Supporting Information

Selective and Efficient Magnetic Separation of Pb^{2+} *via* Gold Nanoparticles-based Visual Binding Enrichment

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Materials and reagents

All chemicals used were of analytical grade or of the highest purity available. $HAuCl_4 \cdot 3H_2O$ was purchased from Shang Hai Chemical Reagent CO.LTD., China. Sodium borohydride ($NaBH_4$, 98%) was purchased from Tianjin Chemical Reagent Plant, China. Diethanolamine, EDTA Disodium salt (EDTA), L-(-)-malic acid, $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 3H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Ammonium hydroxide was purchased from Zhongtian Chemical Reagent Co., Ltd, China. Water used in this experiment was purified by distillation of deionized water.

Characterization

The morphology and size of DEA-Au NPs were characterized by transmission electron microscopy (TEM) by a Philips TecnaiG2 TEM using an accelerating voltage of 200kV. The UV-visible (UV-vis) absorption spectra were taken at room temperature on a UV-2501 spectrophotometer (SHIMADZU CORPORATION) with a variable wavelength between 200 and 1000 nm using a glass cuvette with 0.5cm optical path. The content of metal ions in solution was analyzed by Atomic Absorption Spectrophotometer (TAS-990). The infrared (IR) spectra were collected on a Thermo Nicolet NEXUS IR spectrometer in the wavenumber range 400-4000cm^{-1} at a resolution of 4 cm^{-1}. The samples were prepared in the form of pellets together with KBr.

Synthesis of DEA-Au NPs

100 mL aqueous solution of $HAuCl_4 \cdot 3H_2O$ (1mL, 8.9 mg/mL), 0.1 mL of 10^{-3} M sodium citrate and diethanolamine (10^{-3} M, 0.75mL) which had been ultrasonic with CS_2 stoichiometry, were mixed stirring for 20 min, then the $HAuCl_4$ was reduced by

fresh sodium borohydride solution ($NaBH_4$, 1 mL, 4 mg/mL). After addition of $NaBH_4$, stirred the gold colloidal solution for 2 h at room temperature to obtained diethanolamine modified Au NPs (DEA-Au NPs). The as-synthesized DEA-Au NPs were purified by centrifugation and redispersion in water twice. UV-vis spectra: DEA-Au NPs (524 nm, 0.6302). The average size is about 6 nm (Fig. S4). According to Beer's law using the molar extinction coefficient of ca. 1.1×10^7 $M^{-1}cm^{-1}$ for Au NPs of 5.6±0.4 nm diameter,[1] the particle concentration of the AuNPs (ca. 57.29 nM) was determined.

Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were synthesized via aqueous coprecipitation of $FeCl_3$ and $FeSO_4$ in the precence of ammonium hydroxide.[2] Degassed and deionized water was used to prepare all the solutions. To prepare Fe_3O_4 nanoparticles, 1 M aqueous $FeCl_3$ (10 ml) solution was mixed with 1 M aqueous $FeSO_4$ (5 ml) solution in a flask under a nitrogen atmosphere. Ammonium hydroxide solution (about 30 ml) was slowly added with vigorous stirring until a pH between 11 and 12 was reached. Vigorous stirring was continued for another 30 min. The solution color could be seen to alter from orange to black, leading to black Fe_3O_4 nanoparticles. The magnetic nanoparticles were isolated by applying a permanent external magnet. The supernatant was decanted and discarded. Deionized and degassed water was then added to wash the particles thoroughly and was repeated for 5 times to remove excess ions and salts. Finally particles were washed with ethanol twice and stored as dispersion in ethanol.

L-(-)-malic acid modified Fe_3O_4(MA- Fe_3O_4)

Before midification, the Fe_3O_4 nanoparticles were separated from ethanol by a permanent external magnet and dried. Then, 0.1 g Fe_3O_4 nanoparticles were dispersed in 9 mL of deionized water and 1 mL of 10^{-3} M malic acid was added, the mixture were ultrasonic for 30 min. The resulting MA- Fe_3O_4 were purified via isolated by a permanent external magnet and finally redispersed in water.

Sample preparation for detecting Pb^{2+} in drinking water, the Yangtze water and the East Lake water

The Yangtze water and the East Lake water collected from Yangtze River and East Lake (Wuhan, China) were first filtered through a standard 0.2 μm filter, then mixed with 30 mg sodium bicarbonate and boiled for about 30 minutes. After cooling to room temperature, the solution was filtered with funnel twice. Then, 0.2 M HCl solution was used to regulate filtrate until the pH value achieve to 5~6.

The real water samples (drinking water, the Yangtze water and the East Lake water) were spiked with Pb^{2+} at different concentrations and stored at ambient condition until used.

Colorimetric test

The colorimetric tests of DEA-Au NPs responding to transition metal ions are operated as follows: 0.5 mL of 10^{-4} M the transition metal ions were added to 1.5 mL of Au colloids (ca. 57.29 nM) and after combining 10 min, the solutions were test.

The colorimetric tests of DEA-Au NPs responding to Pb^{2+} with increasing concentrations are operated as follows: 0.5 mL of Pb^{2+} (10^{-7}, 5×10^{-7}, 10^{-6}, 5×10^{-6}, 10^{-5}, 2.5×10^{-5}, 5×10^{-5}, 7.5×10^{-5}, 10^{-4}, 2.5×10^{-4}, 5×10^{-4}, 7.5×10^{-4}, 10^{-3} M) were added to 1.5 mL of Au colloids (ca. 57.29 nM), respectively, and after combining 10 min, the solutions were test.

Lead ions removal test

MA-Fe_3O_4 (10 mg/mL, 140 μL) were added to the aggregated Au colloid (2 mL) under sonicating. Then, a permanent magnet was set beside the bottle, after 15 min, Pb^{2+}-Au aggregation and Fe_3O_4 were completely attracted toward the magnet, leaving behind a clear solution. The supernatant was analyzed by FAAS.

Lead ions release test and reuse of Fe_3O_4 recovered

It's operated as follows: 1.75 mL of deionized water was added to the sedimentation that included Pb^{2+}-Au aggregation and Fe_3O_4 and sonicated for about 2 min to make the sedimentation dispersed. Then 0.25 mL of 2×10^{-3} M EDTA was added to chelate Pb^{2+}. Finally, Au NPs and Fe_3O_4 MNPs were separated by centrifugation at 8500 *g* for 1 min and the Pb solution was obtained which was analyzed by FAAs. The recovered Fe_3O_4 was reused to separated Pb^{2+}-Au aggregation again.

Supplementary figures

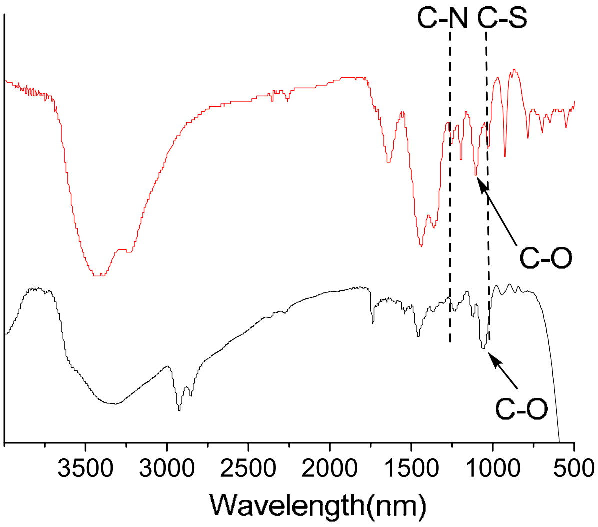

Fig. S1 The FT-IR spectra of diethanolamine (black line) and DEA-Au NPs (red line). The IR spectrum of DEA-Au NPs exhibits the characteristic features C–O stretching mode at 1104 cm^{-1}. Besides, new bands at 1028 and 1253 cm^{-1} which corresponds to stretching mode of C–N and C–S bond are observed for DEA-Au NPs, indicating a successful formation of the DTC-DEA ligand. The result indicated that DEA was successfully modified on the surface of Au NPs via the carbodithioate ($–CS_2$) linkage.

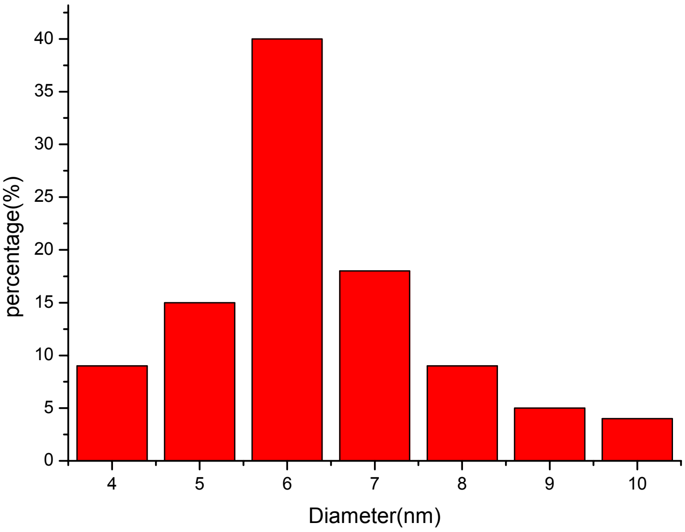

Fig. S2 The size distribution of DEA-Au NPs. 100 particles are measured to get the size distribution. According to the size distribution, the diameter of DEA-Au NPs is about 6 nm.

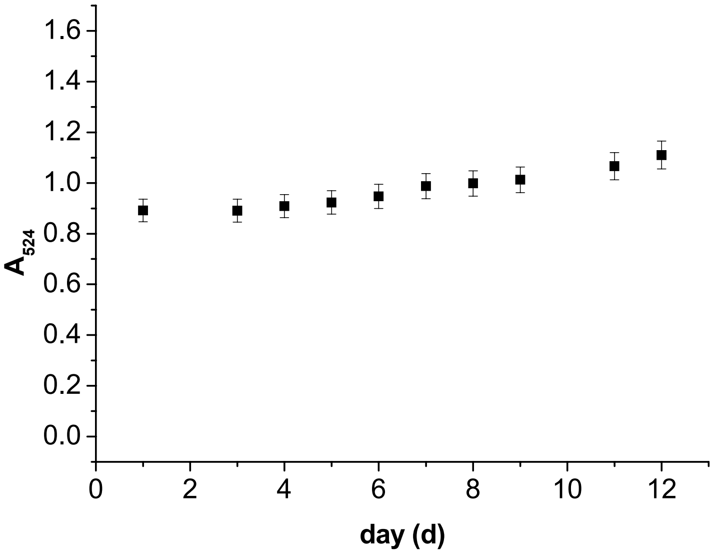

Fig. S3 UV-vis spectroscopy of DEA-Au NPs by day at 524 nm.

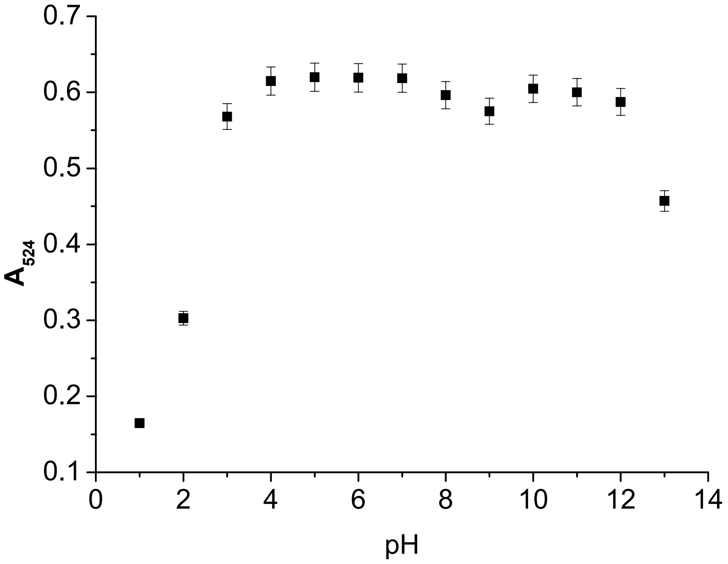

Fig. S4 UV-vis spectroscopy of DEA-Au NPs affected by different pH at 524 nm.

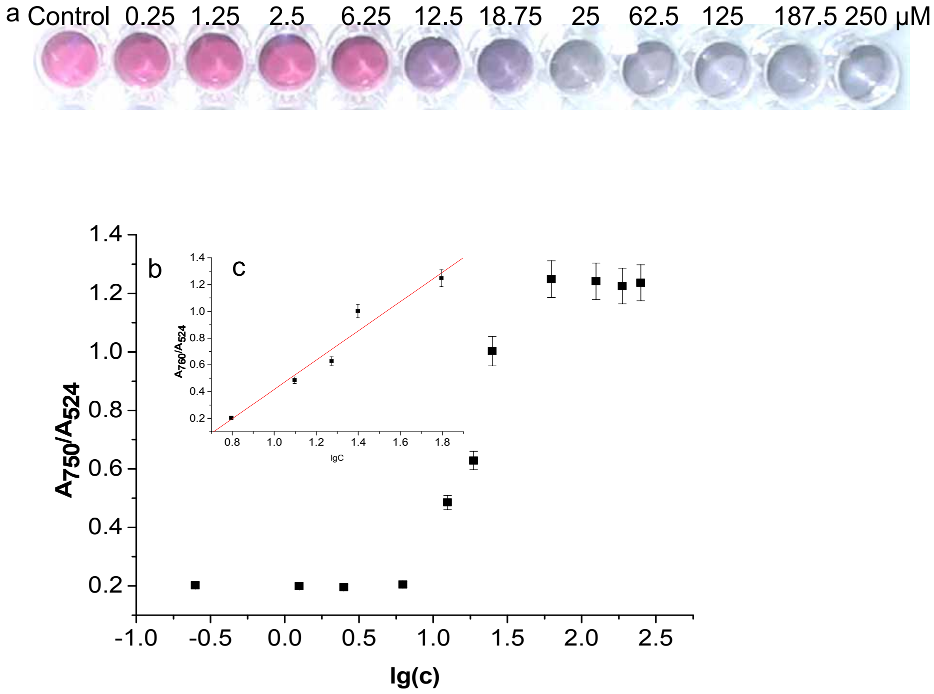

Fig. S5 Color progression of DEA-Au colloids respond to lead concentrations (a), and a plot of extinction ratio ($R=A_{750}/A_{524}$) versus logarithm of the Pb^{2+} concentration C over the range of 0.25 μM to 250 μM (b), and a linear relationship ($R^2=0.97557$) between the $R=A_{750}/A_{524}$ and logarithm of the Pb^{2+} concentration C was obtained in the range of 12.5 μM to 62.5 μM (c).

Table S1 The complex constants between DEA and transition metal ions.

M	Ag^+	Co^{2+}	Mn^{2+}	Pb^{2+}	Cd^{2+}	Ni^{2+}	Cu^{2+}	Hg^{2+}	Zn^{2+}	Fe^{3+}	Au^{3+}
$Ks(10^4)$	0.46	0.18	0.37	1.41	0.19	0.15	0.062	1.02	0.77	0.073	0.67

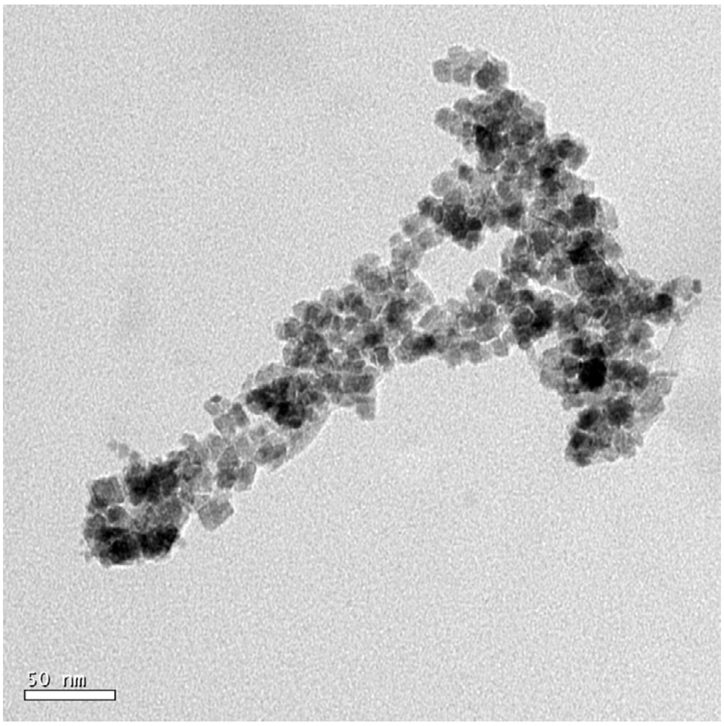

Fig. S6 TEM image of the as-synthesized Fe_3O_4 nanoparticles.

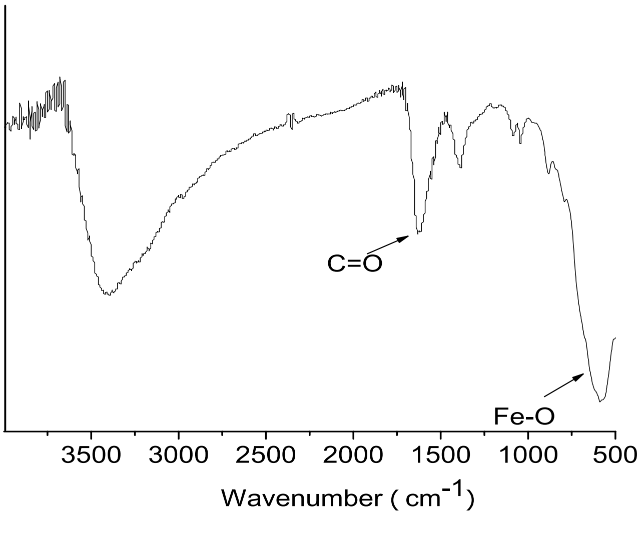

Fig. S7 FT-IR spectrum of L-(-)-malic acid modified Fe_3O_4. The IR spectrum exhibits the characteristic features Fe–O stretching mode at 589 cm^{-1}. Besides, C=O stretching mode at 1631 cm^{-1} is observed indicating malic acid was successfully bound to Fe_3O_4 nanoparticles.

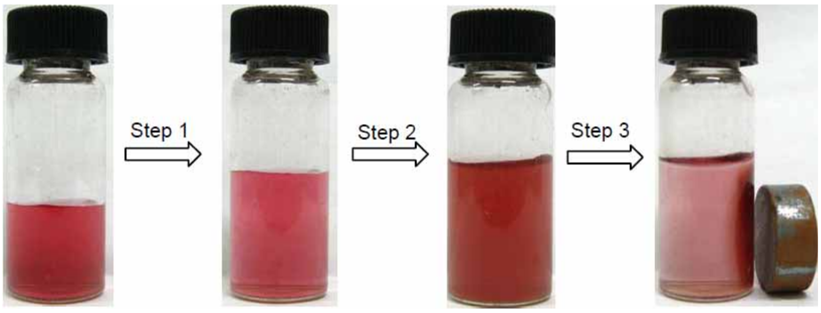

Fig. S8 The photos of overall process of DEA-Au NPs/Co^{2+} absorbed by Fe_3O_4 nanoparticles in turn: well-dispersed DEA-Au NPs, addition of Co^{2+}, then addition of MA-Fe_3O_4,and portion of Au NPs and Fe_3O_4 were attracted toward the magnet when a permanent magnet was set beside the bottle (the fourth photo). The process of DEA-Au NPs/M (M=Ag^+, Mn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+}, Zn^{2+}, Fe^{3+}, Au^{3+}) absorbed by Fe_3O_4 is similar to DEA-Au NPs/Co^{2+}.

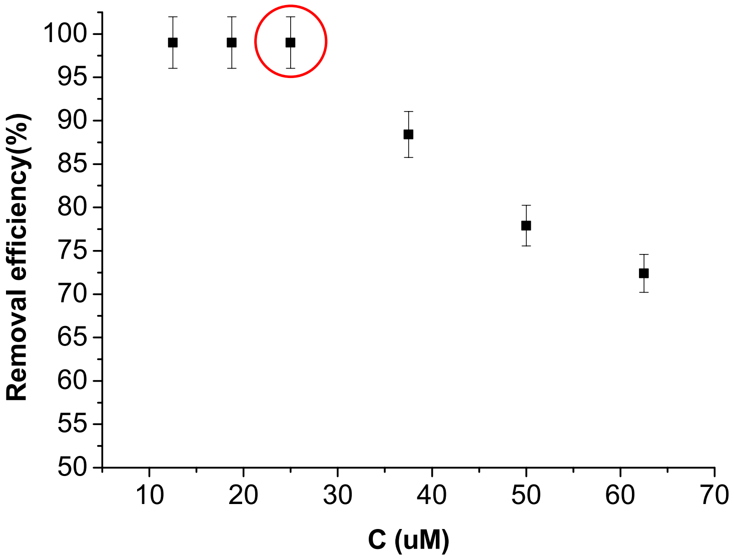

Fig. S9 A plot of removal efficiency versus Pb^{2+} concentration C over the range of 12.5 μM to 62.5 μM (final concentration). The point in the red circle indicates that the maximum adsorption capacity of lead is 25 μM for Au colloid (57.29 nM, 1.5 mL). When the concentration of Pb^{2+} increasing (>25 μM), the volume of Au colloid should increase according to the equation:

$$\frac{0.05\ \mu\text{mol}}{n} = \frac{1.5\ \text{mL}}{V}$$

it calculated as:

$$V = 30n$$

where V (in mL) is the volume of DEA-Au colloid and n (in μmol) is the amount of Pb^{2+}.

Table S2 Detail analysis of release experiments of Pb^{2+}

Concentration of Pb^{2+} before separation / μM	Removal efficiency of Pb^{2+} / %	Release efficiency of Pb^{2+} / %
25	>99	78
12.5	>99	85

Table S3 Reuse of Fe_3O_4 for separation test

Concentration of Pb^{2+} before separation / μM	Removal efficiency of $Pb^{2+\,a}$ / %	Removal efficiency of $Pb^{2+\,b}$ / %
25	>99	56
12.5	>99	65

[a] separated by freshly prepared MA-Fe_3O_4;

[b] separated by MA-Fe_3O_4 recovered.

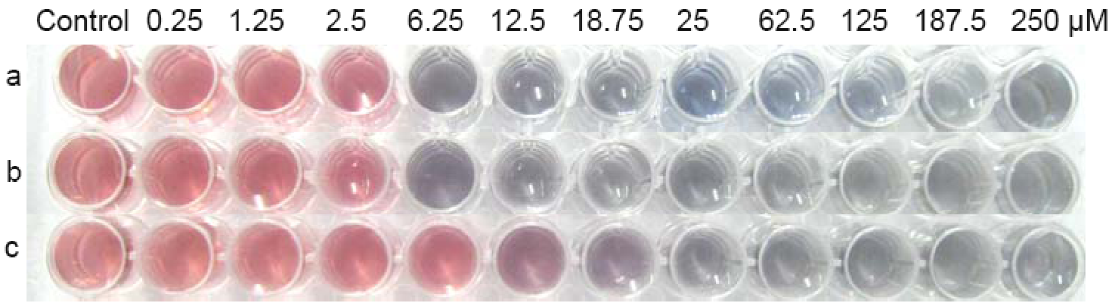

Fig. S10 Color progression of DEA-Au colloids response to lead solution with increasing concentrations in East Lake sample (a), Yangtze sample (b) and drinking water (c). Detection limit of Pb^{2+} in drinking water is 12.5 μM while the detection limit is a little lower (6.25 μM) in Yangtze River and East Lake sample, which is attributed to the impurity such as salt in the water sample that impels Au NPs color change at lower concentration (Fig. S10). [3]

Table S4 the removal efficiency of Pb^{2+} in drinking water, Yangtze River sample and East Lake sample

Concentration of Pb^{2+} / μM	Removal efficiency (drinking water)/%	Removal efficiency (Yangtze River)/%	Removal efficiency (East Lake)/%
25	>99	79	90
18.75	>99	>99	>99
12.5	>99	>99	>99

Reference

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