Well-defined Surface Magnetic Ion-Imprinted Microspheres for Facile onsite Monitoring of Lead Ion at Trace Level in Water[†]

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Experimental Section

Materials and reagents

- Trisodium citrate (Na₃Cit), Ethylene glycol dimethacrylate (EGDMA, AR) Methacrylic acid 10 (MAA, CP), 2,2-azobisisobutyronitrile (AIBN, CP), tetraethyl orthosilicate(TEOS, AR), 3-(trimethoxysilyl)propyl methacrylate (MPS, AR) was purchased was purchased from (Aladdin Reagent Inc, Shanghai, China). All metal stock solutions (1000 mg L⁻¹)(the National Research Center for Certified Reference Materials) were further diluted to the desired concentrations prior to use according to standard method^[1]. All other reagents were of AR grade and used without further
- 15 purification. Geological water was collected from Huangpu River, Shanghai, China. The water samples were filtered through a 0.45 μ m polytetrafluoroethylene (PTFE) millipore filter and acidified to a pH of about 2 with concentrated HCl prior to storage for use. Tap water samples taken from our research laboratory were analyzed without pretreatment.

Synthesis and surface modification of Fe₃O₄@SiO₂@IIPs microspheres



Fig. S1 Synthesis of Fe₃O₄@SiO₂@IIPs microsphere.

Magnetite particles were synthesized according the previous report^[2]. 3.0 g of FeCl₃•6H₂O, 0.72 g of trisodium citrate and 4.8 g of sodium acetate were dissolved in 100 mL of ethylene glycol under vigorous stirring for 30 min. The resultant mixture was then transferred into a Teflon-lined 25 stainless-steel autoclave for heating at 200 °C for 8h. The as-made black products were thoroughly washed with ethanol and deioned water for several times, and finally vacuum dried at 25°C. To synthesize Fe₃O₄@SiO₂ microspheres, 50 mg of magnetite particles were fully dispersed in a solution containing 160 mL of ethanol, 40 ml of H₂O and 2.0 mL of concentrated aqua ammonia(28 wt%) under ultrasonication vibration. Then, 0.8 ml of tetraorthosilicate (TEOS) was added by injection to

the resultant basic dispersion, followed by mechanically stirring for 12h. The obtained Fe₃O₄@SiO₂ microspheres were washed with ethanol for several times to remove blank silica nanoparticles. In order to modify the surface of Fe₃O₄@SiO₂ microspheres with MPS silane coupling agent, the purified Fe₃O₄@SiO₂ microspheres were redispersed in 80 mL of ethanol and 0.5 mL of MPS was added to the 5 dispersion. After mechanically stirred for 48h, the Fe₃O₄@SiO₂@MPS microspheres were washed with ethanol with the help of a magnet, and redispersed in 50 mL of ethanol for further use.

The Fe₃O₄@SiO₂@IIPs microspheres were synthesized via a distillation precipitation polymerization. Typically, in a two-necked round bottom flask, 195 mg PbO was suspended in 10 mL of acetonitrile, then 150 MMA were dissolved in the suspension and heated at 50°C for 1h to obtain 10 chelating ligand. After cooling to room temperature , the solution were mixed with 10 mL of acetonitrile containing 28 mg of Fe₃O₄@SiO₂@MPS microspheres under mechanically stirring. Then 89 mg EGDMA and 10 mg AIBN were dissolved in the suspension and the resultant dispersion was bubbled with high-purity nitrogen gas for 0.5 h. The flask attaching with a fractionating column, Liebig condenser and receiver was submerged in a oil bath. The reaction mixture was heated from 15 ambient temperature till the boiling state within 20 min and the reaction system was kept under refluxing state for further 20 min. Then the polymerization was carried out with distilling the solvent out of the reaction system and the reaction was ended after 8 mL of acetonitrile was distilled off the reaction mixture within 60 min. After the polymerization, the resultant Fe₃O₄@SiO₂@IIPs microspheres were harvested and washed by magnetic separation. The template (Pb(II)) was removed 20 using 2 mol L⁻¹HNO₃ until Pb(II) ions cannot be detected by EDX and ICP-OES.

The non-imprinted polymer Fe₃O₄@SiO₂@NIIPs was synthesized in a similar way but pure MMA monomers was used instead of chelating ligand.

Characterizations of Fe₃O₄@SiO₂@IIPs magnetic microsphere

- A scanning electronic microscopy (SEM) (Model Quanta 200 FEG, FEI Co., USA) was used to 25 measure the size and shape of materials. A transmission electron microscopy (TEM) with energy dispersive X-ray detector (Model TECNAI G2 S-TWIN, FEI Co., USA) was used to study surface morphology and element content of materials. The FT-IR spectra of the hybrids were obtained, using an infrared spectrometer system (Model Equinoxss/hyperion 2000, BRUKER Co., Germany). Thermogravimetry (TG) haracterization was performed by using TG 209F1 libra (Netzsch Co.). An
- 30 Optima 2100DV inductively coupled plasma optical emission spectrometer (ICP-OES), PerkinElmer(Franklin, MA, USA) was used for metal ions determination. The instrumental parameters were those recommended by the manufacturer. The wavelengths of Pb(II) selected was 220.23nm. The portable electrochemical instrument (**PG581**) was purchased from uniscan instruments Ltd. A

imprinted three-electrode consisted of a carbon, Ag/AgCl, and a platinum wire as working, reference and counter electrodes, respectively (CH Instruments, Inc.).

Magnetic solid phase extraction proceduce.

5 Bath method

A series of standard or sample solutions containing Pb(II) were transferred into 10 mL beakers, and the pH value was adjusted to the desired value with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NH₃·H₂O. Then the volume was adjusted to 10 mL with DDW. Fe₃O₄@SiO₂@ IIPs and Fe₃O₄@SiO₂@NIIPs (10 mg) was added, and the mixture was shaken vigorously for 15 min to facilitate adsorption of the metal 10 ions on to the materials. Then the extractants were collected with the help of an external magnetic force and the concentration of the metal ions in the solution was determined by ICP-OES.

Magnetic-SPE procedure

40 mg of Fe₃O₄@SiO₂@IIPs was used for the preconcentration of Pb(II) ions from aqueous standard or sample solutions. Before use, the material was washed by 5mL of 2 mol L^{-1} HNO₃ and 15 DDW successively in order to equilibrate, clean and neutralize it. Portions of aqueous standard or sample solutions containing Pb(II) were prepared, and the pH value was adjusted to the desired pH value with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NH₃·H₂O. The extractant was added into each solution and shaken vigorously for 15 min. Afterwards, the extractant was collected with the help of an external magnetic force and the metal ions retained on the material were eluted with 2 mol L^{-1} HNO₃ solution 20 and the Pb(II) in the elution were determined by different systems.

Onsite determination of Pb(II) at trace level from water samples

For the colorimetric determination, the acidic eluate was transferred into a 5-mL colorimetric tube and the colorization tablet was then added into the elution, which consists of colorant, masking reagent and pH adjusting reagent. 0.3 mg chlorophosphonazo III (CPA-III) was used as colorant because its 25 violet to blue colour reaction with Pb(II) at pH 4.0. The pH adjusting reagent was prepared with 0.6 g NaHCO₃ and 0.15 NaOAc and 0.1 g thiourea was applied as masking reagent to mask the trace copper ions in the elution. After shaken vigorously for 5 min, the elution was eyeballed by the comparison with the defined color gradation. Similarly, the pH adjusting reagent was added into the elution to adjust the pH to 4.0 before measured by hand-hold electrochemical unit. The accumulation potential of 30 electrochemical determination was -1.3v, the accumulation time was 120s and the scan rate was

200mv/s.



5 Fig. S2 TEM images of a) Fe₃O₄ particles, b) Fe₃O₄@SiO₂@NIIPs, c) Fe₃O₄@SiO₂@IIPs with different thickness of imprinted layer



Fig. S3 a) Effect of pH on adsorption of Fe₃O₄@SiO₂@IIPs and b) Adsorption capacity curve of Fe₃O₄@SiO₂@IIPs and Fe₃O₄@SiO₂@NIIPs.



Fig. S4 Evaluation of adsorption selectivity of Fe₃O₄@SiO₂@IIPs and Fe₃O₄@SiO₂@NIIPs. Sample volume: 10 mL; amount of adsorbent: 40 mg(excess); concentration of metal ions: 0.5 ppm; extraction time: 15 min.

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Table. S1The results for the elution-recovery tests for the Pb(II).

Optimization of eluent concentration (the volume of nitric acid was 10.0 mL)						
Concentration (mol L^{-1})	0.5	1.0	1.5	2.0	3.0	
Recovery (%)	83.1	88.7	96.2	99.6	100.7	
Optimization of eluent volume (the concentration of nitric acidwas 2 mol L^{-1})						
Volume (mL)	3.0	4.0	5.0	6.0	7.0	
Recovery (%)	89.5	98.5	99.7	99.4	99.6	

Table. S2 The concentration of Pb(II) in the eluent after elution for 20 times

Thickness of the Shell	10-20 nm	40-60 nm	60-80 nm	80-100nm
The concentration of Pb(II)in elution	No detected	0.028ppm	0.87ppm	1.25ppm

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Fig. S5 Effect of the sample volume on adsorption.



Fig. S6 The content of the Pb(II) in imprinted layer detected by EDX before a) and after elution b).



Fig. S7 Onsite colorimetric determination of lead from water samples: the defined color gradation with different concentration of Pb(II) (a), the elution without adding the colorization tablet (b), the elution after adding the colorization tablet.





Fig. S8 The calibration curve of the peak current and the concentration of pb(II) by the M-SPE procedure and determination of the electrochemical device with printed electrode.

10 Table.S3 The results for the addition-recovery te	ests for the Pb(II) in some real samples $(n = 3)$.
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Sample from	Pb(II) Added (µg L ⁻¹)	Pb(II) Found by ICP-OES* (μ g L ⁻¹)	Recovery (%)	Pb(II) Found by EC(μ g L ⁻¹)	Recovery (%)
Tap water	0	1.06	-	1.17	-
	5.00	5.73	94.55	5.56	90.11
	10.00	10.68	96.56	9.80	87.74

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Industrial wastewater	0	23.01	-	24.87	-
	5.00	28.45	101.57	28.14	94.21
	10.00	33.68	102.03	32.46	93.09

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[1] Y. Cui, S. Liu, Z. J. Hu, X. H. Liu, H. W. Gao, Microchimica Acta 2011, 174, 107.

[2] a) B. Luo, X. J. Song, F. Zhang, A. Xia, W. L. Yang, J. H. Hu, C. C. Wang, *Langmuir* **2010**, *26*, 1674; b) H. Chen, C. Deng, X. Zhang, *Angewandte Chemie-International Edition* **2010**, *49*, 607.

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