Electronic Supplementary Material (ESI) for RSC Advances.

Chemodosimeter functionalized magnetic silica yolk-shell nanoparticles for sensing and removal of Hg^{2+}

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Experimental details

1. Chemicals

Deionized water was used throughout.

Oleic acid (OA), 1-octadecane (ODE), Igepal CO-520, N-[3-(Trimethoxysilyl) propyl] ethylene diamine (TSD, 95%) were purchased from Sigma-*Aldrich*.

$FeCl_3$, sodium oleate were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd.

Cyclohexane were of analytical grade and purchased from Shanghai Dahe Chemical Reagent Co., Ltd.

Absolute ethanol was of analytical grade and purchased from Shanghai Zhenxing No. 1 Chemical Plant.

Hydrofluoric acid (40%) and ammonia solution (25%) were of analytical grade and purchased from Jiangsu Tongcheng Chemical Reagent Co., Ltd.

Ethyl silicate (TEOS) was of analytical grade and purchased from Shanghai Lingfeng Chemical reagent Co., LTD.

All the materials were used without further treatment.

2. Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were synthesized according to the literature with slightly modification.[16]

In a typical process, firstly, iron-oleate complex was prepared by iron chloride ($FeCl_3$, 3.24 g) and sodium oleate (10.95 g) dissolved in a mixture solvent of composed of 24 ml ethanol, 18 ml distilled water and 42 ml cyclohexane. The resulting solution was heated to 75 ^oC and kept at that temperature for five hours. When the reation was completed, the upper organic layer containing the iron-oleate complex was washed three times with 30 ml distilled water in a separatory funnel. After washing, cyclohexane was evaporated off.

Secondly, iron-complex (3g) synthesized and 1 ml oleic acid were dissolved in 1-octadecene (15ml) at room temperature. The reaction was heated to 120 ^oC for 3 h under a N_2 atmosphere, then 320 ^oC kept for 40 min. The resulting solution containing the nanoparticles was cooled to room temperature, and Fe_3O_4 nanoparticles were collected and washed by centrifugation using ethanol/cyclohexane (3/1 v/v). The production was kept in cyclohexane.

3. Synthesis of Fe_3O_4 silica Yolk-shell structure (Fe_3O_4-YS)

Igepal CO-520 (5g) was dispersed in cyclohexane (25 ml) by stirring, while Fe_3O_4 nanoparticles (50 mg) were dispersed in cyclohexane (25 ml) and ultrasonicated for 20 min. Then, the two bottles of solution was mixed and stirred for 1 hour. After added ammonia solution (25%, 500 ul), the mixture was continuously stirred for another 3 hours. After all, TEOS (75 ul) was dropped for the first day, TEOS (200 ul) and TSD (12.5 ul) were dropped for the second day, and TEOS (150 ul) the third day. After 3 days of reaction, the resulting silica coating Fe_3O_4 nanoparticles were collected and washed by centrifugation using water/cyclohexane/ethanol (5/5/1 v/v). The production was dispersed in ethanol.

To prepare Fe_3O_4-YS, the synthesized silica coating Fe_3O_4 nanoparticles (10 mg) were dispersed in water (10 ml) with ethanol (2 ml), then hydrofluoric acid (1%, 2ml) was added and the solution was stirred for 6 hours at 30 ^oC. The resulting Fe_3O_4-YS were collected and washed by centrifugation using water and ethanol. The production was dispersed in ethanol.

4. Prepare Fe_3O_4 silica Yolk-shell structure loaded N719 (Fe_3O_4-YS-N719).

Fe_3O_4-YS (10 mg) and N719 (1 mg) were dispersed in ethanol (5ml), then the solution was stirred overnight and the solvent was evaporated. Free N719 was removed by washing the product with ethanol/water (1/10 v/v). The production was dispersed in water.

5. Characterization

Nanoparticles were dispersed in cyclohexane or ethanol or water, and then dropped on the surface of a copper grid for transmission electron microscope (TEM) characterization performed on a JEOL JEM-2010 low to high resolution TEM (HR-TEM) instrument operated at 200 kV. Energy-dispersive X-ray analysis (EDXA) of the nanoparticles was also performed during HRTEM measurements to obtain the elements of samples.

Powder X-ray diffraction measurements were performed on a Bruker D4 diffractometer at a scanning rate of 1^o/min with the 2θ from 10^o to 90^o (Cu Kα radiation, $\lambda = 1.54056$ Å).

The magnetic hysteresis loops was recorded using a superconducting quantum interference device (SQUID) magnetometer with field up to 5T.

N2 adsorption was measured on a Quadrasorb SI at -196 ^oC, and samples were degassed at 300 ^oC under vacuum for 3 h before measurements.

Fourier transform infrared spectra were obtained from an IRPRESTIGE-21 spectroscope (Shimadzu) with KBr pellets.

UV-vis absorption spectra were measure using a Shimadzu UV-2550 ultraviolet-visible-near infrared spectrometer.

Photos were taken by the camera function of mobile phone NOKIA Lumia710.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis was performed on a Thermo E. IRIS Duo System.

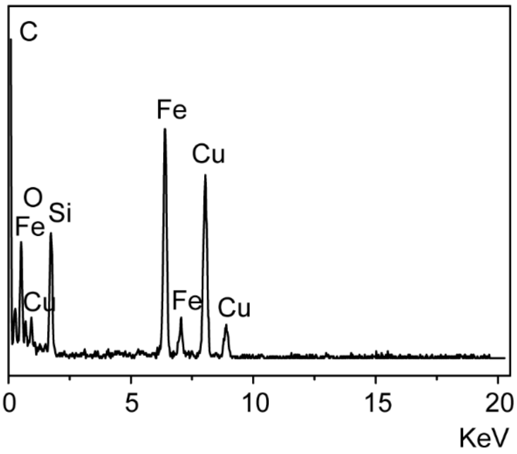

Figure S1. EDXA spectrum of Fe_3O_4 Silica Yolk-Shell structure.

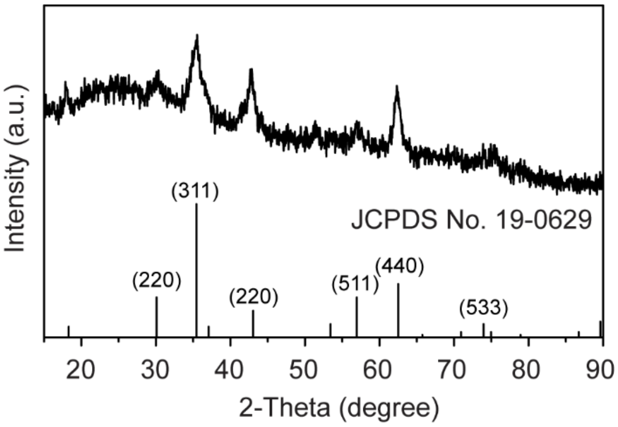

Figure S2. XRD pattern of Fe_3O_4 Silica Yolk-Shell structure.

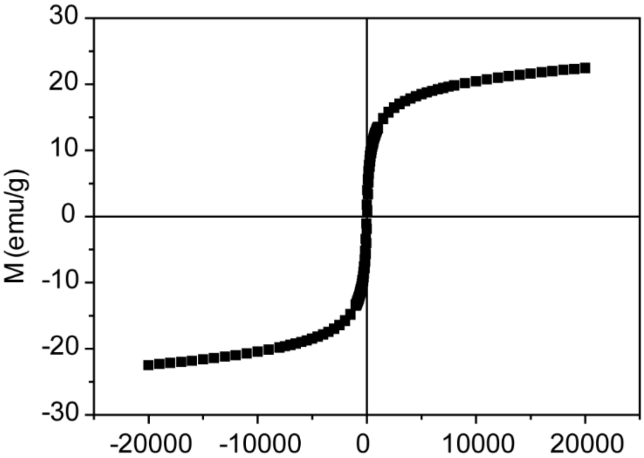

Figure S3. The magnetic hysteresis loops at 300 K of Fe_3O_4-Silica-Yolk-Shell.

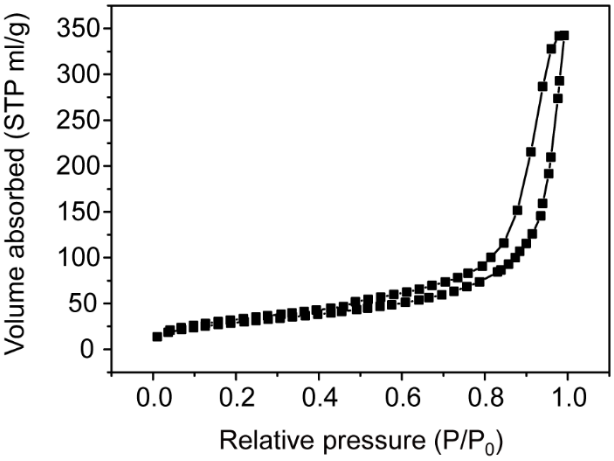

Figure S4. The nitrogen adsorption-desorption isotherms of Fe$_3$O$_4$-Silica-Yolk-Shell.

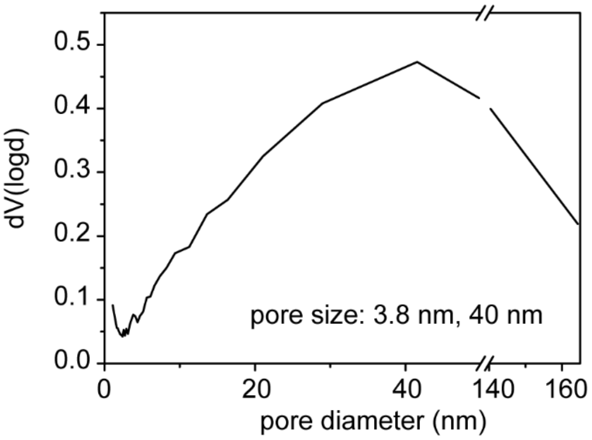

Figure S5. The corresponding Barrett-Joiner-Halenda (BJH) pore distributions of Fe$_3$O$_4$-Silica-Yolk-Shell.

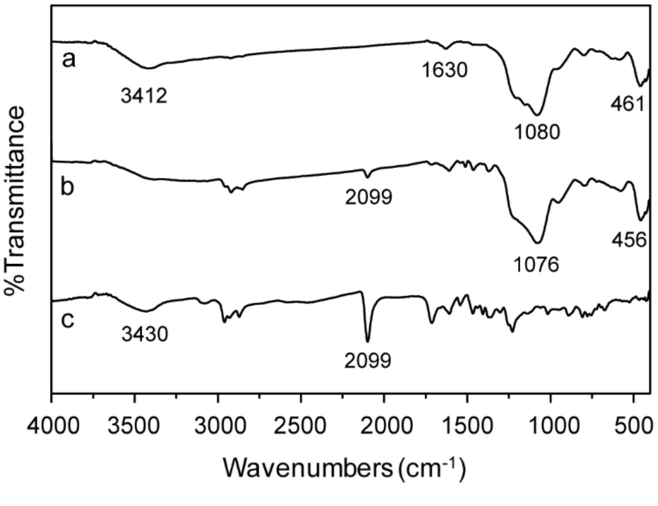

Figure S6. FTIR spectra of (a) Fe_3O_4-Silica-Yolk-Shell, (b) Fe_3O_4-YS-N719, (c) N719.

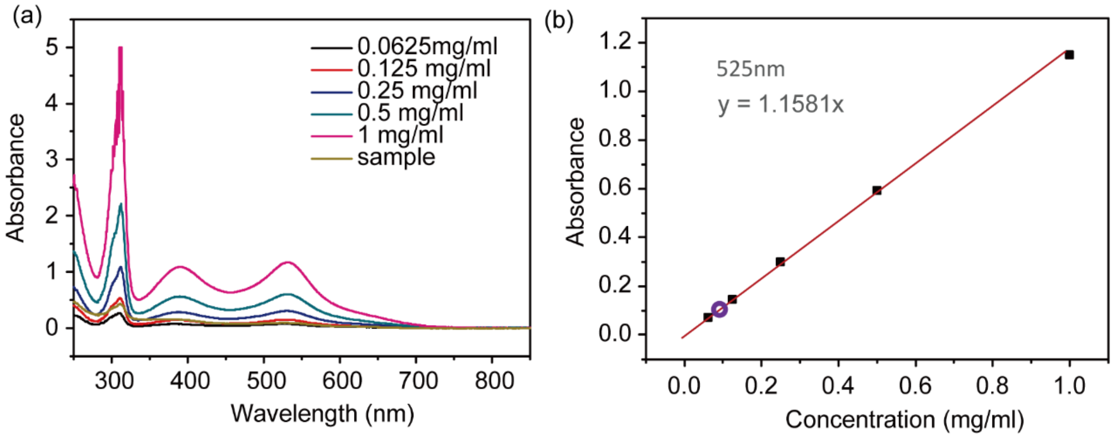

Figure S7. (a) UV-vis absorption spectra of N719 with different concentrations. (b)The absorbance at 530 nm as a function of N719 concentration. The N719 content on Fe_3O_4-YS-N719 was determined to be 5.3 wt%.

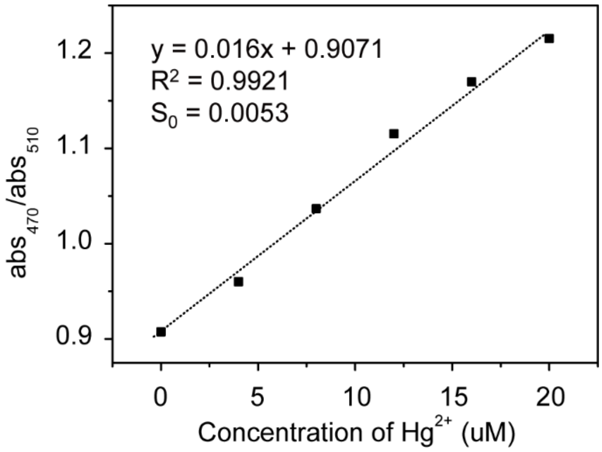

Figure S8. The sensitivity test of Fe_3O_4-YS-N719 using UV-vis absorption spectra. The detection limit of Hg^{2+} was estimated to be 1 uM (200 ppb).

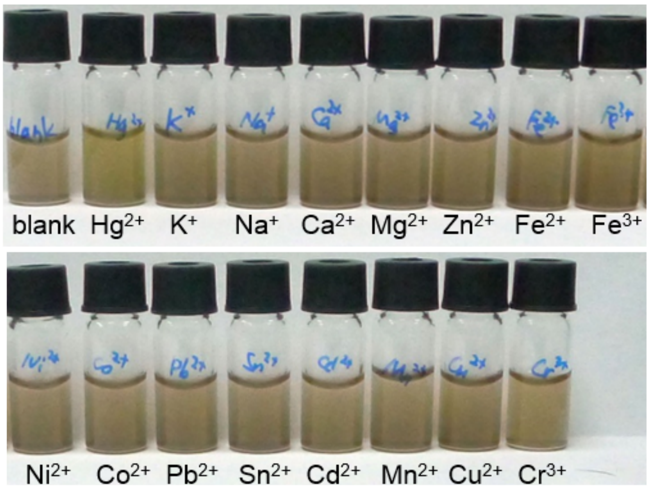

Figure S9. Color change of the aqueous solution of Fe_3O_4-YS-N719 in the presence of various representative metal ions.