT Q600) apparatus. The samples were heated from room temperature up to 715℃ with heating rate of 10 ℃/min and N_2 flow rate of 120 mL/min at atmospheric pressure. The suspension of delaminated LDH was deposited on mica substrate and its shape was detected by Nanoscope E multimode atomic force microscope (AFM) in air at room temperature. The zeta potential measurement of the exfoliated LDH suspension and the dynamic light scanning (DLS) were conducted using Malvern Zetasizer Nano ZS. The size and shape of the presented compounds were characterized by SEM (SU-70) and TEM (Tecnai G2 F20 S-TWIN). The chemical structures of salen ligand were confirmed by H^1 NMR (DMX-500). Fourier-transform infrared (FT-IR) spectra in the frequency range of 400~4000 cm^{-1} were recorded on aNexus 670 spectro-meter. Electron spin resonance (ESR) spectra were recorded on Bruker A300.



Scheme S1. The image of exfoliated LDH suspension in formamide with different LDH concerntrations-10g/L, 20g/L, 30g/L and 40g/L (a) after ultrasonic treatment; (b) rested for several days to months.

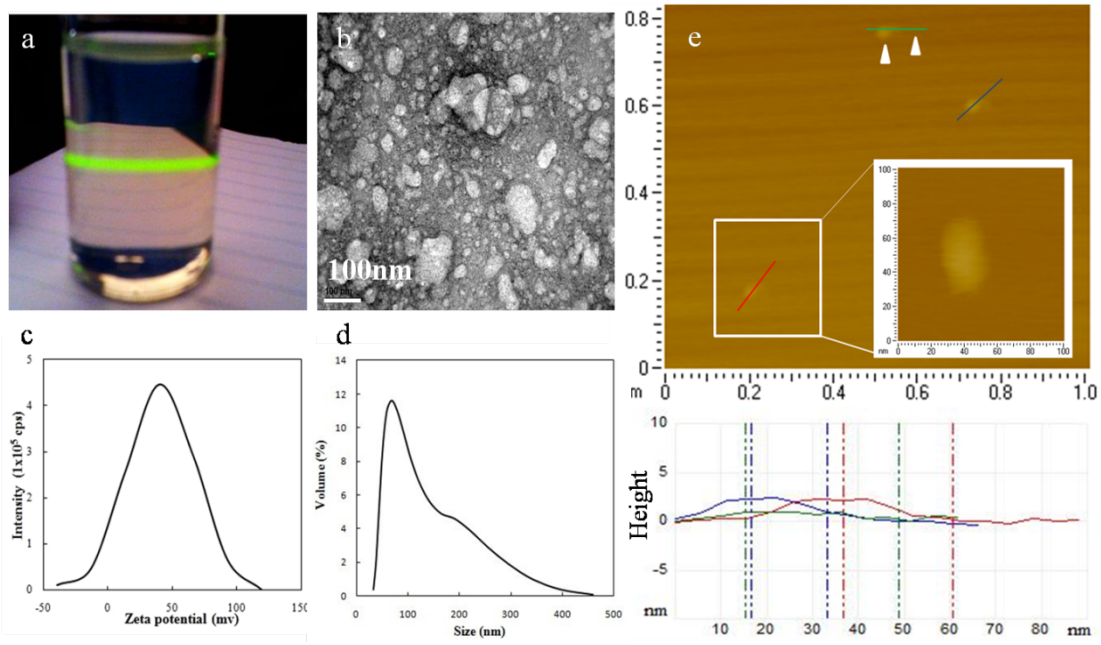
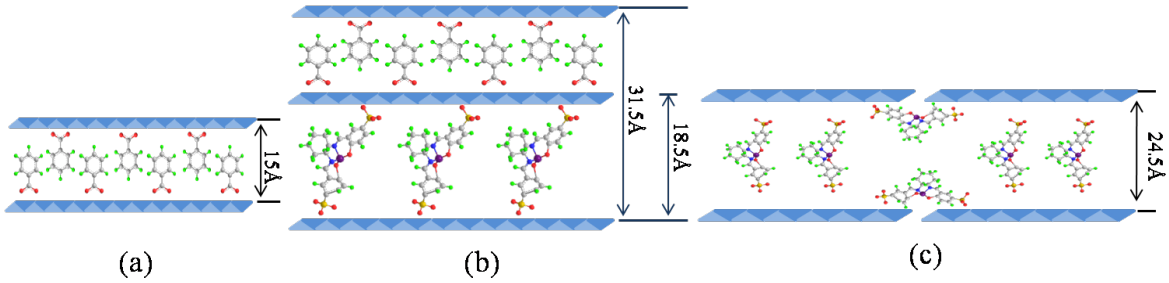


Figure S1. (a) Image of delaminated LDH-BA suspension (10g/L). (b) TEM image. (c)& (d) Zeta potential and DLS curves of LDH-BA nanosheets sol. (e) AFM image of delaminated LDH-BA deposited on a mica substrate and its height profile.

Table S1

Element analysis of Cat.1, Cat.2 and their homogeneous analogue.

compound	Analytical Data (%)			
	C	H	N	Mn
LDH-BA	21.42	4.68	0.33	--
Salen Complex	33.18	3.34	4.11	8.10
Cat.1	15.82	4.49	1.08	1.64
Cat.2	17.85	4.46	1.19	1.80



Scheme S1 Structure diagram of (a) LDH-BA, (b) Cat.1 and (c) Cat.2

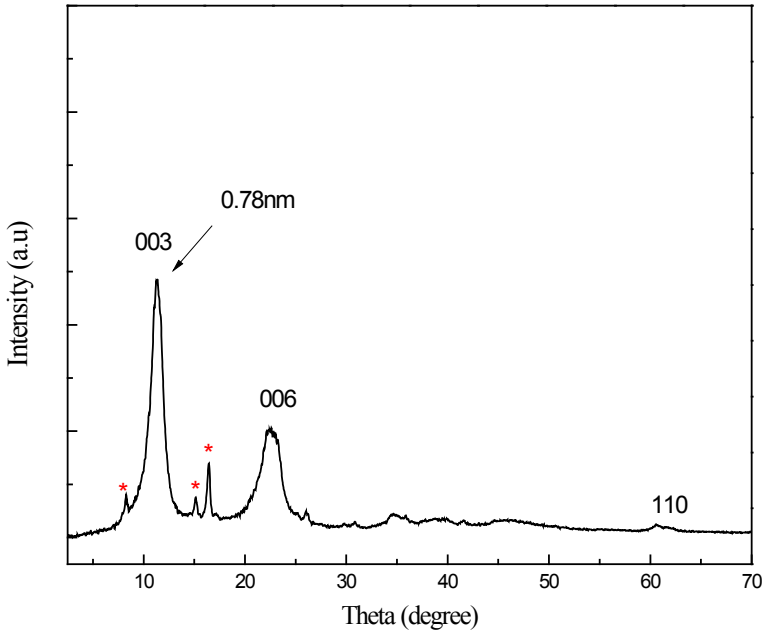


Figure S2 XRD pattern of complex prepared by adding salen complex solution dropwised into LDH-BA nanosheets suspension

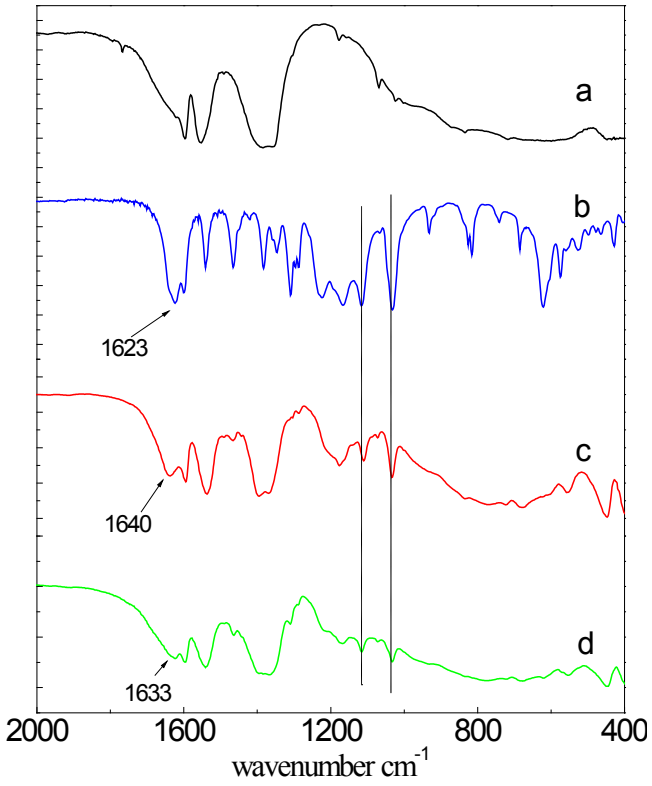


Figure S3 FTIR spectra of (a) LDH-BA, (b) Free Mn(II) salen ligand, (c)Cat.1 and (d) Cat2.

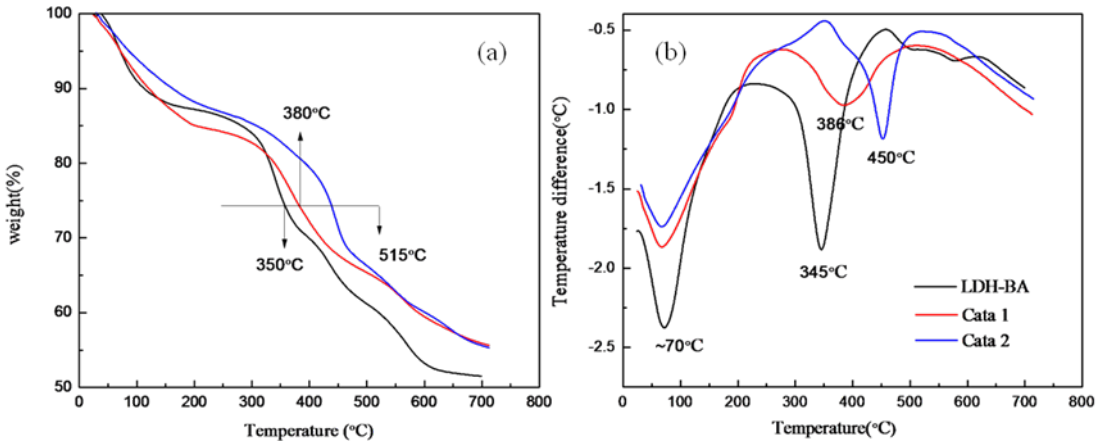


Figure S4 The (a)TGA and (b) DTA spectras of LDH-BA, Cat.1 and Cat2.

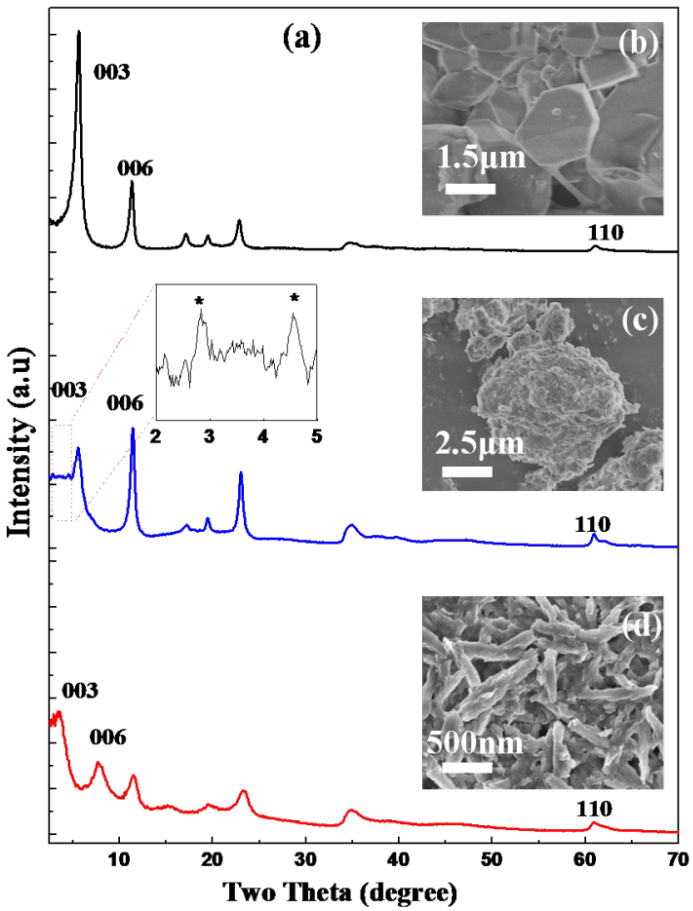


Figure 1 (a) XRD patterns of LDH-BA, Cat.1 and Cat.2 SEM images of (b) LDH-BA, (c) Cat.1 and (d) Cat.2

Table 1 The N-Oxidation of 4-picoline using Cat.1, Cat.2 and their homogeneous analogue[a]

Entry	Catalyst	oxidant	Time/h	Yield(%)[b]	TOF [c]
1	Mono-Salen	H_2O_2	5	77	42
2	Mono-Salen	O_2	24	56	6.2
3	Cat.1	H_2O_2	8	84(83)[d]	176
4	Cat.1	O_2	24	--	--
5	Cat.2	H_2O_2	3.5	95(93)[d]	415
6	Cat.2	O_2	24	22	14
7	LDH	H_2O_2	24	--	--
8	--	H_2O_2	24	--	--

[a] All reactions were carried out using 10mmol 4-picoline and 20 mg catalyst in 20 mL DD water with 0.68g (30mmol) H_2O_2 at room temperature. [b] The yield was detected by HPLC. [c] TOF (turnover frequency) = mmol of product per mmol of catalyst per hour. [d] product yields after 6 recycles.

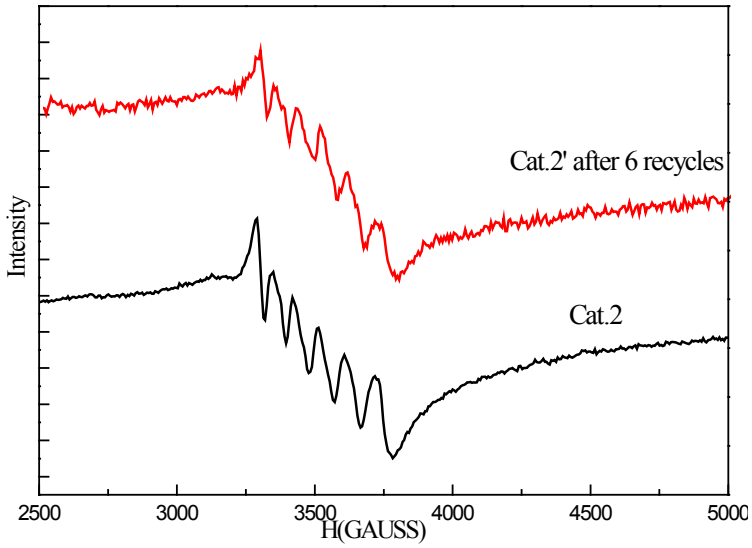


Fig.2 ESR spectra of Cat.2 and Cat.2'(after 6 recycles); EPR spectra: 9.85 GHz, room temperature, 102mW microwave power.

Table S2 The effect of reaction solvent on N-Oxidation of 4-picoline using Cat.2 [a]

Entry	Solvent	Time/h	Yield(%)[b]
1	H_2O	12	95
2	Methanol	12	7.3
3	Ethanol	12	7.5
4	Acetonitrile	12	32
5	Dechloromethane	12	14.3

[a] All reactions were carried out using 10mmol 4-picoline and 20 mg catalyst in 20 mL solvent with 0.68g (30mmol) H_2O_2 at room temperature. [b] The yield was detected by HPLC.