

Supporting Information

Facile fabrication of chiral hybrid organic-inorganic nanomaterial with large optical activity for Selective and Sensitive Detection of Trace Hg²⁺

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Chemicals and Materials: All chemicals used were of at least analytical grade. Ultrapure water (18.2 MΩ cm) obtained from a WaterPro water purification system (Labconco Corporation, Kansas City, MO, USA) was used throughout this work. A standard stock solution of 10 mg L⁻¹ of Hg²⁺ was prepared from HgCl₂ (The Second Chemical Co., Beijing, China). L-Cysteine was from Beijing Newprobe Biotechnology Co. Ltd. (Beijing, China). Silver nitrate was from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Aqueous solutions of K⁺, Na⁺, Ca²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Fe³⁺, Cu²⁺, Pb²⁺, Cd²⁺, Cr₂O₇²⁻ and Zn²⁺ were prepared from KNO₃, NaCl, Ca(NO₃)₂·4H₂O, MgCl₂·6H₂O, MnCl₂·4H₂O, NiCl₂·6H₂O, FeCl₃·6H₂O, CuCl₂·2H₂O, Pb(NO₃)₂, CdCl₂, K₂Cr₂O₇ and Zn(NO₃)₂·7H₂O, respectively. All solutions were freshly prepared everyday.

Characterization: The XRD spectra were collected on a Rigaku D/max-2500 X-ray diffractometer (Rigaku, Japan) with Cu K_α radiation. The XPS measurements were carried out on a Kratos Axis Ultra DLD spectrometer fitted with a monochromated Al-K_α X-ray source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics, a multi-channel plate, and delay line detector. The TEM images of nanoparticles were recorded on JEOL 100 CXII (JEOL Ltd., Japan) microscope with an accelerating voltage of 100 kV. All XPS spectra were recorded using an aperture slot of 300×700 microns. Survey spectra were recorded with a pass energy of 160 eV, and high resolution spectra with a pass energy of 40 eV. All the results were corrected with charge shift. The FT-IR spectra of (400-4,000 cm⁻¹) were measured on Nicolet IR AVATAR-360 spectrometer with pure KBr as the background. All CD spectra were measured on a Jasco J-715 spectropolarimeter at ambient temperature (Cell length: 1 cm; data pitch: 0.1 nm; band width: 1 nm; scanning speed: 500 nm/min; accumulation: 3). The solution should be shaken before every CD measurement.

Procedures for Detecting Hg²⁺: The colloids of chiral Ag-L-cysteine complex nanoparticles (1) were facilely fabricated by mixing equal volumes of AgNO₃ (20 μM) and L-cysteine (22 μM) aqueous solutions under sonication (120 W) in a water bath at 37 °C for 30 min. The prepared colloids of the Ag-L-cysteine complex nanoparticles were directly used to detect Hg²⁺ without further purification and separation.

For preparing a calibration curve, to 10 mL calibrated flask, 2.0 mL of the colloids of the chiral Ag-L-cysteine complex nanoparticles and 0-1 mL of 10 μM Hg²⁺ standard solution were added,

and diluted to volume with ultrapure water. The mixture solution was shaken for 200 s before CD measurement. The pH of the mixture solution was 5.8.

For detecting Hg^{2+} in water sample, to 10 mL calibrated flask, 2.0 mL of the colloids of the chiral Ag–L-cysteine complex nanoparticles and 8.0 mL of water sample were added, and diluted to volume with ultrapure water. The mixture solution was shaken for 200 s before CD measurement.

For evaluating the selectivity, to 10 mL calibrated flask, 2.0 mL of the colloids of the chiral Ag–L-cysteine complex nanoparticles and certain amounts of interfering ion standard were added, and diluted to volume with ultrapure water. The mixture solution was shaken for 200 s before CD measurement.

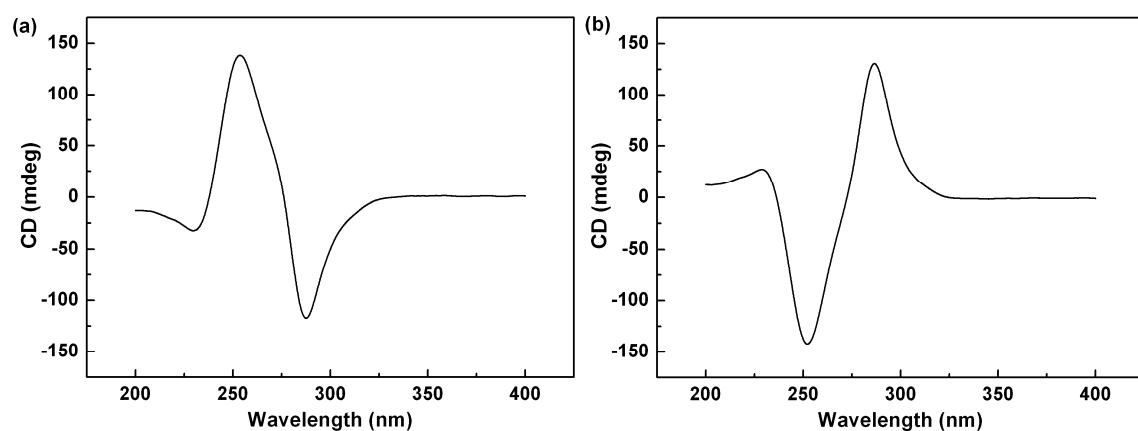


Figure S1. CD spectra of the mixture of (a) L-cysteine (10 µM) and Ag⁺ (11 µM), (b) D-cysteine (10 µM) and Ag⁺ (11 µM) measured after ultrasonication (120 W) in a water bath at 37°C for 30 min.

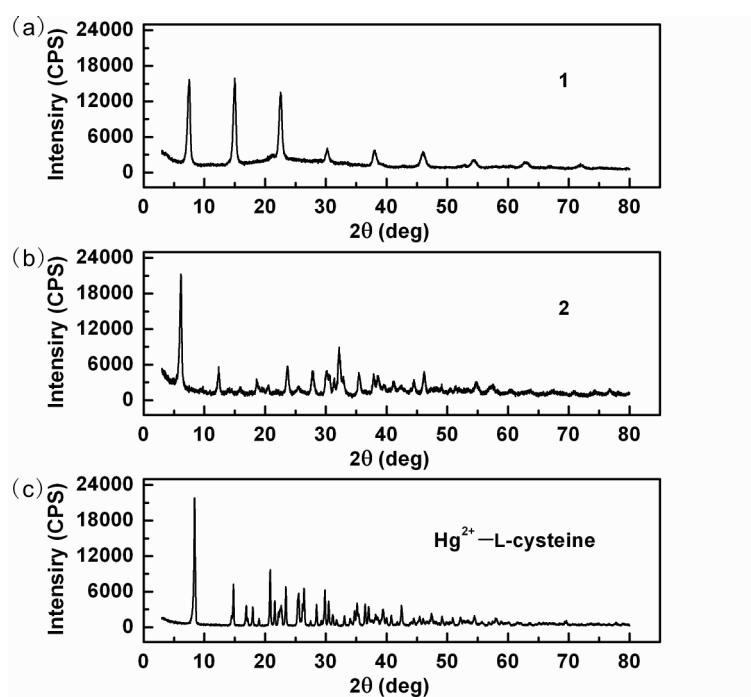


Figure S2. X-ray diffraction (XRD) patterns of (a) **1**, (b) **2**, (c) Hg^{2+} —L-cysteine. The precipitate **1** was obtained by centrifugation (12000 rpm) of the mixture of L-cysteine (1 mM) and Ag^+ (1 mM) after ultrasonication (120 W) in a water bath at 37°C for 30 min, and subsequent vacuum drying. The precipitate **2** was obtained by centrifugation (12000 rpm) of the mixture after mixing **1** and Hg^{2+} (0.5 mM) for 5 minutes, and subsequent vacuum drying. The precipitate Hg^{2+} —L-cysteine was obtained by centrifugation (12000 rpm) of the mixture of L-cysteine (1 mM) and Hg^{2+} (0.5 mM) in 50:50 aqueous ethanol, and subsequent vacuum drying.

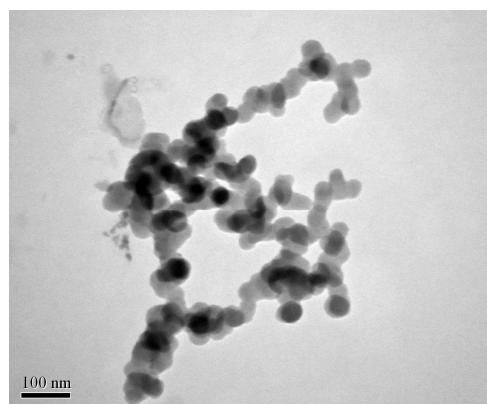


Figure S3. TEM images of the chiral Ag–L-cysteine complex nanoparticles. The sample was prepared from the aqueous mixture of L-cysteine (50 μ M) and Ag(I) (50 μ M) after ultrasonication (120 W) in a water bath at 37°C for 30 min.

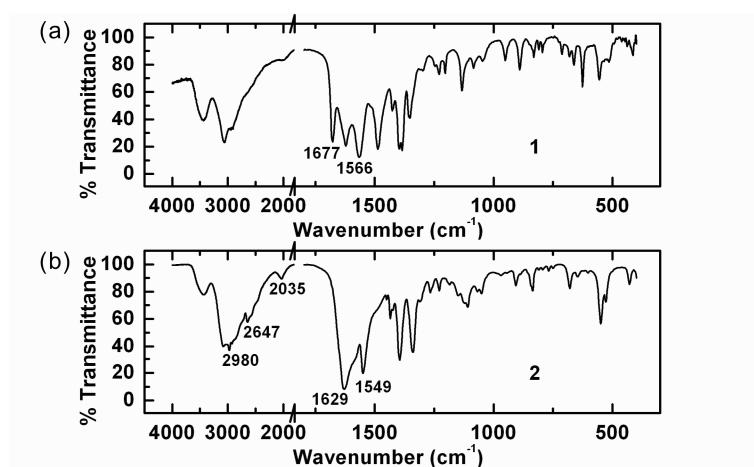


Figure S4. FT-IR spectra of (a) **1** and (b) **2**. The precipitate **1** was obtained by centrifugation (12000 rpm) of the mixture of L-cysteine (1 mM) and Ag⁺ (1 mM) after ultrasonication (120 W) in a water bath at 37°C for 30 min, and subsequent vacuum drying. The precipitate **2** was obtained by centrifugation (12000 rpm) of the mixture after mixing **1** and Hg²⁺ (0.5 mM) for 5 minutes, and subsequent vacuum drying.

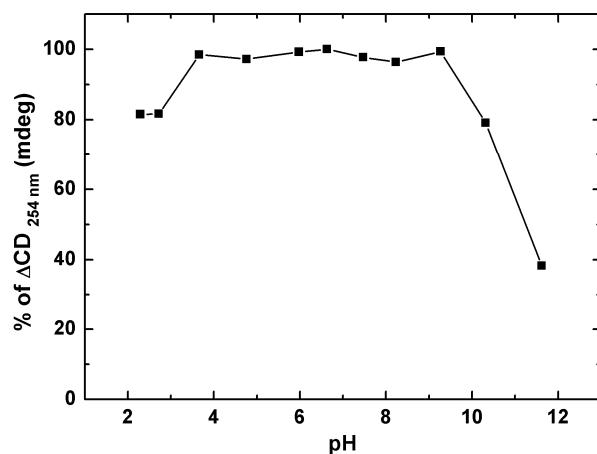


Figure S5. Influence of sample pH on the detection of Hg^{2+} (500 nM).

Table 1. Analytical Results for the Determination of Hg²⁺ In Spiked Pond Samples

Samples	Spiked Hg ²⁺ (nM)	Measured by the developed method (nM) (mean ± s, n=3)	Recovery (%) (mean ± s, n=3)	Measured by ICP-MS (nM) (mean ± s, n=3)
Pond water 1	100	105.1 ± 4.9	105.1 ± 4.7	102.2 ± 0.9
	200	203.3 ± 9.1	101.7 ± 4.5	209.6 ± 3.6
Pond water 2	100	94.1 ± 4.6	94.1 ± 4.9	91.8 ± 0.7
	200	194.5 ± 9.0	97.3 ± 4.6	197.8 ± 3.0
Pond water 3	100	107.8 ± 3.6	107.8 ± 3.3	104.0 ± 0.9
	200	206.6 ± 5.4	103.3 ± 2.6	213.6 ± 3.0