

Supporting Information

Water-soluble Fe₃O₄ superparamagnetic nanocomposites for the removal of low concentration mercury(II) ions from water

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Materials and methods

Materials

Styrene (St), 9H-carbazole were all purchased from Shanghai Chemical Reagent Co., Ltd., as analytical reagents and used without further purification. 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), 1-hydroxybenzotriazole (HOBT), diethyl 2,2'-azanediyldiacetate, Azobisisobutyronitrile (AIBN) (chemically pure, Shanghai Chemical Reagent Co., Ltd.) was recrystallized from anhydrous methanol. Methacryloyl chloride was produced by Haimen Best Fine Chemical Industry Co. Ltd. and used after distillation. Tetrahydrofuran (THF) and cyclohexanone were purified by reduced pressure distillation. All other reagents were commercially available and used as received.

Characterization

¹H NMR spectra were measured by a Bruker 400 MHz NMR spectrometer using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal reference at ambient temperature. Molecular weight (M_n) and polydispersity (M_w/M_n) relative to PS were measured on a gel permeation chromatography using a Waters 1515 pump and differential refractometer. THF was used as the mobile phase at a flow rate of 1.0 mL/min. The samples for transmission electron microscopy (TEM) observations were prepared by placing a drop of the micelle solution (0.2 mg/mL) on copper grids, which were coated with thin films of Formvar and then carbon. TEM images were obtained using a TecnaiG220 electron microscope at an acceleration voltage of 200 kV.

FTIR analysis: KBr pellet were prepared and the proportion of sample/KBr was 1/100. The background was obtained from the scan of pure KBr. Perkin-Elmer spectrum RX/FTIR system was used for FT-IR analysis of samples.

The crystalline phase of the particles was identified by X-ray powder diffraction of the dried samples using a Philips X'Pert X-ray diffractometer equipped with a Cu K α monochromatic radiation source.

Magnetization measurements were conducted using Quantum Design PPMS

(Physical Properties Measurement System) and SQUID (Superconducting Quantum Interference Device) systems.

Removal percent and adsorbed amount of Hg were determined by cold vapor atomic absorption spectrophotometric (CVAAS) measurement of the sample solution before and after removing process.

Preparation of magnetic nanoparticles

Magnetite nanoparticles were synthesized by thermal decomposition of iron-oleate complex following published procedures. ^[1,2] FeCl₃ · 6H₂O (2.7 g, 10 mmol) and sodium oleate (9.125 g, 30 mmol) were added to a mixture of ethanol (20 mL), deionized water (15 mL), and hexane (35 mL). The mixture was refluxed at 70 °C for 4 h; the upper reddish brown hexane solution containing iron-oleate complex was then separated, and washed three times with deionized water (10 mL) in a separatory funnel. Hexane was then evaporated in a rotary evaporator, yielding a dark reddish brown, oily iron-oleate complex. Using a standard Schlenk line, iron oleate complex (9 g, 10 mmol) was dissolved in 25 g of 1-octadecene; oleic acid (1.41 g, 5 mmol) or sodium oleate (1.52 g, 5 mmol) was then added. The mixture was heated to 320 °C at a ramp of 3–5 °C min⁻¹ for 30 min under argon. The resulting black nanocrystal solution was cooled to room temperature, and 2-propanol (50 mL) was added to precipitate the magnetic nanoparticles. After centrifugation, nanoparticles were washed with hexane and ethanol three times, and then redispersed in hexane or toluene.

Preparation of polystyrene-N(CH₂COOH)₂ (PS(CH₂COOH)₂)

Polymers were prepared according to our previous work. ^[3]

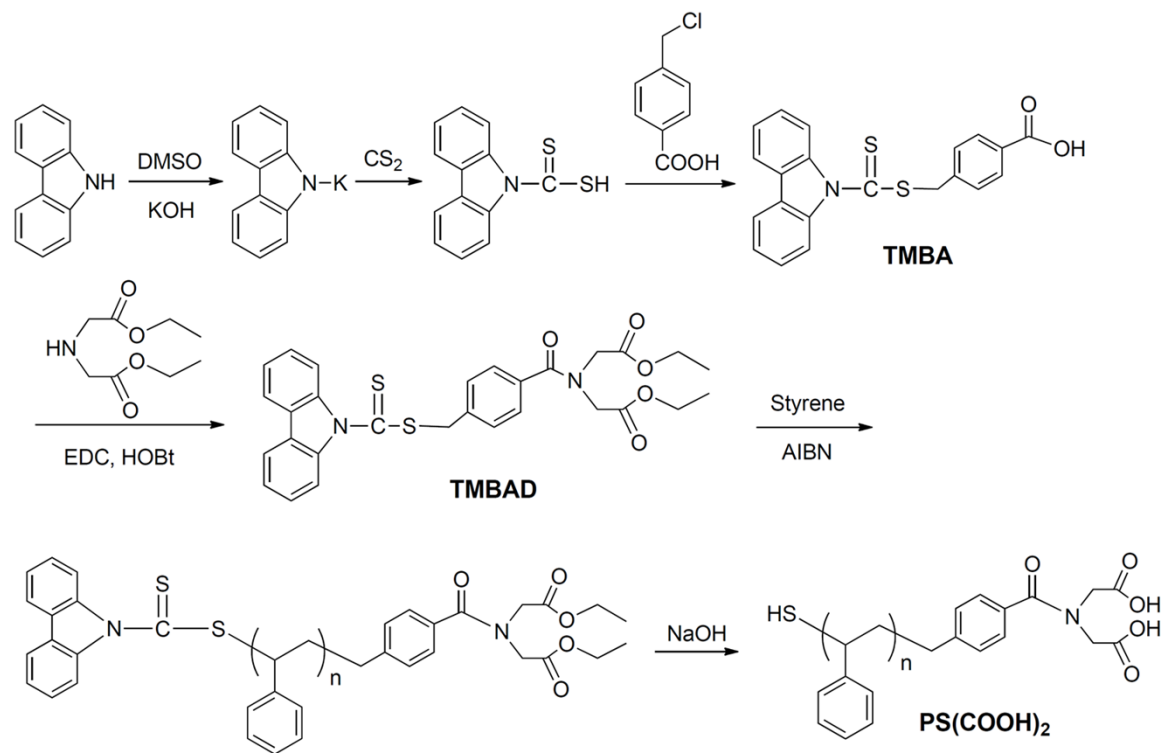
Synthesis of 4-(((9H-carbazole-9-carbonothioyl)thio)methyl)benzoic acid (TMBA). 9H-carbazole (8 g, 0.048 mol) was dissolved in anhydrous DMSO, and then potassiumhydroxide (3.36 g, 0.06 mol) were added. The mixture was stirred at room temperature for 4~5 hours until completely dissolved and was subsequently cooled to 0 °C. Then CS₂ (4.57 g, 0.06 mol) was added dropwisely. The reaction mixture was

stirred for another 4~5 h, followed by addition of 4-(chloromethyl) benzoic acid (10.23 g, 0.06 mol) and stirring overnight. The crude product was isolated by precipitation from massive water and recrystallized from anhydrous ethanol, then light yellow crystal was obtained (yield: 65%). ¹H NMR(400MHz, CDCl₃, δ, ppm): 4.79(*s*, 2H, CH₂), 7.37(*t*, 2H, C₆H₄ in carbazole ring), 7.43(*t*, 2H, C₆H₄ in carbazole ring), 7.58(*d*, 2H, C₆H₄ in benzene ring), 7.98(*d*, 2H, C₆H₄ in benzene ring), 8.11(*d*, 2H, C₆H₄ in carbazole ring), 8.44(*d*, 2H, C₆H₄ in carbazole ring). ESI-MS (+): calcd=378.0617 for [M + H]⁺, found = 378.0618.

Synthesis of diethyl 2,2'-((4-(((9H-carbazole-9-carbonothioyl)thio)methyl)-benzoyl)azanediyl)diacetate (TMBAD). TMBA (0.33 g, 0.87 mmol), diethyl 2,2'-azanediyl diacetate (0.15 g, 0.79 mmol), EDC (0.183 g, 0.95 mmol), HOBT (0.129 g, 0.95 mmol) were added in anhydrous THF. The reaction mixture was stirred for 24 h at room temperature. After the solvent was evaporated under reduced pressure, the crude product was column chromatographed on silica-gel (elution with EtOAc/petroleum = 1:2) to give bright yellow crystal (yield: 82%). ¹H NMR(400 MHz, CDCl₃, δ, ppm): 1.24(*t*, 6H, CH₃), 4.08(*q*, 4H, CH₂CH₃), 4.20(*dd*, 4H, NCH₂COO), 4.72(*s*, 2H, CH₂), 7.36(*t*, 2H, C₆H₄ in carbazole ring), 7.43(*t*, 2H, C₆H₄ in carbazole ring), 7.51(*d*, 2H, C₆H₄ in benzene ring), 7.55(*d*, 2H, C₆H₄ in carbazole ring), 7.98(*d*, 2H, C₆H₄ in benzene ring), 8.43(*d*, 2H, C₆H₄ in carbazole ring). TOF-MS (EI): calcd for C₂₉H₂₈N₂O₅S₂: 548.1440, found: 548.1451.

Preparation of PS(COOH)₂. To a solution of monomer St (520.7 mg, 5 mmol) and RAFT agent TMBA (548.1 mg, 1 mmol) in cyclohexanone (2.0 mL), AIBN (82.1 mg, 0.5 mmol) was added. The resulting solution was degassed by three freeze-evacuate-thaw cycles and heated at 70 °C for 4 h under argon. The mixture was added into a large amount of cooled anhydrous ethanol (100 mL). The precipitate was filtered and dissolved in hot ethanol (250 mL), followed by adding aqueous solution of NaOH (20 mL, 10%). Under stirring, the reaction mixture was refluxed for 3 h and cooled to room temperature, followed by adding hydrochloric acid until the pH of the solution reaching 3. The precipitate was filtered and dried under vacuum at ambient

temperature for 24 h to obtain the polymer (PS-N(CH₂COOH)₂) (yield: 31%). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 1.5-2.5 (CH₂CHC₆H₅), 4.0-4.5 (N(CH₂COOH)₂), 6.5-7.5 (-C₆H₅), 8.0-8.2 (NCOC(CHCH)₂C).



Scheme S1 Synthetic route of PS(CH₂COOH)₂

Preparation of polymer coated magnetic nanoparticles

Predetermined amount of MNPs and polymer were dispersed in hexane and water, respectively. After placed in an ultrasonic bath for half an hour, the mixture was separated to remove the phase of hexane. The obtained water phase was placed near magnetic field and dark brown solids were separated from water. They were then washed three times with water and freeze-dried.

Adsorption procedure

A batch procedure was applied for the removal process. The adsorption of Hg²⁺ by M-MSPNPs was carried out in a pH 7 solution at 298K. In General, 8 mg of M-MSPNPs was added to a 20 mL solution of Hg²⁺ (50µg/L) adjusted to pH 7. After shaking for 10 min with a speed of 350 rpm, magnetic nano-adsorbents were separated magnetically from solution by the magnet. Removal percent and adsorbed

amount of Hg were determined by cold vapor atomic absorption spectrophotometric (CVAAS) measurement of the sample solution before and after removing process.

Removal % = $(C_0 - C_e) \times 100 / C_0$, where C_0 and C_e are the initial and equilibrium concentrations of mercury ion ($\mu\text{g/L}$) in the solution.

$$\text{Removal \%} = (C_0 - C_e) \times 100 / C_0$$

Equilibrium model

The adsorption isotherms for Hg ion on M-MSPNPs were obtained for concentrations ranging from 200 to 5000 $\mu\text{g/L}$, while keeping all other parameters constant. These parameters are: amount of M-MSPNPs = 8mg, shaking time = 10 min, shaking speed = 350 rpm and pH = 7.

q_e ($\mu\text{g Hg/g}$ adsorbent) is the equilibrium adsorption amount of Hg, which is calculated by: $q_e = (C_0 - C_e)V/W$, where C_0 and C_e are the initial and equilibrium concentrations of mercury ion ($\mu\text{g/L}$) in the solution, V is the volume of solution (L), and W is the weight of adsorbent (g) in the mixture.

Freundlich adsorption isotherm is an empirical model developed by Freundlich in 1906, can be applied to multilayer sorption as well as non ideal sorption on heterogeneous surfaces and is given by the following equation [4]:

$$\ln(q_e) = \ln(K_f) + (1/n) \times \ln(C_e).$$

Where K_f and n are Freundlich constants denoting adsorption capacity and intensity of adsorption.

Langmuir adsorption isotherm, developed by Langmuir in 1916, derived from simple mass action kinetics is based on the assumptions that molecules are adsorbed as a saturated monolayer of one molecule thickness with no transmigration in the plane of the surface, and interaction between adsorbed molecules are negligible with energy of adsorption remaining constant. The Langmuir model is given by the following equation [5]:

$$C_e/q_e = 1/(Kq_m) + C_e/q_m.$$

In this model, q_m (mg/g) is the amount of adsorption corresponding to complete

monolayer coverage and K (L/mg) is the Langmuir constant related to the energy or net enthalpy of adsorption.

Competitive adsorption experiments

In order to study the effects of salinity changes on the adsorption capacity of PMMNPs, 8 mg of particles were added to solutions spiked with Hg^{2+} (50 $\mu\text{g/L}$) and concentration range of 0.01 – 1.00 mol/L of NaCl.

Model and real samples

As real wastewater sample, Jinji Lake water was collected from Suzhou industrial park in Suzhou, in Jiangsu Province, China, were spiked with Hg^{2+} and the final concentrations were 5, 10, 20, 50 $\mu\text{g/L}$. As model wastewater sample, added with 50 mg/L of usual ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}), were spiked with Hg^{2+} and the final concentrations were 5, 10, 20, 50 $\mu\text{g/L}$.

Samples for selectivity

M-MSPNPs were mixed with Hg^{2+} (50 $\mu\text{g/L}$) and up to 100-fold molar excess of lead, zinc, or cadmium ions.

Reusability

The Hg^{2+} -adsorbed PMMNPs was mixed with 2 mL of the extraction buffer (50 mM 2-mercaptoethanol), the regenerated PMMNPs were separated by a magnet and washed with deionized water.

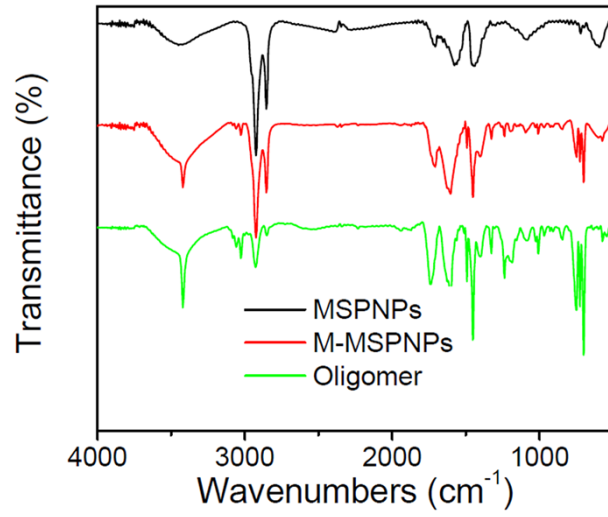


Fig. S1 FT-IR spectrum of MSPNPs before and after modification

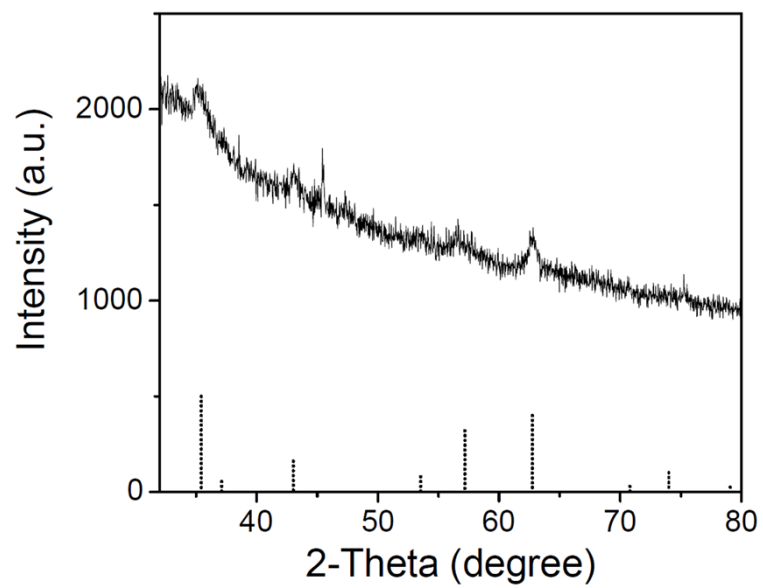


Fig. S2 XRD pattern of M-MSPNPs with peaks corresponding to (···) Fe_3O_4

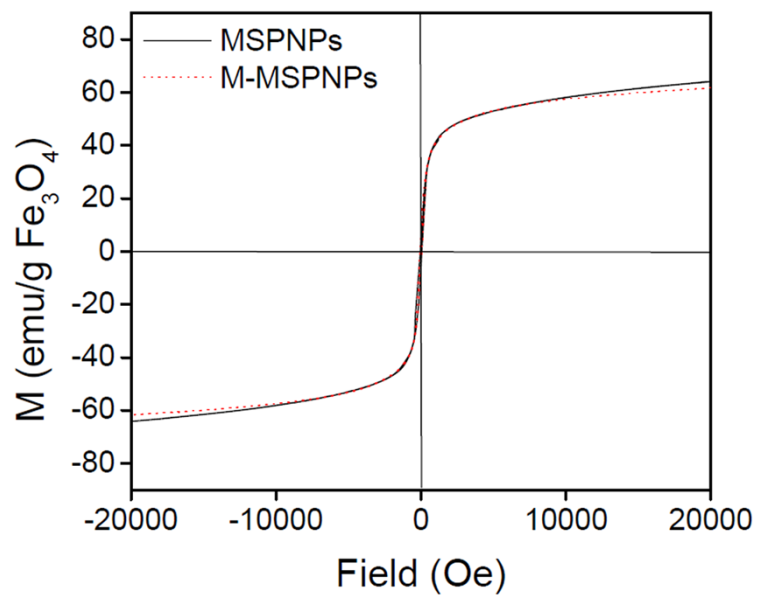


Fig. S3 Magnetic hysteresis loops of MSPNPs and M-MSPNPs measured at 6K

References

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