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# Highly efficient extraction of uranium from aqueous solution by imidazole functionalized core-shell sunflower-like superparamagnetic polymer microspheres : Understanding adsorption and binding mechanism

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#### Synthesis of Fe<sub>3</sub>O<sub>4</sub> hollow microspheres prepared by solvothermal method

Water-dispersible monodisperse hollow  $Fe_3O_4$  microspheres were synthesized using a hydrothermal method. In a typical experiment, 5 mmol  $FeCl_3 \cdot 6H_2O$ , 10 mmol sodium citrate were dissolved in 80 ml distilled water to form yellow transparent solution. Then 1 g urea was added in above solution, followed by the addition of 0.6 g PAAS. After 30 min vigorously magnetic stirring, the viscous transparent mixture was transferred to a 100 ml Teflon-lined stainless-steel autoclave and maintained at 200 °C for 12 h. The product was collected with a magnet and washed with distilled water and ethanol for several times. Finally, the sample was dried in a vacuum oven at 45 °C for 12 h.

#### Detailed experiments of activated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> microspheres by KH570

Amounts of 0.3 g of Fe<sub>3</sub>O<sub>4</sub> microspheres, 128.0 ml of ethanol and 4.0 ml of KH570 were dissolved in 36.0 ml of distilled water in a 250 ml three-neck flask, and then 4.0 ml of  $NH_3$ · $H_2O$  was added. The obtained mixture was incubated at 40 °C with moderate shaking at 190 rpm for 12 h. Then, the product was separated using a magnet, washed several times with ethanol and deionized water and dried by lyophilization.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-GMA) by distillation-precipitation polymerization

In a typical run, an amount of 0.15 g of the surface activated hollow Fe<sub>3</sub>O<sub>4</sub> microspheres was immersed in 80.0 mL of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 1.0 g of MBA and 2.0 g of glycidyl methacrylate (GMA) were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained product was separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization to get the epoxy functionalized magnetic adsorbent, which was abbreviated as  $Fe_3O_4/P$  (MBA-GMA).

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-HEMA) by distillation-precipitation polymerization

In a typical run, an amount of 0.15 g of the surface activated hollow Fe<sub>3</sub>O<sub>4</sub> microspheres was immersed in 80.0 mL of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 1.0 g of MBA and 2.0 g of hydroxyethyl methacrylate (HEMA) were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained product was separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization to get the hydroxyl functionalized magnetic adsorbent, which was abbreviated as Fe<sub>3</sub>O<sub>4</sub>/P (MBA-HEMA).

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-MMA) by distillation-precipitation polymerization

In a typical run, an amount of 0.15 g of the surface activated hollow Fe<sub>3</sub>O<sub>4</sub> microspheres

was immersed in 80.0 mL of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 1.0 g of MBA and 2.0 g of methyl methacrylate (MMA) were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained product was separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization to get the ester functionalized magnetic adsorbent, which was abbreviated as  $Fe_3O_4/P$  (MBA-MMA).

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)-1 by distillation-precipitation polymerization

In a typical run, an amount of 0.15 g of the surface activated hollow Fe<sub>3</sub>O<sub>4</sub> microspheres was immersed in 80.0 mL of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 1.5 g of MBA and 1.5 g of VIM were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained product was separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization to get the imidazole functionalized magnetic adsorbent, which was abbreviated as Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)-1.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)-2 by distillation-precipitation polymerization

In a typical run, an amount of 0.15 g of the surface activated hollow Fe<sub>3</sub>O<sub>4</sub> microspheres was immersed in 80.0 mL of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 2.0 g of MBA and 1.0 g of VIM were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained product was separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization to get the imidazole functionalized magnetic adsorbent, which was abbreviated as Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)-2.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)-3 by distillation-precipitation polymerization

In a typical run, an amount of 0.15 g of the surface activated hollow Fe<sub>3</sub>O<sub>4</sub> microspheres was immersed in 80.0 mL of acetonitrile in a 150 mL three-neck flask, and then 0.08 g of AIBN, 2.5 g of MBA and 0.5 g of VIM were added to the mixture. Thereafter, the mixture was heated to 90 °C with a ramping rate of 1 °C per minute for 2 h with a mechanical stirring rate of 200 rpm. Then, the obtained product was separated using an external magnet, washed several times with ethanol and deionized water and dried by lyophilization to get the imidazole functionalized magnetic adsorbent, which was abbreviated as Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)-3.

# Synthesis of Fe<sub>3</sub>O<sub>4</sub>/P (AA-MMA-VIM) by controlled radical polymerization in the presence of 1,1- diphenylethylene

Firstly, 1,1- diphenylethylene (DPE) (0.06 g), MMA (3 g) and AA (0.25 g) constituted the oil phase. Then the mixture was charged in a four-necked flask equipped with a stirrer, a condenser and heated with water bath. When the mixture was heated to 80 °C, KPS (0.1 g) which had been dissolved in 10 ml water was added. After 0.5 h, magnetic nanoparticles  $Fe_3O_4$  (10%, w/w in water) were added in 3 min. The mixture was maintained at 80 °C for 4 h, cooled to room temperature. After the mixture was heated at 80°C again, VIM (7.5 g) and KPS (0.05 g) dissolved in 10 mL water were added. The mixture was maintained at 80 °C for 4 h once again, and the resulting microspheres were separated by the magnet, washed with deionized water to remove the excess stabilizer and other impurities and to adjust required pH value. Finally, the separated product was dried in a vacuum oven at 45 °C for 24 h to give yellow magnetic adsorbent Fe<sub>3</sub>O<sub>4</sub>/P (AA-MMA-VIM).

$$\ln K_{\rm d} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad \text{Eqn (S1)}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{0} \qquad \text{Eqn (S2)}$$

Where  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ , and  $\Delta G^{\circ}$  stands for the enthalpy (KJ mol<sup>-1</sup>), entropy (J mol<sup>-1</sup> K<sup>-1</sup>) and Gibbs free energy (KJ mol<sup>-1</sup>).



Fig. S1 The measurement of water contact angle for  $Fe_3O_4/P$  (MBA-VIM)



Fig. S2 The TEM image of Fe<sub>3</sub>O<sub>4</sub>/P (AA-VMMA-VIM) prepared by controlled radical polymerization in the presence of 1, 1- diphenylethylene



Fig. S3 Pseudo-first-order model



Fig. S4 Pseudo-second-order model



Fig. S5 Intra-particle diffusion model



Fig. S6 The Langmuir model fitted the absorption isotherms of uranium at pH of 4.5



Fig. S7 The Freundlich model fitted the absorption isotherms of uranium at pH of 4.5



Fig. S8 The Langmuir-Freundlich model fitted the absorption isotherms of uranium at pH of

4.5



Fig. S9 Thermodynamic fitting plot of the sorption at pH of 4.5



Fig. S10 The TEM image of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM) after the sixth adsorption cycle



Fig. S11 The FT-IR spectrum of Fe $_3O_4/P$  (MBA-VIM) after the sixth adsorption cycle



Fig. S12 The XRD pattern of Fe $_3O_4/P$  (MBA-VIM) after the sixth adsorption cycle

Table. S1 Effect of the concentration of imidazole group on the uranium adsorption rate of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)  $^{a}$ 

Adsorbent	Equilibrium	The concentration of imidazole groups (mmol $a^{-1}$ )
Ausorbent	time (s)	The concentration of minuazone groups (minor g)
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)	180	7.2
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)-1	450	5.0
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)-2	600	3.3
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)-3	1200	1.7

<sup>a</sup> Sorption condition (T=298 K, pH=4.5, t=180 sec, and m/V=0.4 g L<sup>-1</sup>)

**Table. S2** Comparison of adsorption rate of the imidazole functionalized magnetic adsorbent developed by distillation precipitation polymerization and controlled radical polymerization in the presence of 1, 1- diphenylethylene <sup>a</sup>

Adsorbents	Equilibrium time (s)	SBET	The concentration of	Contact
		(m <sup>2</sup>	imidazole groups (mmol	angel (°)
		g <sup>-1</sup> )	g <sup>-1</sup> )	
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)	180	76.5	7.2	10
b				
Fe <sub>3</sub> O <sub>4</sub> /P	720	23.4	7.3	9
(AA-MMA-VIM) <sup>c</sup>				

<sup>a</sup> Sorption condition (T=298 K, pH=4.5, t=180 sec, and m/V=0.4 g  $L^{-1}$ ).

<sup>b</sup> developed by distillation-precipitation polymerization.

<sup>c</sup> controlled radical polymerization in the presence of 1, 1- diphenylethylene

## Table. S3

Kinetic parameters for uranium adsorption on Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)

Kinetic model	Parameter	Value
	$k_1 (1 \text{ sec}^{-1})$	0.0447
Pseudo-first-order	$q_{e. cal} (mg g^{-1})$	138.3
	$\mathbb{R}^2$	0.9794
	$k_2 [g (mg^{-1} sec^{-1})]$	0.0007
Pseudo-second-order	$q_{e. cal} (mg g^{-1})$	243.3
	$\mathbb{R}^2$	0.9996
	$K_{int} [mg (g^{-1} sec^{-1/2})]$	4.187
Intraparticle diffusion	c (mg g <sup>-1</sup> )	184.6
	$\mathbb{R}^2$	0.732

# Table. S4

Adsorption isotherms parameters for uranium on Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)

Adsorbent	Model	Parameter	Value
		b (L mg <sup>-1</sup> )	0.0778
	Langmuir	$q_{\max} (\mathrm{mg \ g}^{-1})$	800.0
		$\mathbb{R}^2$	0.9902
		$K_F(\text{mg g}^{-1})$	127.74
	Freundlich	$\mathbf{n}_F$	2.4184
		$\mathbb{R}^2$	0.8777
		$q_{\max} \ (\mathrm{mg \ g}^{-1})$	490.1
	Longmuin Engundlich	Κ	0.5818
	Langmun-Fleununen	n	0.2083
		$\mathbb{R}^2$	0.9354

### Table. S5

Thermodynamic parameters of uranium adsorption on Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)						
$\Delta H^{\circ} (kJ mol^{-1})$	$\Delta S^{\circ} (J \text{ mol}^{-1} \text{ K}^{-1})$	$\Delta G^{\circ} (kJ \text{ mol}^{-1})$				
21.14	157.6	278 K	288 K	298 K	308 K	318 K
21.14	137.0	-22.67	-24.25	-25.82	-27.4	-28.98

**Table. S6** Comparison of adsorption capacity of uranium on various adsorbents also developed by distillation precipitation polymerization <sup>a</sup>

Adsorbents	$q_e (\mathrm{mg \ g}^{-1})$
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)	233.7
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-MMA)	45.3
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-HEMA)	78.2
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-GMA)	62.3

<sup>a</sup> Sorption condition (T=298 K, pH=4.5, t=180 sec, and m/V=0.4 g L<sup>-1</sup>).

Table. S7 Effect of the concentration of imidazole group on the uranium adsorption capacity of Fe<sub>3</sub>O<sub>4</sub>/P (MBA-VIM)  $^{a}$ 

Adsorbent	$q_e (\mathrm{mg \ g}^{-1})$	The concentration of imidazole groups (mmol g <sup>-1</sup> )
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)	233.7	7.2
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)-1	161.3	5.0
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)-2	107.5	3.3
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)-3	65.2	1.7

<sup>a</sup> Sorption condition (T=298 K, pH=4.5, t=180 sec, and m/V=0.4 g L<sup>-1</sup>)

**Table. S8** Comparison of adsorption of uranium on the imidazole functionalized magnetic adsorbent developed by distillation precipitation polymerization and controlled radical polymerization in the presence of 1, 1- diphenylethylene <sup>a</sup>

	$q_e ({ m mg}$	$S_{BET}$ (m <sup>2</sup>	The concentration of imidazole groups
Adsorbents	g <sup>-1</sup> ) <sup>a</sup>	g <sup>-1</sup> )	$(mmol g^{-1})$
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM) <sup>b</sup>	233.7	76.5	7.2
Fe <sub>3</sub> O <sub>4</sub> /P	157.2	23.4	7.3
(AA-MMA-VIM) <sup>c</sup>			

<sup>a</sup> Sorption condition (T=298 K, pH=4.5, t=180 sec, and m/V=0.4 g  $L^{-1}$ ).

<sup>b</sup> developed by distillation-precipitation polymerization.

<sup>c</sup> developed by controlled radical polymerization in the presence of 1, 1- diphenylethylene.

**Table. S9** Calculated interaction energy parameter for the complexation of  $UO_2^{2+}$  with imidazole group anchored onto the polymer chain of P (MBA-VIM)

Model	$\Delta E_{gas}$ (kcal mol <sup>-1</sup> )	
1:1 of $UO_2^{2+}$ with imidazole group	-204.0	
1:2 of $UO_2^{2+}$ with the two adjacent imidazole groups anchored	106.0	
onto the same polymer chain	-196.0	
1:2 of $UO_2^{2+}$ with the two non-adjacent imidazole groups	200.0	
anchored onto the same polymer chain	-209.0	
1:2 of $UO_2^{2+}$ with the two imidazole groups anchored onto the	206.0	
two-distinct polymer chains	-306.0	

**Table. S10** The comparison of  $q_{DFT}$  derived from DFT calculations with the saturated adsorption experimental data  $q_{max}$  obtained from the Langmuir model

Adsorbent	$q_{DFT} (\mathrm{mg}~\mathrm{g}^{-1})$	$q_{\max} (\mathrm{mg \ g^{-1}})$
Fe <sub>3</sub> O <sub>4</sub> /P (MBA-VIM)	856.8	800.0