ELECTRONIC SUPPLEMENTARY MATERIAL

Highly-Dispersed Layered Double Oxide Hollow Spheres with Sufficient Active Sites for Adsorption towards Methyl Blue

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1. Experimental Section

Materials

The chemicals used in this experiment were all analytical grade reagents. Typically, $Mg(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, Na_2CO_3, NaOH, D-glucose and boric acid were purchased from Beijing Chemical Reagent Company (Beijing, China). Methyl blue ($C_{37}H_{27}N_3O_9S_3 \cdot Na_2$, biological stain) was obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). In this work, all reagents were used without further purification, and all the aqueous solutions were prepared with deionized water.

Preparation of Carbon Spheres

Carbon spheres (CSs) were synthesized in a hydrothermal reaction containing D-glucose and boric acid.[1] Typically, D-glucose (2.2 mol/L) and boric acid (0.8 mol/L) were dissolved in deionized water by ultrasonic irradiation for 30 min. The solution was transferred to a Teflon-lined stainless steel autoclave and heated at 160 °C for 8 h. The autoclave was then cooled to room temperature. Black precipitates were collected and washed with ethanol for three times. Finally, the brown CSs were obtained and dried in vacuum drying oven at 65 °C.

Preparation of MgFe-layered double hydroxides

MgFe-layered double hydroxides (LDHs) were prepared *via* the co-precipitation method. Briefly, Na_2CO_3 solution (0.5 mol/L, 50.0 mL) was added into a 500 mL four-necked flask. Salt solution, containing 3.8 mmol $Mg(NO_3)_2 \cdot 6H_2O$ and 1.3 mmol $Fe(NO_3)_3 \cdot 9H_2O$, and NaOH solution (50.0 mL, 1.0 mol/L) were simultaneously added into the flask under vigorous stirring. In the whole process, the pH value of the suspension was remained at ~13. The mixture was

aged for 24 h at room temperature. Finally, the product was washed with deionized water for three times and re-dispersed in deionized water for further use.

Preparation of hollow MgFe-layered double oxide (LDO) and ordinary MgFe-LDO

The CSs (0.1 g) was mixed in the as-prepared MgFe-LDHs colloid solution (8.0 mmol/L, 8.0 mL) under ultrasonic irradiation for 15 min. The suspensions were then centrifuged at 3000 r/min for 2 min to remove the excess LDHs. The collected CSs@MgFe-LDHs composites were dried in vacuum drying oven at 65 $^{\circ}$C. The CSs@MgFe-LDHs composites were then calcined in muffle at 500 $^{\circ}$C for 5 h to prepare hollow MgFe-LDO (Scheme S1, the heating rate was set at 5 $^{\circ}$C/min).

Moreover, ordinary MgFe-LDO was prepared as a control experiment. MgFe-LDHs were calcined at the same conditions above. After cooling to room temperature, ordinary MgFe-LDO was obtained.

Adsorption Experiments

The removal efficiency of methyl blue (MB) with different adsorbent dosages was firstly studied: hollow MgFe-LDO powder with quantities ranged from 0.10 g/L to 1.0 g/L was added into MB (80 mg/L, 20.0 mL) aqueous solution under continuous stirring. During the adsorption process, 1.0 mL of suspension was sampled every 5 min until 90 min. The adsorbent in the suspension was collected and the residual MB was analyzed by UV-vis spectrophotometer. For adsorption isotherms, hollow MgFe-LDO of 0.5 g/L and MB ranged in 80−240 mg/L were adopted. For adsorption kinetics, 0.4 g/L hollow MgFe-LDO was selected for the absorption of MB (80 mg/L). To compare the adsorption capacity of hollow MgFe-LDO with ordinary MgFe-LDO, the removal percentage of MB (80 mg/L) was recorded in the presence of 0.5 g/L

absorbents. In addition, the reusability of hollow MgFe-LDO (0.5 g/L) was studied by the repeated calcination and adsorption in MB solution (80 mg/L) for five times. All the adsorption experiments were carried out at room temperature.

Sample Characterizations

The powder X-ray diffractometer (XRD) measurements were carried out on a D8 ADVANCE XRD (Bruker, Germany), operating at a scan rate of 10 °/min with Cu Kα radiation (λ = 1.5406 Å). The 2θ angle of the diffractometer was stepped from 5° to 90°. The zeta potentials of all samples were tested on a Zetasizer 3000HS nanogranularity analyzer (Malvern, UK). FT-IR spectra were measured on a Nicolet 6700 FT-IR spectrometer (Thermo, USA) (resolution of 4.0 cm^{-1}; number of scans: 32). The morphological characterizations of CSs, MgFe-LDHs, CSs@MgFe-LDHs composites and hollow MgFe-LDO were complemented on SUPRA55 scanning electron microscope (SEM) (Zeiss, Germany). High Resolution Transmission electron microscope (HRTEM) images of all samples were recorded on Tecnai G2 F30 with the accelerating voltage of 300 kV (FEI, USA), equipped with energy-dispersive X-ray spectroscopy (EDX) mapping attachment. The ratios of Mg/Fe for all samples were calculated by inductively coupled plasma (ICP) results, which were tested on the iCAP6300 Radial (Thermo Fisher Scientific, US). UV-vis spectra were recorded on UV-3600 (Shimadzu, Japan) in the range of 250−800 nm, and the slit width was set at 1.0 nm. N$_2$ adsorption-desorption isotherms were measured at 77 K by ASAP 2020 nitrogen adsorption apparatus (Micromeritics Ins. Corp., USA). Specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) equation. The pore-size distributions of samples were calculated from Barrett-Joyner-Halenda (BJH) plot.
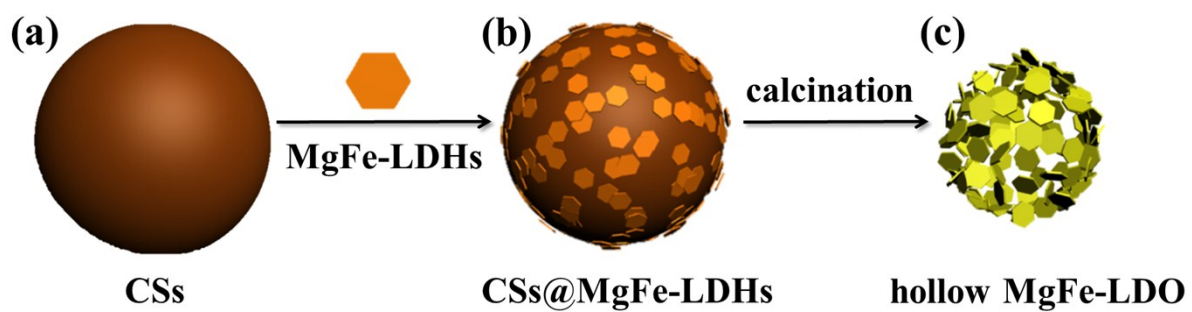
Scheme S1. Schematic representation for the preparation of the hollow MgFe-LDO by CSs and MgFe-LDHs

Table S1. Zeta potentials of CSs, MgFe-LDHs, CSs@ MgFe-LDHs and hollow MgFe-LDO

Sample	Zeta potential/mV
CSs	−36.6
MgFe-LDHs	+17.2
CSs@MgFe-LDHs	−0.535
hollow MgFe-LDO	+9.45

Table S2. ICP results of MgFe-LDH, CSs@MgFe-LDHs and hollow MgFe-LDO

samples	ratio of Mg/Fe from ICP results	feed ratio of Mg/Fe
MgFe-LDH	3.00	3.00
MgFe-LDHs@CSs	2.96	3.00
Hollow MgFe-LDO	2.99	3.00
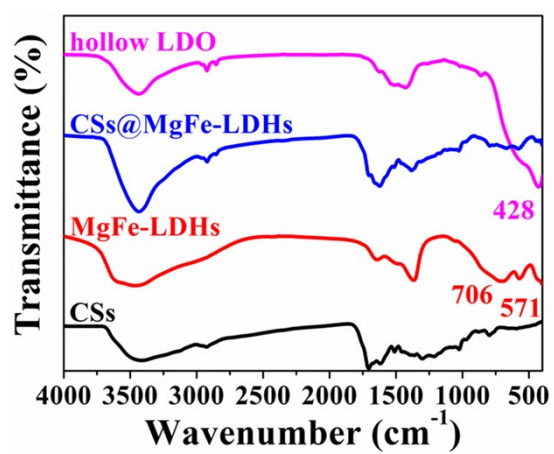
Fig. S1 FT-IR spectra of CSs (black line), MgFe-LDHs (red line), CSs@MgFe-LDHs (blue line) and hollow MgFe-LDO (magenta line).
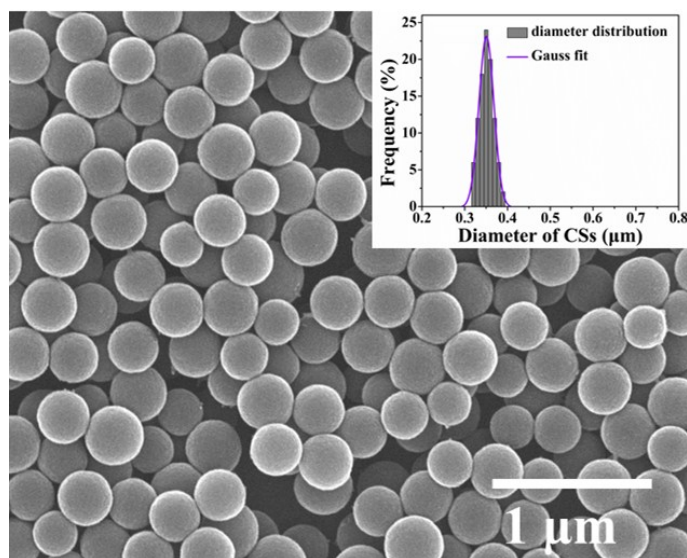
Fig. S2 SEM image and diameter distribution of CSs.
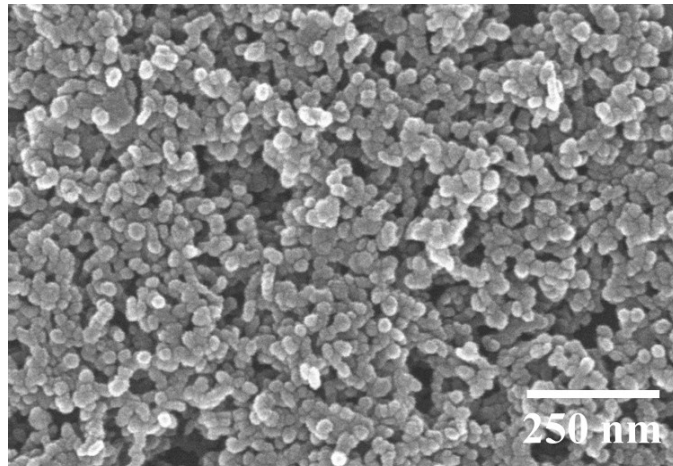
Fig. S3 SEM image of MgFe-LDH nanoparticles.
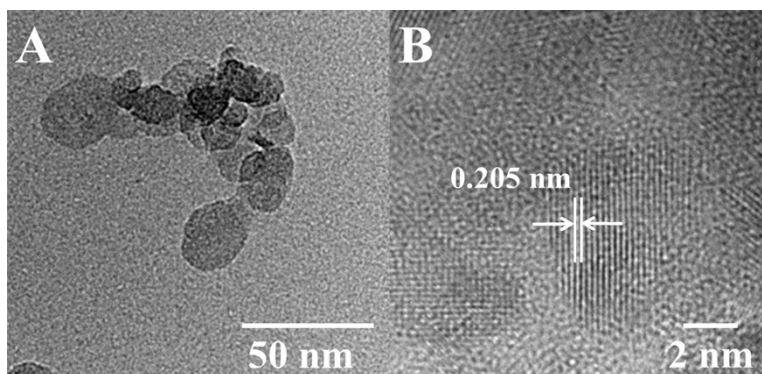
Fig. S4 (A) HRTEM images and (B) the corresponding lattice fringes of the fresh MgFe-LDHs.
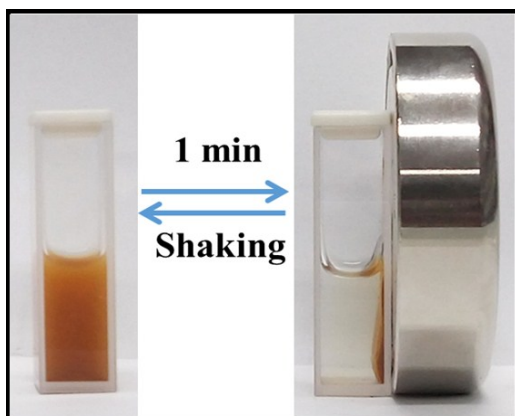
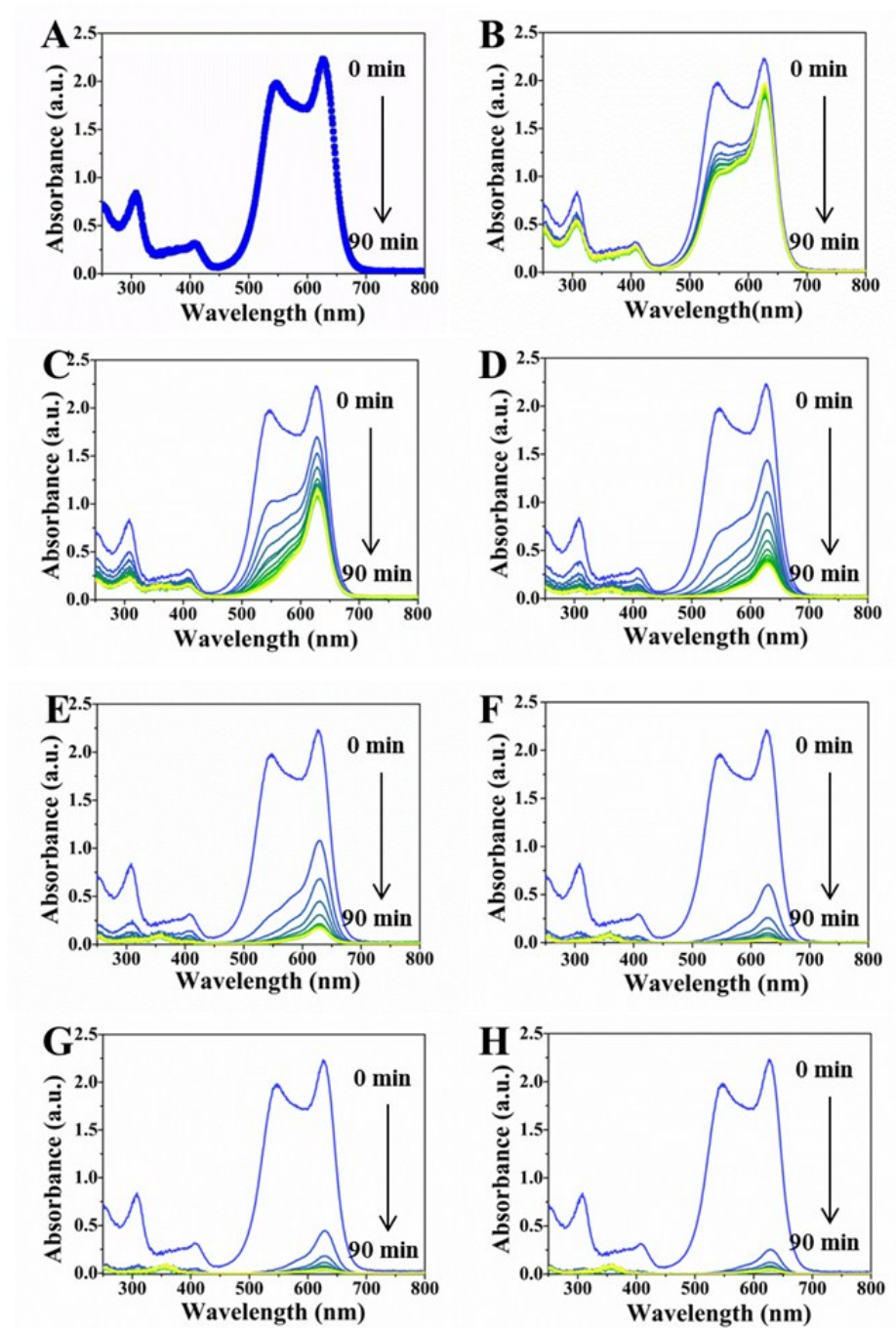**Fig. S5** Magnetic separation and re-dispersion process of hollow MgFe-LDO.

Fig. S6 UV-vis spectra of methyl blue (MB) after adsorption by the hollow MgFe-LDO with different adsorbent dosages: (A) 0 g/L, (B) 0.1 g/L, (C) 0.2 g/L, (D) 0.3 g/L, (E) 0.4 g/L, (F) 0.5 g/L, (G) 0.75 g/L and (H) 1.0 g/L (MB: 80 mg/L).
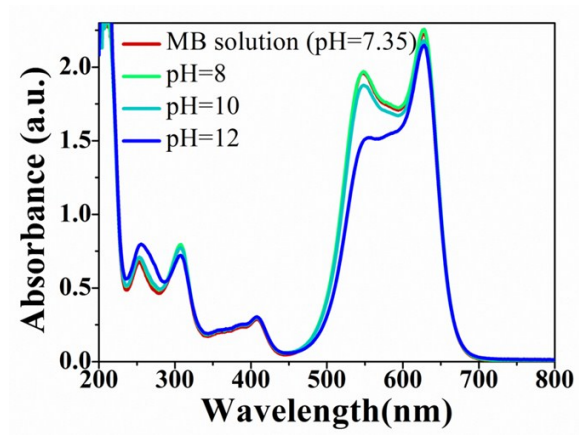
Fig. S7 UV-vis spectra of MB solution (80 mg/L) at different pH values.

Table S3. Removal efficiency of MB after adsorption by hollow MgFe-LDO at different time

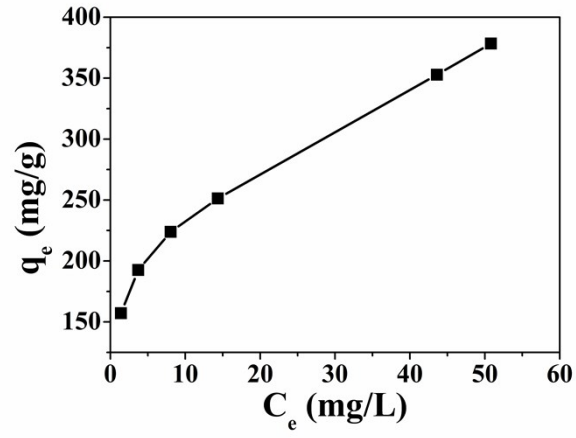| Time (min) Adsorbent dosage (g/L)	0	5	10	15	20	60
0.10	0.00%	12.6%	14.7%	15.2%	16.7%	16.1%
0.20	0.00%	23.5%	31.6%	37.8%	45.9%	52.4%
0.30	0.00%	35.7%	50.2%	60.4%	68.2%	84.0%
0.40	0.00%	51.5%	69.6%	80.1%	86.2%	91.6%
0.50	0.00%	74.6%	90.1%	95.6%	98.4%	98.2%
0.75	0.00%	80.1%	92.0%	97.8%	98.1%	98.5%
1.0	0.00%	88.6%	94.6%	98.1%	98.1%	98.2%

Fig. S8 Adsorption isotherm of MB by hollow MgFe-LDO.

Table S4. Langmuir and Freundlich isotherm parameters of the adsorption of MB by hollow MgFe-LDO (adsorbent dose: 0.5 g/L, MB: 80−240 mg/L)

isotherm	parameters	value	R^2
Langmuir	q_{max} (mg·g^{-1})	398.4	0.9925
	b (L·mg^{-1})	0.2430	
Freundlich	k_f (mg·g^{-1})	140.3	0.9919
	$1/n$	0.2456	

Table S5. Adsorption efficiency comparisons for different systems

adsorbent	adsorption capacity (mg·g⁻¹)	equilibrium time (min)	ref
Polyacrylonitrile fiber	161.0	250	2
Layered double hydroxide−carbon dot	185.0	20	3
Magnetic chitosan and graphene oxide	95.16	60	4
Fe_3O_4@PDA/PEI	170.0	60	5
Konjac glucomannan/graphene oxide hydrogel	92.30	480	6
Mn/MCM-41	45.38	120	7
Hollow MgFe-LDO	398.0	20	In our work

Table S6. Parameters of kinetic models for the adsorption of MB by the hollow MgFe-LDO (adsorbent dose: 0.4 g/L, MB: 80 mg/L)

kinetic models	parameters	value	R^2
pseudo–first–order	q_e (mg·g^{-1})	188.4	0.9884
	$k_1 \times 10^3$ (min^{-1})	141.4	
pseudo–second–order	q_e (mg·g^{-1})	226.8	0.9999
	$k_2 \times 10^3$ (g·mg^{-1}·min^{-1})	4.410	
intra–particle diffusion	k_i (mg·g^{-1}·min$^{0.5}$)	28.43	0.9606
	C	44.71	
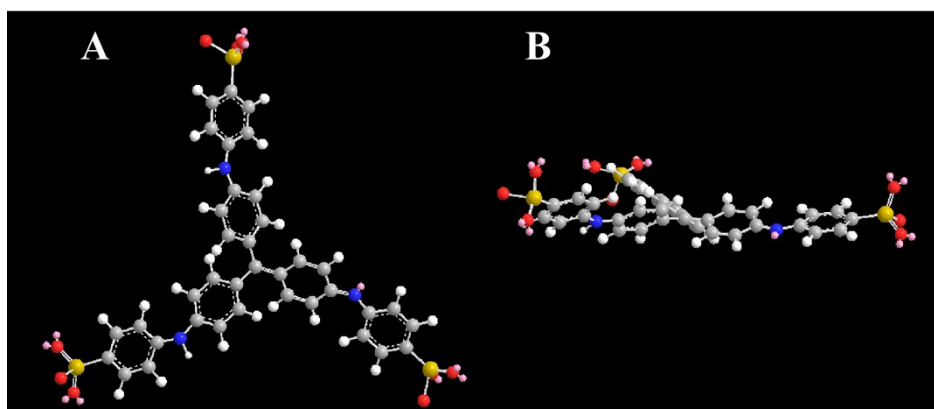
Fig. S9 Schematic diagrams of the molecular structure of MB in different directions.
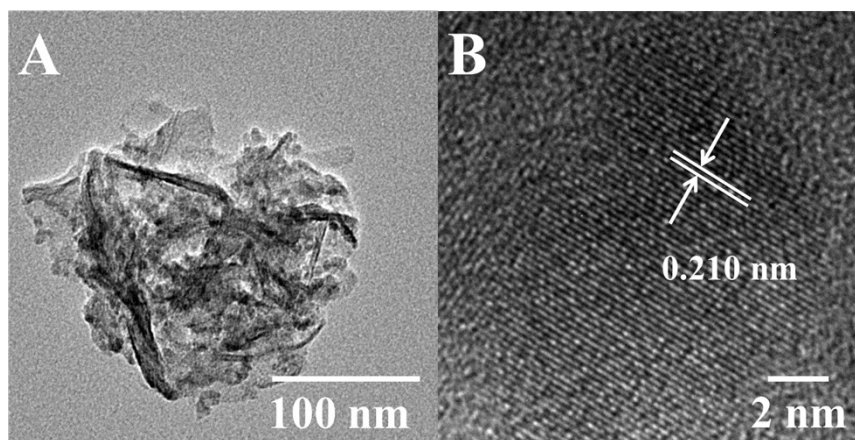
Fig. S10 (A) HRTEM images and (B) the corresponding lattice fringes of used hollow MgFe-LDO.
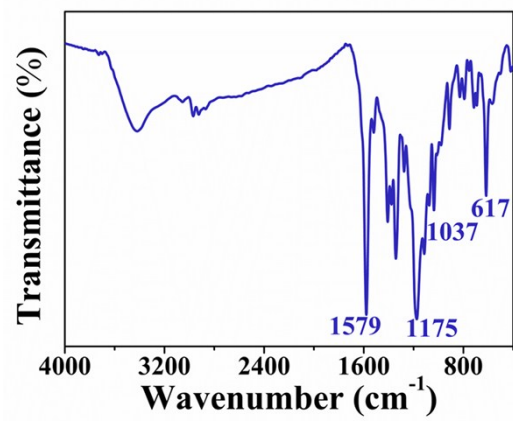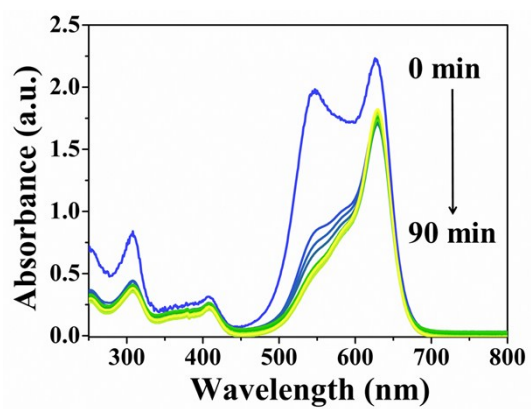
Fig. S11 FT-IR spectrum of MB powder.

Fig. S12 UV-vis spectra of MB after adsorption by the ordinary LDO (adsorbent dosage: 0.5 g/L, MB: 80 mg/L).
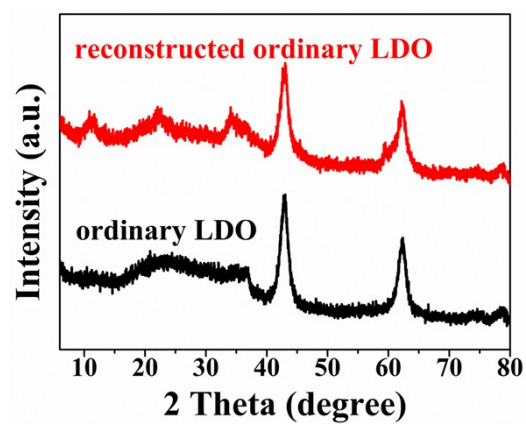
Fig. S13 XRD patterns of ordinary MgFe-LDO before and after adsorption of MB (ordinary MgFe-LDO: 0.5 g/L, MB: 80 mg/L).
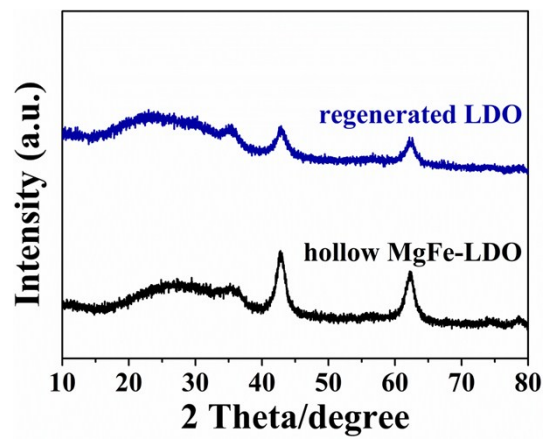
Fig. S14 XRD patterns of hollow MgFe-LDO after the regenerated calcination process.
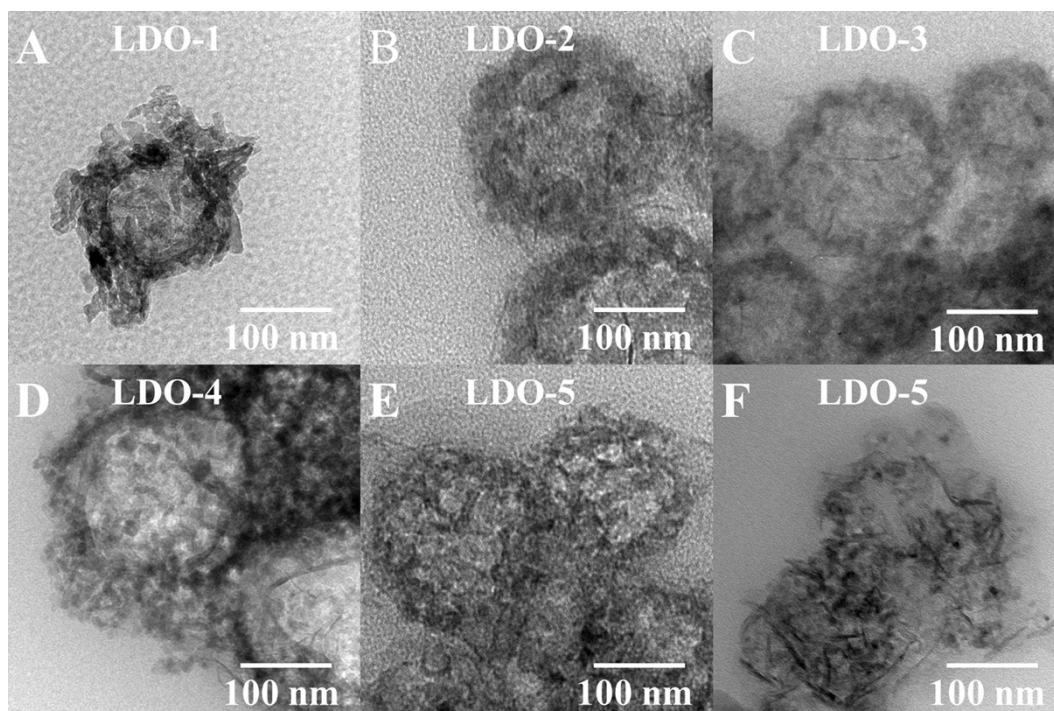
Fig. S15 TEM images of regenerated hollow MgFe-LDO for the five-time cycling measurements, LDO-*n* (*n*＞1) were the products after thermal regenerations of hollow LDO.
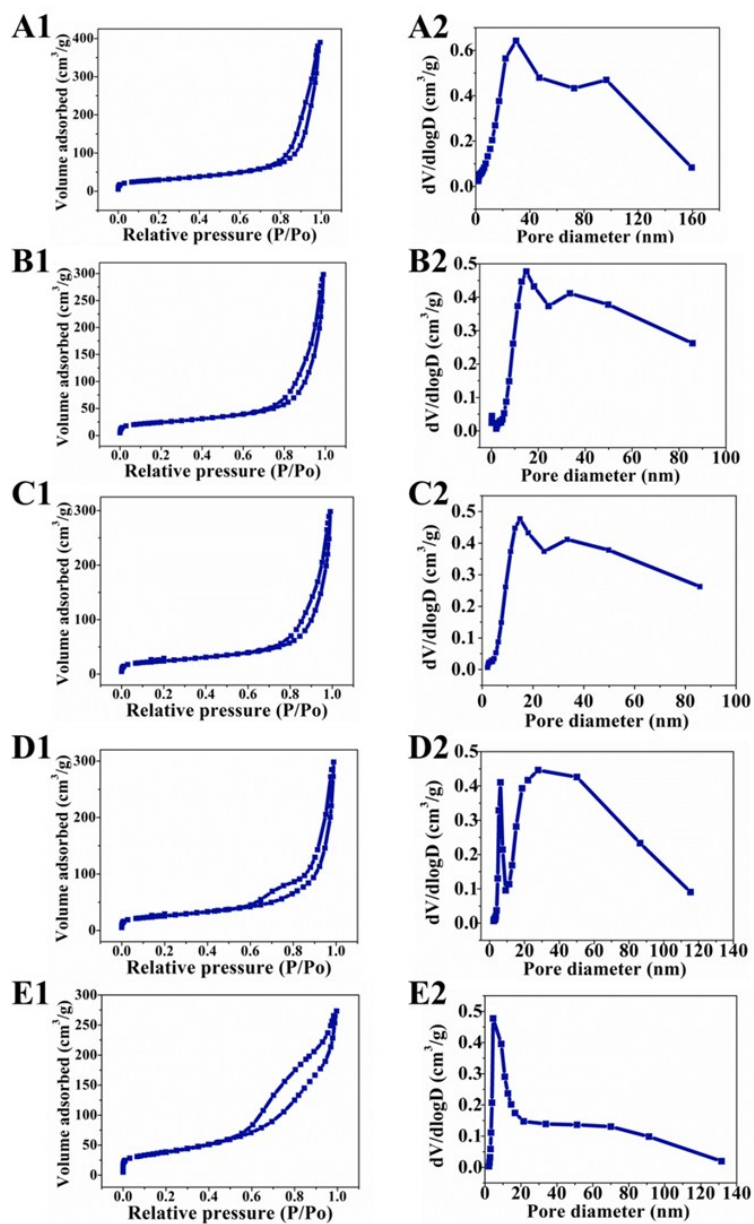
Fig. S16 (A1~E1) N$_2$ adsorption−desorption isotherms and (A2~E2) pore size distributions of LDO-*n*, LDO-*n* (*n*＞1) were the products after thermal regenerations of hollow LDO.

Table S7. Structural parameters of hollow MgFe-LDO during five-time cycling test

samples	BET surface area (m^2/g)	total pore volume (cm^3/g)	average pore width (nm)
LDO-1	99.3	0.655	23.3
LDO-2	105	0.604	19.1
LDO-3	86.8	0.461	17.7
LDO-4	92.8	0.461	16.4
LDO-5	138	0.414	8.20

Reference:

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