Supporting information

Synthesis and characterization of magnetic mesoporous nanoparticles Fe₃O₄@mSiO₂-DODGA for adsorption of 16 rare earth elements

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**Material preparation**

**Synthesis of Fe₃O₄@mSiO₂@NH₂**

Fe₃O₄ magnetic nanoparticles were synthesized by solvothermal reaction according to the literature\(^1\). Typically, FeCl₃ (6 m mol, 1.62 g) and carbamide (30 m mol, 1.80 g) were dissolved in ethylene glycol (58 mL) and water (2 mL). The obtained mixture was stirred vigorously at room temperature for 30 min and added subsequently into a Teflon-lined stainless autoclave. The autoclave was sealed and placed in a muffle furnace. The increasing temperature programmed was set from room temperature to 200 °C in 1 h and remained 200 °C for 16 h, followed by cooling to room temperature. The black precipitate was collected by an external magnetic field and purified by washing sequentially with ethanol and ultrapure water for three times, respectively.

The Fe₃O₄@mSiO₂ particles were synthesized according to the reported method\(^2,3\). Briefly, Fe₃O₄ magnetic nanoparticles (0.3 g) was added into a mixed solution of ethanol (160 mL) and ultrapure water (40 mL). The dispersion mixture was sonicated for 30 min to make the nanoparticles disperse evenly. After that, the concentrated ammonia aqueous solution (5 mL, 25 wt%) and TEOS (3.1 m mol, 0.7 mL) was added to make sol-gel reaction occurred on the surface of the particles. The mixture was stirring for 8 h at 40 °C. Finally, the Fe₃O₄@mSiO₂ particles were separated and washed with ethanol and ultrapure water respectively, dried under vacuum.

The mesoporous SiO2 layer coated on SiO2 shell was prepared with the following method. Typically, Fe₃O₄@mSiO₂ particles (0.4 g) was added into a mixed solution of ethanol (30 mL) and ultrapure water (20 mL). The dispersion mixture was sonicated for 10 min. the concentrated ammonia aqueous solution (1 mL, 28 wt%), CTAB (0.9 g) and TEOS (9 mmol, 2.0 mL) was added subsequently. The mixture was stirring for 10 h at room temperature. The Fe₃O₄@mSiO₂ particles were separated and washed with ethanol and ultrapure water. To remove CTAB\(^4\), the obtained Fe₃O₄@mSiO₂ particles were added into a mixed solution of ethanol (150 mL) and NH₄NO₃ (0.9 g). The mixture was refluxed for 3 h.

Amine functionalization nanoparticles Fe₃O₄@mSiO₂@NH₂ were prepared by reacting with APTES\(^5\). Briefly, anhydrous toluene (50 mL) and Fe₃O₄@mSiO₂ particles (0.4 g) were added in a three-neck flask. The mixture was sonicated for 30 min to make the particles disperse. APTES (4 mL) was added into the flask. The reaction was going on under nitrogen gas protection at 120 °C for 24 h. The resultant Fe₃O₄@mSiO₂@NH₂ nanoparticles were washed with anhydrous toluene and acetone for three times, respectively, and dried under vacuum.

**Synthesis of DODGA-Cl**

The synthesis of DODGA-Cl was referred the literature\(^6,7\). Diglycolic acid (37.3 mM, 5.0 g) was dissolved in acid anhydride (132.2 mM, 12.5 mL) under a nitrogen atmosphere. The mixture was stirred and heated to reflux. After refluxing for 10 min, 3 drops of
phosphoric acid were added into the reaction mixture to catalysis the reaction. The solution was stirred under reflux conditions for 2 hour. The resulting solution was concentrated through rotary evaporation under reduced pressure. The final solution was poured into the toluene to recrystallize the products. After filtrating the solid generated in toluene, a white needle-like product (3.6 g, 83% yield) was obtained to be used directly in the next synthesis step.

In the second step, didocylamine (16.0 m mol, 3.86 g) was placed in a 250 ml round bottom flask and dissolved in DCM (150 ml), glycolic anhydride (22.4 m mol, 2.62 g) was added, and the mixture was stirred at room temperature for 2 h. The end of the reaction was controlled by TLC (DCM/MeOH 8:2). The mixture was concentrated; and the residue was taken up in ethyl acetate, washed successively with 0.1N HCl (∼2) and sat. NaCl, and dried over Na2SO4. Evaporation of the solvent gave the title compound as an oil which crystallized on standing (5.00 g, 87.5%).

Converting the DODGA-OH to its acyl chloride derivative was referred the normal organic reaction operation. Typically, DODGA-OH (10 m mol, 3.60 g) was dissolved in the solvent of CH2Cl2 (30 mL). Anhydrous oxalyl chloride (15 m mol, 1.3mL) was added into the mixture. After stirring for 10 min, 2 drops of DMF was added to catalyze the reaction. The reaction was monitored by thin layer chromatography. At the end of the reaction, the solvent and excessive oxalyl chloride was removed by rotary evaporating. The residue was DODGA-Cl (3.30 g, 87.2%) that could be used directly to modify magnetic particles.

Modifying the Fe3O4 particles with the functional unit of DODGA

The functionalized Fe3O4 particles were prepared by the reaction between the anime groups on the surface of the Fe3O4@mSiO2@NH2 and the DODGA-Cl. Briefly, the Fe3O4@mSiO2@NH2 (0.3 g) and TEA( 15 m mol, 2.1 mL) was added into the solvent of anhydrous CH2Cl2 ( 30 mL). The mixture was sonicated for 15min. the solution of DODGA-Cl (10 m mol, 3.75 g) in anhydrous CH2Cl2 (10 mL) was dropped slowly into the mixture. The reaction was going on at room temperature for 8 h. The resultant particles were washed with CH2Cl2 and methanol three times respectively, and dried under vacuum.
Figure S1. The mass spectra of DODGA

Figure S2. The mass spectra of Glycolic anhydride
Figure S3. The $^1$H NMR spectra of DODGA
$^1$H NMR (400 MHz, Chloroform-$d$) δ 4.41 (s, 1H), 4.23 (s, 1H), 3.37 (dd, $J = 9.0, 6.6$ Hz, 1H), 3.19-3.03 (m, 1H), 1.68-1.50 (m, 2H), 1.31 (s, 10H), 0.91 (td, $J = 6.8, 3.0$ Hz, 3H).

Figure S4. The $^1$H NMR spectra of Glycolic anhydride
$^1$H NMR (400 MHz, Chloroform-$d$) δ 4.42 (d, $J = 1.4$ Hz, 4H).
Figure S5. The $^{13}$C NMR spectra of DODGA

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.84, 170.61, 72.94, 71.20, 46.87, 46.84, 31.75, 31.69, 29.25, 29.18, 29.16, 29.11, 28.61, 27.39, 26.92, 26.80, 22.60, 22.57, 14.05, 14.03. MS (ESI): calcd. for C$_{20}$H$_{39}$NO$_4$: 357.29; found:358.60.

Figure S6. The $^{13}$C NMR spectra of Glycolic anhydride

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 162.87, 64.67. MS (ESI): calcd. for C$_4$H$_4$O$_4$: 116.01; found:117.10.
Adsorption kinetics

Pseudo-first order kinetic model

\[ q_t = q_e \left(1 - e^{-k_1 t}\right) \]

Where \( q_e (\text{mg} \cdot \text{g}^{-1}) \) and \( q_t (\text{mg} \cdot \text{g}^{-1}) \) refer to the amounts of REEs adsorbed at equilibrium and designed time, respectively. \( k_1 (\text{min}^{-1}) \) Pseudo-first order reaction rate constant.

| Elements | Equation | Parameter | \( R^2 \) | \( q_e \) | \( k_1 \) |
|----------|----------|-----------|---------|--------|--------|
| Nd       | \( q_e=57.36(1-e^{-0.089t}) \) | 0.9000 | 57.362 | 0.0891 |
| Sm       | \( q_e=26.65(1-e^{-0.066t}) \) | 0.9755 | 26.6529 | 0.0665 |
| Eu       | \( q_e=35.40(1-e^{-0.188t}) \) | 0.7948 | 35.3960 | 0.1882 |
| Ho       | \( q_e=16.43(1-e^{-0.095t}) \) | 0.9561 | 16.428 | 0.0927 |
| Yb       | \( q_e=33.16(1-e^{-0.160t}) \) | 0.9761 | 33.1592 | 0.1052 |
| Lu       | \( q_e=39.29(1-e^{-0.265t}) \) | 0.5491 | 39.2897 | 0.2851 |
| Y        | \( q_e=15.60(1-e^{-0.103t}) \) | 0.9592 | 15.6051 | 0.1032 |
| Sc       | \( q_e=13.85(1-e^{-0.088t}) \) | 0.9106 | 13.8479 | 0.0881 |

Pseudo-second-order model

\[ \frac{t}{q_t} = \frac{1}{2k_2q_e^2} + \frac{1}{q_e} \]

Where \( k_2 \) was pseudo-second-order reaction rate constant \( (\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}) \), the initial adsorption rate \( h (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}) \) was calculated from the following equation: \( h = k_2q_e^2 \)

| Elements | Equation | Parameter | \( R^2 \) | \( q_e \) | \( k_2 \) |
|----------|----------|-----------|---------|--------|--------|
| Nd       | \( t/q_e=0.1484+0.0162t \) | 0.9997 | 61.7584 | 282.7313 |
| Sm       | \( t/q_e=0.3136+0.0357t \) | 0.9998 | 28.0112 | 123.0296 |
| Eu       | \( t/q_e=0.0828+0.027t \) | 1.0000 | 37.0370 | 56.7901 |
| Ho       | \( t/q_e=0.4107+0.0578t \) | 0.9997 | 17.3010 | 61.4666 |
| Yb       | \( t/q_e=0.1515+0.0289t \) | 0.9999 | 34.6021 | 90.6958 |
| Lu       | \( t/q_e=0.095+0.0237t \) | 0.9998 | 42.1941 | 84.5662 |
| Y        | \( t/q_e=0.3802+0.0608t \) | 0.9999 | 16.4474 | 51.4251 |
| Sc       | \( t/q_e=0.5058+0.0687t \) | 0.9997 | 14.5506 | 53.5840 |
Intra-particle diffusion model

\[ q_t = k_i t^{1/2} + C \]

Where \( k_i \) was intra-particle diffusion rate constant (mg·g\(^{-1}\)·min\(^{-1/2}\)), \( C \) represented the boundary layer diffusion effect. The larger the value of \( C \), the greater the diffusion effect of the boundary layer.

Table S3. The result of data processing according to intra-particle diffusion model

| Elements | Equation | Parameter |
|----------|----------|-----------|
|          |          | \( R^2 \) | \( k_i \) | \( C \) |
| Nd       | \( q_t = 35.996 + 1.4109 t^{1/2} \) | 0.6592 | 1.4109 | 35.996 |
| Sm       | \( q_t = 14.789 + 0.7398 t^{1/2} \) | 0.5851 | 0.7398 | 14.789 |
| Eu       | \( q_t = 28.686 + 0.4675 t^{1/2} \) | 0.5898 | 0.4675 | 28.686 |
| Ho       | \( q_t = 10.433 + 0.3864 t^{1/2} \) | 0.4838 | 0.3864 | 10.433 |
| Yb       | \( q_t = 22.532 + 0.6897 t^{1/2} \) | 0.5001 | 0.6897 | 22.532 |
| Lu       | \( q_t = 33.574 + 0.4466 t^{1/2} \) | 0.8311 | 0.4466 | 33.574 |
| Y        | \( q_t = 10.419 + 0.3384 t^{1/2} \) | 0.4985 | 0.3384 | 10.419 |
| Sc       | \( q_t = 8.7572 + 0.3277 t^{1/2} \) | 0.4386 | 0.3277 | 8.7572 |

Elovich model

\[ q_t = \frac{\ln (\alpha \beta)}{\beta} + \frac{\ln t}{\beta} \]

Where \( \alpha \) (mg·g\(^{-1}\)·min\(^{-1}\)) was the initial adsorption rate constant, \( \beta \) (mg·g\(^{-1}\)·min\(^{-1}\)) was a parameter related to the surface coverage of the adsorbent and the activation energy of chemical adsorption.

Table S4. The result of data processing according to Elovich model

| Elements | Equation | Parameter |
|----------|----------|-----------|
|          |          | \( R^2 \) | \( \alpha \) | \( \beta \) |
| Nd       | \( q_t = 26.945 \ln t + 14.218 \) | 0.9612 | 45.6711 | 0.03711 |
| Sm       | \( q_t = 14.724 \ln t + 2.5879 \) | 0.9266 | 17.5533 | 0.06792 |
| Eu       | \( q_t = 9.2842 \ln t + 21.003 \) | 0.9298 | 89.1700 | 0.10771 |
| Ho       | \( q_t = 8.2165 \ln t + 3.3692 \) | 0.8744 | 12.38142 | 0.12171 |
| Yb       | \( q_t = 14.55 \ln t + 10.074 \) | 0.8899 | 29.0774 | 0.06873 |
| Lu       | \( q_t = 7.696 \ln t + 27.774 \) | 0.9867 | 284.1745 | 0.12994 |
| Y        | \( q_t = 7.1041 \ln t + 4.3537 \) | 0.8782 | 13.1118 | 0.14076 |
| Sc       | \( q_t = 7.0795 \ln t + 4.3537 \) | 0.8181 | 13.0943 | 0.14125 |
Figure S7. Different adsorption kinetic model of Fe₃O₄@mSiO₂-TODGA for REEs (a. pseudo-first-order, b. pseudo-second-order, c. intra-particle diffusion, d. Elovich model)

Adsorption isotherms

**Langmuir model**

\[
\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}}
\]

Where \(Q_e(\text{mg g}^{-1})\) and \(C_e(\text{mg L}^{-1})\) was the amount of nanoparticles adsorbed and the concentration of REEs in the solution under the equilibrium, respectively; \(Q_{max}(\text{mg g}^{-1})\) was the saturated monolayer adsorption, and \(K_L(\text{L mg}^{-1})\) was the Langmuir constant, which is related to the binding energy of the adsorption system.

| Elements | Equation | Parameter |
|----------|----------|-----------|
|          |          | \(R^2\)  | \(Q_{max}\) | \(K_L\)  | \(R_L\)  |
| Nd       | \(C_e/q_e=0.0145 C_e +0.0109\) | 0.9327  | 68.9655 | 1.3303 | 0.4291 |
| Sm       | \(C_e/q_e=0.0350 C_e +0.0102\) | 0.9987  | 28.5714 | 3.4314 | 0.2256 |
| Eu       | \(C_e/q_e=0.0249 C_e +0.0211\) | 0.9981  | 40.1606 | 1.1801 | 0.4586 |
| Ho       | \(C_e/q_e=0.0579 C_e +0.0439\) | 0.9892  | 17.2712 | 1.3189 | 0.4312 |
| Yb       | \(C_e/q_e=0.0258 C_e +0.0236\) | 0.9911  | 38.7597 | 1.0932 | 0.4777 |
| Lu       | \(C_e/q_e=0.022 C_e +0.0222\) | 0.9900  | 45.4545 | 0.9910 | 0.5022 |
| Y        | \(C_e/q_e=0.0568 C_e +0.0318\) | 0.9919  | 17.6056 | 1.7862 | 0.3589 |
| Sc       | \(C_e/q_e=0.0674 C_e +0.0105\) | 0.9983  | 14.8368 | 6.4190 | 0.1347 |
Freundlich model

\[
\ln(Q_e) = \ln(K_f) + \frac{1}{n} \ln(C_e)
\]

where \(K_f\) and \(n\) was the Freundlich isotherm constant, respectively. \(K_f\) was related to the adsorption amount, and \(n\) was related to the strength of the adsorption. The value of \(1/n\) between 0.1-0.5 indicated that the adsorption process was favorable.

Table S6. The result of data processing according to Freundlich model

| Elements | Equation | Parameter | \(R^2\) | \(K_f\) | \(n\) |
|----------|----------|-----------|---------|---------|-------|
| Nd       | \(\ln(q_e)=0.4574\ln(C_e)+3.4593\) |           | 0.9972  | 31.7947 | 2.1863 |
| Sm       | \(\ln(q_e)=0.2941\ln(C_e)+2.7919\) |           | 0.9366  | 16.3120 | 3.4002 |
| Eu       | \(\ln(q_e)=0.1542\ln(C_e)+3.2662\) |           | 0.9838  | 26.2115 | 6.4851 |
| Ho       | \(\ln(q_e)=0.1808\ln(C_e)+2.3297\) |           | 0.9950  | 10.2794 | 5.5310 |
| Yb       | \(\ln(q_e)=0.7722\ln(C_e)+2.9209\) |           | 0.9828  | 18.5580 | 1.2950 |
| Lu       | \(\ln(q_e)=0.4854\ln(C_e)+2.8683\) |           | 0.9444  | 17.6071 | 2.0602 |
| Y        | \(\ln(q_e)=0.6547\ln(C_e)+2.1791\) |           | 0.9025  | 8.8383  | 1.5274 |
| Sc       | \(\ln(q_e)=0.3962\ln(C_e)+2.2898\) |           | 0.9429  | 9.8730  | 2.5240 |

D-R model

\[\ln Q_e = \ln Q_m - \beta \varepsilon^2\]
\[\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)\]
\[E = (2\beta)^{-0.5}\]

Where \(\beta\) was a constant (mol²·J⁻²) and related to adsorption energy; \(Q_m\) was the theoretical saturated adsorption capacity (mg·g⁻¹); \(\varepsilon\) was Polanyi potential; \(R\) was gas constant (8.314 J·mol⁻¹·K⁻¹), \(T\) was the absolute temperature (K); \(E\) was the average adsorption energy (kJ·mol⁻¹) and represented the energy required to transfer 1 mol of metal ions from the solution to the surface of the solid phase. The value of \(E\) could reflect whether the adsorption mechanism was a physical reaction or a chemical reaction. When \(E>8\) kJ·mol⁻¹, the adsorption process follows chemical adsorption, while \(E<8\) kJ·mol⁻¹, the adsorption process was a physical reaction.

Table S7. The result of data processing according to D-R model

| Elements | Equation | Parameter | \(R^2\) | \(\beta\) (mol²·J⁻²) | \(E\) (kJ·mol⁻¹) | \(Q_{max}\) (mg·g⁻¹) |
|----------|----------|-----------|---------|----------------------|------------------|----------------------|
| Nd       | \(\ln(Q_e) = 3.6081 - 8.001 \times 10^{-9} \varepsilon^2\) |           | 0.9543  | 8.001 \times 10⁻⁹   | 15.81            | 36.8959              |
| Sm       | \(\ln(Q_e) = 3.2104 - 1.137 \times 10^{-9} \varepsilon^2\) |           | 0.9574  | 1.137 \times 10⁻⁸   | 13.26            | 24.7890              |
| Eu       | \(\ln(Q_e) = 3.4517 - 2.801 \times 10^{-9} \varepsilon^2\) |           | 0.953   | 2.801 \times 10⁻⁸   | 8.45             | 31.5540              |
| Ho       | \(\ln(Q_e) = 2.6778 - 1.200 \times 10^{-9} \varepsilon^2\) |           | 0.9603  | 1.200 \times 10⁻⁸   | 12.91            | 14.5530              |
\[ Q_e = B_T \ln K_T + B_T \ln C_e \]

Where the value of the \( B_T \) was calculated from the following equation: \( B_T = (RT)/b_T \), \( R \) was the gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\)), \( b_T \) was the Tempkin constant (J·mol\(^{-1}\)) and related to adsorption heat. \( K_T \) was the equilibrium binding constant (L·g\(^{-1}\)) and related to the maximum binding energy.

### Table S8. The result of data processing according to Tempkin model

| Elements | Equation          | Parameter | \( R^2 \) | \( B_T \) | \( K_T \)     |
|----------|-------------------|-----------|-----------|-----------|---------------|
| Nd       | \( Q_e = 9.0897 \ln C_e + 37.799 \) | 0.8545    | 9.0897    | 63.9718   |
| Sm       | \( Q_e = 3.8971 \ln C_e + 19.61 \) | 0.9702    | 3.8971    | 153.2310  |
| Eu       | \( Q_e = 7.7306 \ln C_e + 21.578 \) | 0.9665    | 7.7396    | 16.2485   |
| Ho       | \( Q_e = 2.2484 \ln C_e + 10.392 \) | 0.9805    | 2.2484    | 101.6925  |
| Yb       | \( Q_e = 8.0659 \ln C_e + 20.264 \) | 0.9395    | 8.0659    | 12.3333   |
| Lu       | \( Q_e = 7.9296 \ln C_e + 23.234 \) | 0.9650    | 7.9196    | 18.7977   |
| Y        | \( Q_e = 3.4884 \ln C_e + 9.9655 \) | 0.8066    | 3.4884    | 17.4049   |
| Sc       | \( Q_e = 2.3076 \ln C_e + 10.189 \) | 0.8240    | 2.3076    | 82.7157   |

### Table S9. 16 kinds of REEs linear standard curve

| Elements | \( Y \)          | \( R^2 \) | Linear range |
|----------|-------------------|-----------|--------------|
| La       | \( Y = 242.396X + 190.248 \) | 0.99969   | 5~1000 µg/L  |
| Ce       | \( Y = 41.843X + 23.1529 \)  | 0.99986   | 5~1000 µg/L  |
| Pr       | \( Y = 33.372X + 32.615 \)   | 0.99997   | 5~1000 µg/L  |
| Nd       | \( Y = 29.463X + 214.024 \)  | 0.99781   | 5~1000 µg/L  |
| Sm       | \( Y = 53.289X + 17.493 \)   | 0.99986   | 5~1000 µg/L  |
| Eu       | \( Y = 120.374X + 23.768 \)  | 0.99999   | 5~1000 µg/L  |
| Gd       | \( Y = 73.411X + 38.238 \)   | 0.99996   | 5~1000 µg/L  |
| Tb       | \( Y = 49.724X + 14.738 \)   | 0.99995   | 5~1000 µg/L  |
| Dy       | \( Y = 83.063X + 0.00 \)     | 0.99784   | 10~1000 µg/L |
| Ho       | \( Y = 35.289X + 17.842 \)   | 0.99996   | 5~1000 µg/L  |
| Er       | \( Y = 54.089X + 2.625 \)    | 0.99999   | 5~1000 µg/L  |
| Tm       | \( Y = 139.274X + 34.453 \)  | 1.00000   | 5~1000 µg/L  |
| Yb       | \( Y = 611.496X + 120.269 \)| 1.00000   | 5~1000 µg/L  |
Table S10. Comparison of the Fe$_3$O$_4$@mSiO$_2$-DODGA with the other conventional materials

| Entry | Materials | Recycling times          | REEs         | Ref. |
|-------|-----------|--------------------------|--------------|------|
| 1     | Fe@CS-DGA | 5/>90%                   | Pb(II)       | 28   |
| 2     | Fe$_3$O$_4$@TODGA | 3/80%, 92%          | Am(III), Pu(IV) | 29   |
| 3     | Fe$_3$O$_4$@ HA-MNPs | 6/95%            | Eu(III)      | 23   |
| 4     | SBA-15-BSEA- Fe$_3$O$_4$-NPs | 5/95%           | Ce(III)      | 18   |

Figure S8. The pore diameter of Fe$_3$O$_4$@mSiO$_2$-DODGA
Figure S9. The pore structure of Fe₃O₄@SiO₂

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