

# Supporting Information

## Hierarchically Ordered Macroporous-Mesoporous (HOM-m) $\text{MgFe}_2\text{O}_4/\text{MgO}$ for Highly Efficient Adsorption of Ce(III) and La(III): Experimental Study and DFT Calculation Analysis

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**Text S1. Preparation of polystyrene colloidal crystal template.****(1) Preparation of polystyrene microspheres by soap-free emulsion polymerization:**

Firstly, polystyrene was refined. Polystyrene was washed 5-6 times with a 5%-10% mass fraction NaOH solution and neutralized with distilled water. Then, 0.2 g NaCl, 40 mL St, and 550 mL deionized water were sequentially added to a three-necked flask. When the water bath temperature reached 70 °C, potassium persulfate solution was added to initiate the polymerization of styrene. Throughout the polymerization process, N<sub>2</sub> was passed to exclude oxygen. After complete polymerization for 24 hours, the reaction mixture was cooled to room temperature. The upper clear liquid was removed by centrifugation, and the polystyrene microspheres were washed multiple times with water. Finally, the washed polystyrene microspheres were dispersed in H<sub>2</sub>O.

**(2) Preparation of colloidal crystal template by constant temperature suspension film formation method:**

According to the principle of constant temperature suspension film formation, PS microspheres self-assemble into colloidal crystal templates. Since the density of polystyrene is greater than that of water, it settles at the bottom of the container when left at room temperature for a long time. When the emulsion is placed in an environment with a temperature of 70-90 °C, PS microspheres will suspend above the water surface, forming a densely packed thin film. Therefore, heating a 3%-5% mass fraction polystyrene emulsion in a water bath at 80 °C until completely dried can produce a polystyrene colloidal crystal template.

## Text S2. Calculation methods for pore size, pore volume, and specific surface area.

The calculations of pore size, pore volume and specific surface area all refer to the previous literature <sup>[1]</sup>. The Brunauer–Emmett–Teller (BET) theory is developed on the basis of Langmuir monolayer adsorption theory. It assumes that adsorption can be multilayered, and in the process of physical adsorption, the interaction between adsorbate molecules is the van der Waals force.

### (1) Calculation of specific surface area:

Calculate  $V_m$  according to BET Equation (1):

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{P}{P_0} \quad (1)$$

In the formula,  $V_m$  is the adsorption capacity of a single molecular layer, and  $C$  is a constant related to the adsorption heat.  $V$  is the adsorption capacity at different relative pressures, where  $P$  is the equilibrium pressure of the adsorbate and  $P_0$  is the saturated vapor pressure of the adsorbate at that temperature.  $S_{BET}$  according to Equation (2):

$$S_{BET} = \frac{V_m N_A A_m}{22400} \quad (2)$$

$N_A$  is Avogadro's constant and  $A_m$  is the cross-sectional area.

### (2) Calculation of pore size:

During the desorption process, the pore size is calculated by assuming the geometry of the pores (such as a cylindrical shape) based on the adsorption capacity pressure data of the desorption branch.

Calculate pore size according to Equation (3):

$$\ln \frac{P}{P_0} = \frac{2\gamma V_m}{rRT} \quad (3)$$

In the formula,  $\gamma$  is the surface tension of the adsorbate,  $V_m$  is the molar volume of the adsorbate,  $r$  is the radius of the meniscus formed in the mesopore,  $R$  is the gas constant, and  $T$  is the temperature.

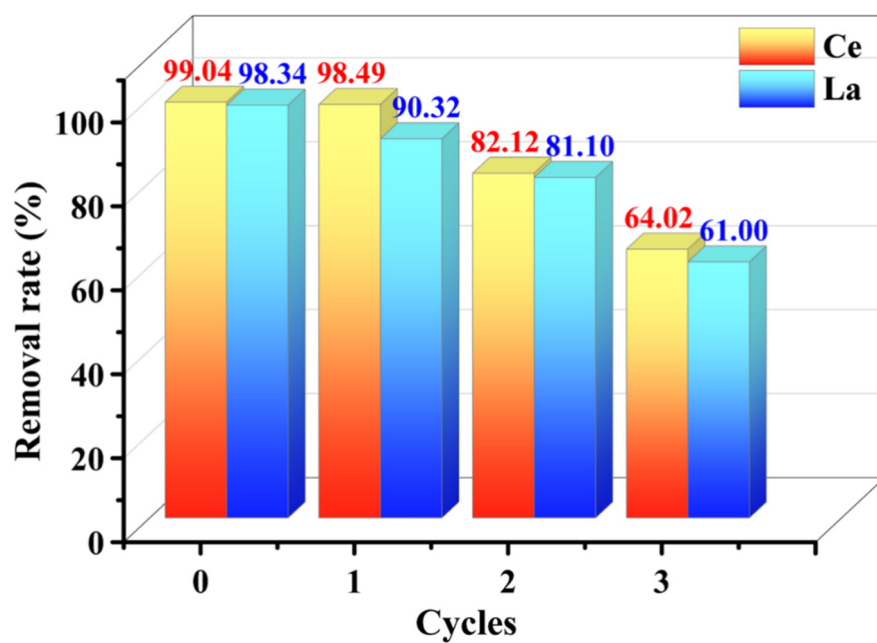
### (3) Calculation of pore volume:

The total pore volume is usually at relatively high pressures (close to but less than 1, usually around 0.99), when the adsorbate (such as nitrogen) almost fills all the pores. Calculate pore volume according to Equation (4):

$$V_p = \frac{V}{V_m} \quad (4)$$

In the formula,  $V_{ads}$  is the adsorption capacity of the adsorbate at a relative pressure close to 1,  $V_m$  is the molar volume of nitrogen gas, and  $V_p$  is the pore volume.

[1] Bardestani R., Patience G. S., Kaliaguine S., 2019. Experimental methods in chemical engineering: specific surface area and pore size distribution measurements BET, BJH, DFT. Can. J. Chem. Eng., 97(11), 2781. <https://doi.org/10.1002/cjce.23632>



**Figure S1.** The removal rate for La(III)和 Ce(III) as a function of adsorption–desorption cycles.

**Table S1**

Supplier, mass fraction purity, and CAS registry number of chemicals.

Component	Mass fraction	Suppliers	CAS Reg. No.
CH <sub>3</sub> CH <sub>2</sub> OH	>99.7%	Xilong Scientific Co., Ltd	64-17-5
NaCl	>99.5%	Xilong Scientific Co., Ltd	7647-14-5
NH <sub>4</sub> Cl	>99.5%	Xilong Scientific Co., Ltd	12125-02-9
AlCl <sub>3</sub> ·6H <sub>2</sub> O	>98.0%	Xilong Scientific Co., Ltd	7784-13-6
CH <sub>3</sub> OH	>99.5%	Xilong Scientific Co., Ltd	67-56-1
C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	>99.5%	Xilong Scientific Co., Ltd	107-21-1
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	>99.0%	Xilong Scientific Co., Ltd	13446-18-9
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	>98.5%	Shanghai Macklin Biochemical Co., Ltd	7782-61-8
La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	>99%	Shanghai Macklin Biochemical Co., Ltd	10277-43-7
Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	>99.5%	Shanghai Macklin Biochemical Co., Ltd	10294-41-4
St	>99.5%	Shanghai Macklin Biochemical Co., Ltd	100-42-5
HCl		Shanghai Macklin Biochemical Co., Ltd	7647-01-0
MgCl <sub>2</sub> ·6H <sub>2</sub> O	>99%	Shanghai Macklin Biochemical Co., Ltd	7786-30-3
FeCl <sub>3</sub> ·6H <sub>2</sub> O	>99.0%	Sinopharm Group Chemical Reagent Co., Ltd	10025-77-1
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	>99.5%	Sinopharm Group Chemical Reagent Co., Ltd	7727-21-1
C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	>99.5%	Sinopharm Group Chemical Reagent Co., Ltd	5949-29-1
CaCl <sub>2</sub>	>96.0%	Tianjin Kemiou Chemical Reagent Co., Ltd	10043-52-4
Pluronic F127		Sigma Aldrich Trading Co., Ltd	9003-11-6

**Table S2**

Equations and parameters used in kinetics and isotherm models.

Model	Equation	Parameters
Pseudo-first-order	$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 \cdot t$	$q_t$ (mg/g) is the adsorption capacity at time $t$ (min), $k_1$ (min <sup>-1</sup> ) is PFOM rate constant
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$	$k_2$ (mg/(g·min)) is PSOM rate constant
Intra-particle diffusion	$q_t = K_i \cdot t^{0.5} + C$	$K_i$ (mg/(g·min <sup>0.5</sup> )) is DI model rate constant
Langmuir	$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$	$q_m$ (mg/g) is maximum adsorption capacity; $K_L$ (L/mg) is Langmuir constant
Freundlich	$q_e = K_F \cdot C_e^{\frac{1}{n}}$	$K_F$ ((mg/g)(L/mg) <sup>1/n</sup> ) is Freundlich constant; $1/n$ is adsorption strength

**Table S3**

Pseudo-first-order kinetic model correlation coefficients of the adsorption of Ce(III) and La(III) by HOM-m MgFe<sub>2</sub>O<sub>4</sub>/MgO.

	$k_1$ (min <sup>-1</sup> )	$q_{e, \text{exp}}$ (mg·g <sup>-1</sup> )	$q_{e, \text{cal}}$ (mg·g <sup>-1</sup> )	$R^2$
Ce(III)	0.0112	835.34	11.0498	0.7396
La(III)	0.0083	663.96	9.9620	0.6071

**Table S4**

Pseudo-second-order kinetic model correlation coefficients of the adsorption of Ce(III) and La(III) by HOM-m MgFe<sub>2</sub>O<sub>4</sub>/MgO.

	$k_2$ (g·mg <sup>-1</sup> ·min <sup>-1</sup> )	$q_{e, \text{exp}}$ (mg·g <sup>-1</sup> )	$q_{e, \text{cal}}$ (mg·g <sup>-1</sup> )	$R^2$
Ce(III)	0.0003	835.34	833.3333	0.99992
La(III)	0.0004	663.96	653.5948	0.99995

**Table S5**

Intra-particle diffusion model correlation coefficients of the adsorption of Ce(III) and La(III) by HOM-m MgFe<sub>2</sub>O<sub>4</sub>/MgO.

	$K_{d1}$	$R_1^2$	$K_{d2}$	$R_2^2$	$K_{d3}$	$R_3^2$
Ce(III)	221.03	0.9683	25.61	0.9716	3.69	0.9961
La(III)	171.74	0.9981	15.68	1.0000	3.05	0.8940

**Table S6**

Adsorption isotherm parameters for Ce(III) and La(III) adsorption on HOM-m MgFe<sub>2</sub>O<sub>4</sub>/MgO.

		Langmuir			Freundlich		
		$q_m$ (mg·g <sup>-1</sup> )	$K_L$	$R^2$	$K_F$	1/n	$R^2$
Ce(III)	25°C	5689.69	0.0014	0.9555	133.7940	0.4514	0.9807
	35°C	5932.56	0.0017	0.9650	150.0198	0.4505	0.9804
	45°C	6320.60	0.0018	0.9632	178.9414	0.4398	0.9834
La(III)	25°C	2123.50	0.0026	0.9626	130.1908	0.3369	0.9842
	35°C	2528.02	0.0029	0.9551	181.5064	0.3200	0.9823
	45°C	2953.45	0.0036	0.9528	263.0802	0.2966	0.9739

**Table S7**

Thermodynamic parameters for Ce(III) and La(III) removal by HOM-m  $\text{MgFe}_2\text{O}_4/\text{MgO}$ .

		$K_p$	$\Delta G^0$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	$\Delta H^0$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	$\Delta S^0$ ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
Ce(III)	25°C	2.4949	-2.46	9.50	37.06
	35°C	2.8190	-2.87		
	45°C	3.0652	-3.20		
La(III)	25°C	2.3953	-2.35	11.19	41.83
	35°C	2.6648	-2.72		
	45°C	3.0543	-3.19		

**Table S8**

The content of XPS elements on the surface of the sample before and after the adsorption of Ce(III) and La(III) by adsorbents.

Sample	Atomic (%)					
	C	O	Mg	Fe	Ce	La
$\text{MgFe}_2\text{O}_4/\text{MgO}$	39.09	43.95	9.94	7.02	-	-
$\text{MgFe}_2\text{O}_4/\text{MgO-Ce}$	34.04	48.53	6.15	6.33	4.95	-
$\text{MgFe}_2\text{O}_4/\text{MgO-La}$	33.60	50.78	5.38	6.00	-	4.23