

Electronic Supporting Information (ESI) for
**Specifically colorimetric recognition of calcium, strontium, barium
ions using 2-mercaptosuccinic acid-functionalized gold nanoparticles
and its use in reliable detection of calcium ion in water**

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1. Experimental sections

1.1. Materials

Hydrogen tetrachloroaurate(III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was purchased from Sigma-Aldrich Co. (USA). DL-Mercaptosuccinic acid was obtained from ACROS ORGANICS (USA). The analytical grade metal salts: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, MgSO_4 , CaCl_2 , $\text{Sr}(\text{NO}_3)_2$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$, and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ were purchased from Beijing Chemical Reagents Co. (China) and used for preparation of standard stock metal ion solutions. Tris-HCl buffer (10 mM) was used for all experiments at pH 7.0. Other chemicals were analytical grade and used directly. Milli-Q water (18.2 M Ω cm) was used throughout the experiment.

1.2. Synthesis of citrate-stabilized AuNPs

The citrate-stabilized AuNPs of an average 13 nm diameter was synthesized according to the Natan's method.^{S1} 1 mL of 0.1 M HAuCl_4 was added with 190 mL of water and brought to a rolling boil with vigorous stirring. Then 10 mL of 38.8 mM trisodium citrate was rapidly added, and the solution kept stirring under heat for 10 min. The obtained ruby red solution continued to be stirred without heat for another 15 min. After cooling down to room temperature, it was stored at 4 °C before use. The concentration of the red AuNPs solution was determined to be ~7.2 nM by UV/Vis spectroscopy, based on an extinction coefficient of $2.7 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 520 \text{ nm}$ for 13 nm AuNPs.^{S2}

S1 K. G. Grabar, R. G. Freeman, M. B. Hommer, and M. J. Natan, *Anal. Chem.*, 1995, **67**, 735.

S2 H. D. Hiller and C. A. Mirkin, *Nat. Protoc.*, 2006, **1**, 324.

1.3 Preparation of MSA-AuNPs probes

For preparation of MSA-AuNPs probes with designate ratios, in a typical experiment, each 2 mL of citrate-stabilized AuNPs solution was added with 1.4, 3.5, 7.0, 14, and 35 μL of MSA (20 mM), respectively. After being stirred for 2 h at room temperature (25 ± 1 °C), each solution was diluted with 2 mL of water. The solutions were stored at the refrigerator (4 °C) for 24 h before any analysis.

2. Instruments and methods

UV/Vis absorption spectra were recorded with a Cary 50 UV/Vis spectrophotometer (USA). Photographs were taken with a Kodak DX 7590 digital camera (USA). TEM images were acquired on the Hitachi H-800 (Japan) transmission electron microscope operated at 200 kV. A filter paper was put under the carbon-coated copper grip when preparing samples to preclude the possibility of aggregation of nanoparticles during sample drying. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was conducted with a Thermo Scientific ICAP6300 ICP-OES (USA).

In the analysis of standard concentration solution, 100 μL of MSA-AuNPs solution was mixed with 100 μL of buffer, followed by the addition of known amount of metal ions. Afterwards, NaCl (10 mM) was injected and the solution was incubated for ~ 8 min before it was spectrally recorded. In the analysis of water samples, no pretreatment was performed except the lake water. It was handled with centrifugation (at 8000 rpm) for ~ 5 min to rid of the larger particles and other insoluble matters.

3. Figures

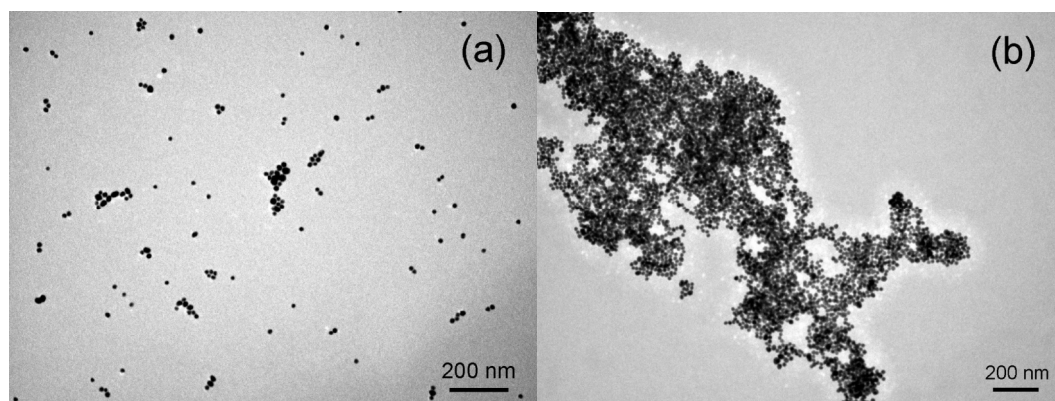


Fig. S1 TEM images of nanoparticles after the addition of (a) 10 mM NaCl and (b) 10 mM NaCl + 50 μM Ca^{2+} to the Au-3 probe solution.

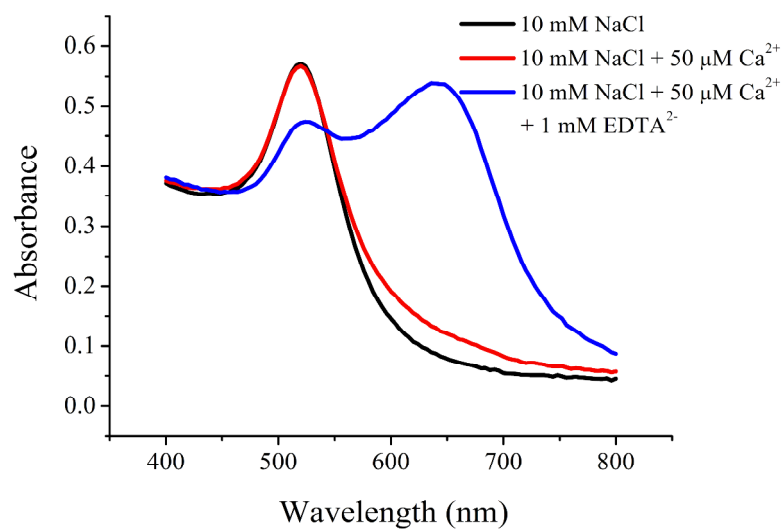


Fig. S2 The optical spectra for the Au-3 system in the presence of 10 mM NaCl, 10 mM NaCl + 50 μM Ca^{2+} , and 10 mM NaCl + 50 μM Ca^{2+} + 1 mM EDTA^{2-} . Note: sodium salt of EDTA^{2-} was added before the addition of Ca^{2+} .

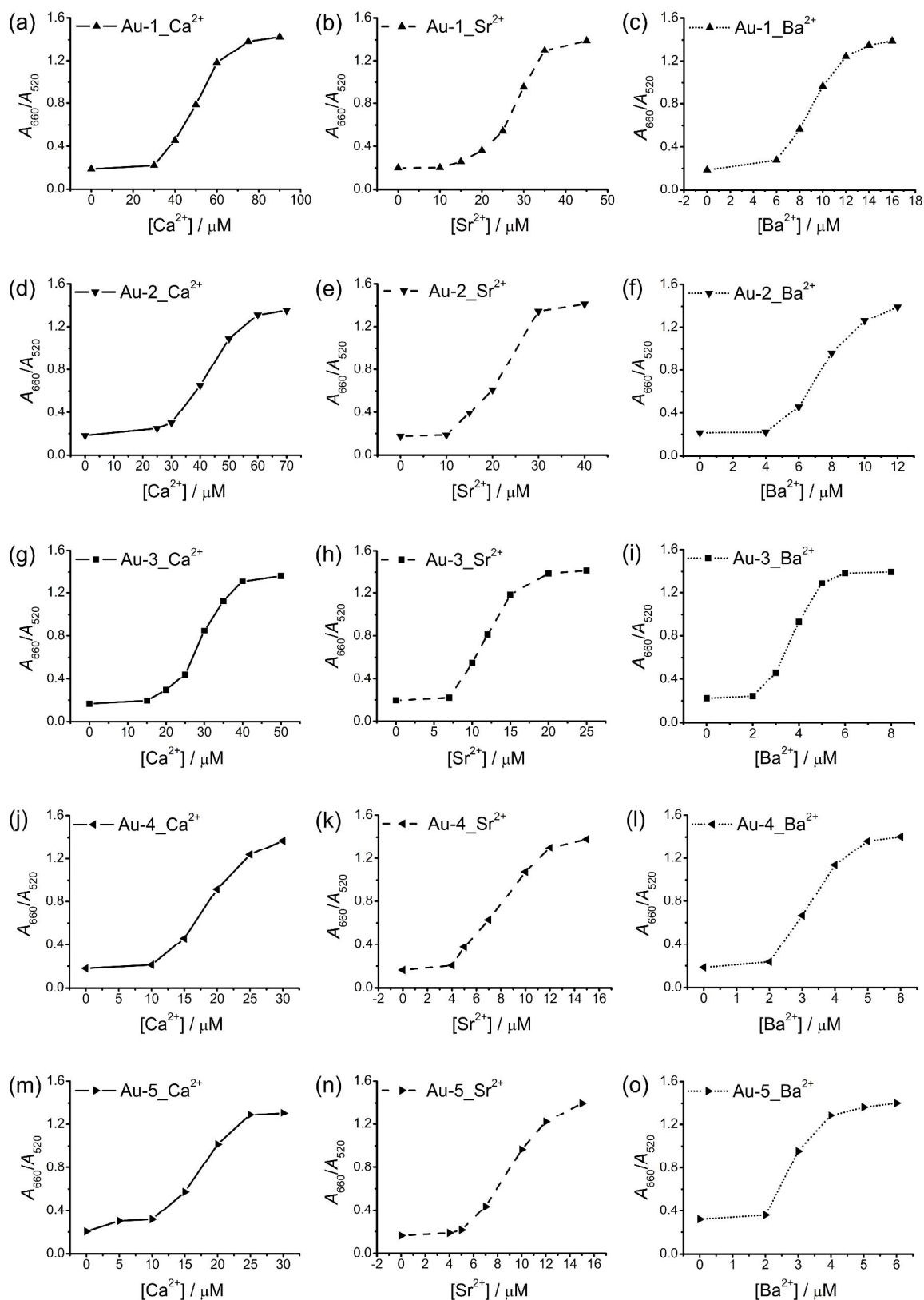


Fig. S3 The performances of detection for Ca^{2+} , Sr^{2+} , Ba^{2+} ions by Au-1 (a-c), Au-2 (d-f), Au-3 (g-i), Au-4 (j-l), and Au-5 (m-o) sensory systems, respectively.

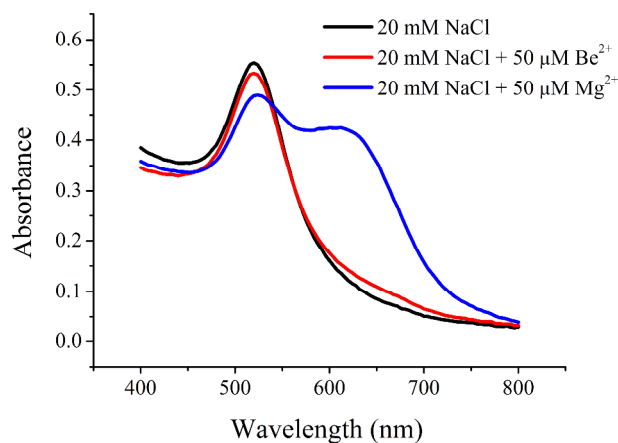


Fig. S4 The optical spectra for the Au-3 system in the presence of 20 mM NaCl, 20 mM NaCl + 50 μM Be²⁺, and 20 mM NaCl + 50 μM Mg²⁺.

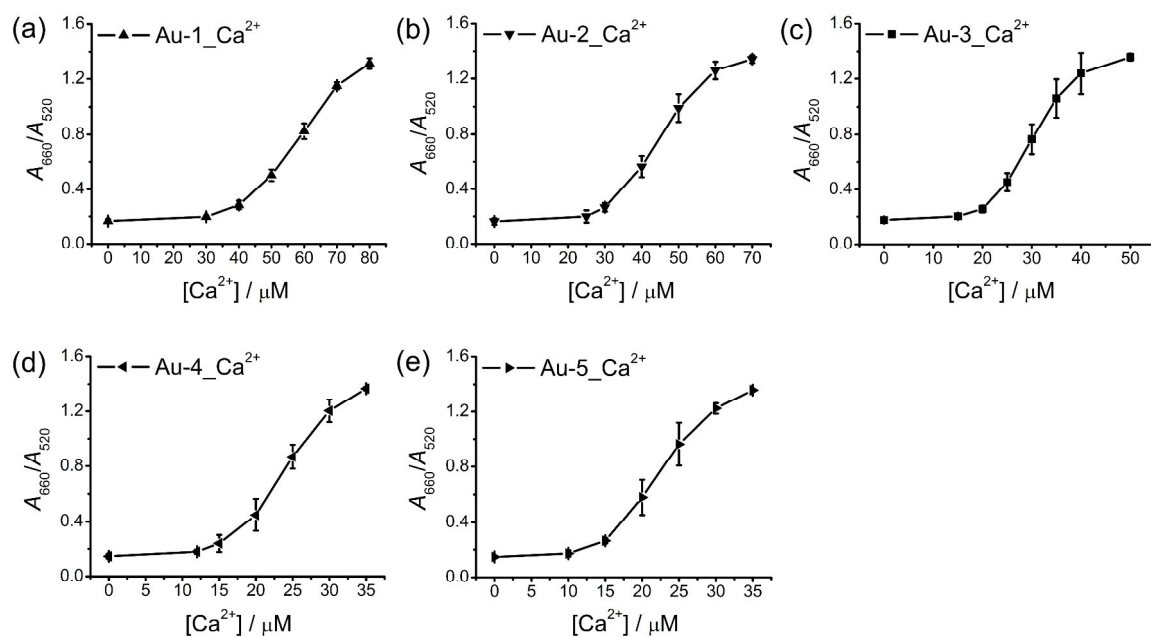


Fig. S5 The dynamic detection concentration ranges of Ca^{2+} ion by Au-1 to Au-5 (a to e) sensory systems. The error bars represent the standard deviations of three parallel measurements.

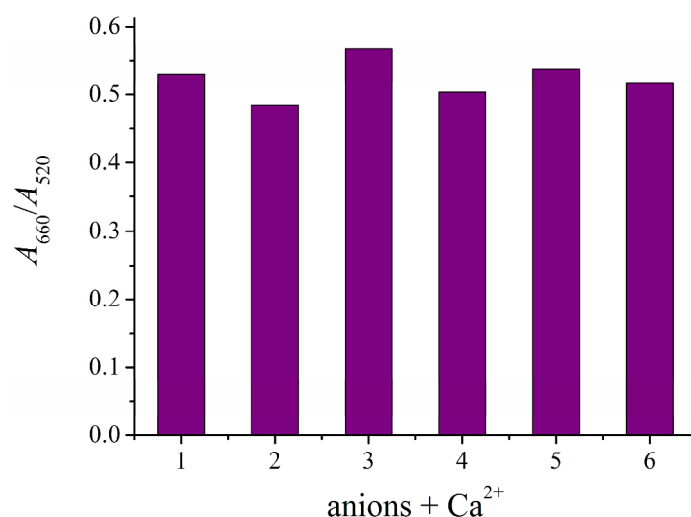


Fig. S6 Interference test by the addition of anions (1 mM) in the calcium (25 μM) assay by the Au-3 probe. The 1-6 represents only Ca^{2+} , $\text{F}^- + \text{Ca}^{2+}$, $\text{Cl}^- + \text{Ca}^{2+}$, $\text{SO}_4^{2-} + \text{Ca}^{2+}$, $\text{PO}_4^{3-} + \text{Ca}^{2+}$, and $\text{NO}_3^- + \text{Ca}^{2+}$, respectively.

4. Table

	Tap water (mM) ^a	Cool boiled water (mM)	Lake water (mM)	Mineral water 1 (mM) ^b	Mineral water 2 (mM) ^c	Purified water (mM) ^d
Au-1	1.53 ± 0.12	0.4 ± 0.04	0.88 ± 0.12	0.2 ± 0.06	0.31 ± 0.08	undetectable
Au-2	1.50 ± 0.13	0.39 ± 0.08	0.9 ± 0.10	0.2 ± 0.06	0.3 ± 0.05	undetectable
Au-3	1.62 ± 0.08	0.4 ± 0.07	1.04 ± 0.08	0.21 ± 0.04	0.33 ± 0.05	undetectable
Au-4	1.65 ± 0.10	0.39 ± 0.08	1.03 ± 0.08	0.21 ± 0.08	0.35 ± 0.10	undetectable
Au-5	1.64 ± 0.08	0.36 ± 0.07	1.0 ± 0.06	0.2 ± 0.05	0.29 ± 0.08	undetectable
ICP-OES	1.57 ± 0.04	0.4 ± 0.05	0.95 ± 0.04	0.2 ± 0.04	0.32 ± 0.05	≤ 0.001

a. Each result related to Au-1 to Au-5 was obtained by an average of three measurements. The same procedure was applied to other water samples.

b. Mineral water 1 is from Nongfu Spring, whose water resource site is located at the mineral water preserve of Jingyu county, Jilin Province.

c. Mineral water 2 is from Masterkong Natural Mineral Water, whose water resource site is located at the Changbaishan Qinglongquan of Jingyu county, Jilin Province.

d. Purified water is from Wahaha purified drinking water, Hangzhou Wahaha group Co., LTD.

Table S1 Comparison of results for Ca^{2+} level assay in several waters by the MSA-AuNPs sensory systems with those by the standard ICP-OES method.