Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Aggregation-induced accelerating peroxidase-like activity of gold nanoclusters and their applications for colorimetric Pb^{2+} detection

Hong Liao, Guangjuan Liu, Yun Liu, Rong Li, Wensheng Fu, Lianzhe Hu*

Chongqing Key Laboratory of Green Synthesis and Applications, and Chongqing Key Laboratory of Inorganic Functional Materials, College of Chemistry, Chongqing Normal University, Chongqing 401331, China

* Corresponding author. Email: lianzhehu@cqnu.edu.cn

Experimental Section

Reagents and materials

L-Glutathione in the reduced form (GSH) and $HAuCl_4 \cdot 3H_2O$ were purchased from Sigma. 3,3′,5,5′-tetramethylbenzidine (TMB), H_2O_2 solution, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), and the metal salts used in this study were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical reagent grade, and used as received. The solutions were prepared with water purified by a Milli-Q system (Millipore, Bedford, MA, USA).

Apparatus

Absorption spectra were recorded with a UV2550 UV-Vis Spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed on a Hitachi Model F-4600 FL Spectrophotometer. Transmission electron microscopy (TEM) images were obtained on a JEM-2100 transmission electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) measurement was carried out on an X-ray photoelectron spectrometer using monochromatized Al Kα radiation (Thermo Fisher Scientific, USA). Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS (Malvern Instruments, UK).

Preparation of Au-NCs

Au-NCs were prepared following previous method. Freshly prepared

aqueous solutions of $HAuCl_4$ (4 mM, 5 mL) and GSH (6 mM, 5 mL) were mixed at 25 °C. The reaction mixture was heated to 70 °C under gentle stirring for 24 h. The obtained solution was then dialyzed using 3000 Da MWCO dialysis bag in double distilled water.

Preparation of Au(I)−thiolate complexes

Solutions of $HAuCl_4$ (4 mM, 5 mL) and GSH (6 mM, 5 mL) were mixed at room temperature for 5 min. A precipitate was formed. NaOH was added to the mixture to bring the pH to ∼7.0 and the precipitate was dissolved within seconds. The solution was aged for ∼1 h, and the oligomeric Au(I)−thiolate complexes formed were used without purification.

Procedure for the detection of Pb^{2+}

A typical colorimetric analysis for Pb^{2+} was realized as follows. Firstly, 50 μL TMB (5 mM), 50 μL H_2O_2 (100 mM), 50 μL Au-NCs (50 μg/mL), and 50 μL Pb^{2+} with different concentration were added into 300 μL 10 mM phosphate buffer (pH 6.0). Secondly, the mixed solution was incubated for 25 min at room temperature. Finally, the solution was used for adsorption spectroscopy measurement. The lake water sample was filtered using a 0.22 μM membrane filter before analysis.

Kinetic analysis

Kinetic measurements were carried out by monitoring the absorbance change at 650 nm. Experiments were conducted using 5

μg/mL Au-NCs in 10 mM phosphate buffer (pH 6.0) containing 0.5 mM TMB. The Michaelis-Menten constant was calculated using Lineweaver-Burk plots of the double reciprocal of the Michaelis-Menten equation.

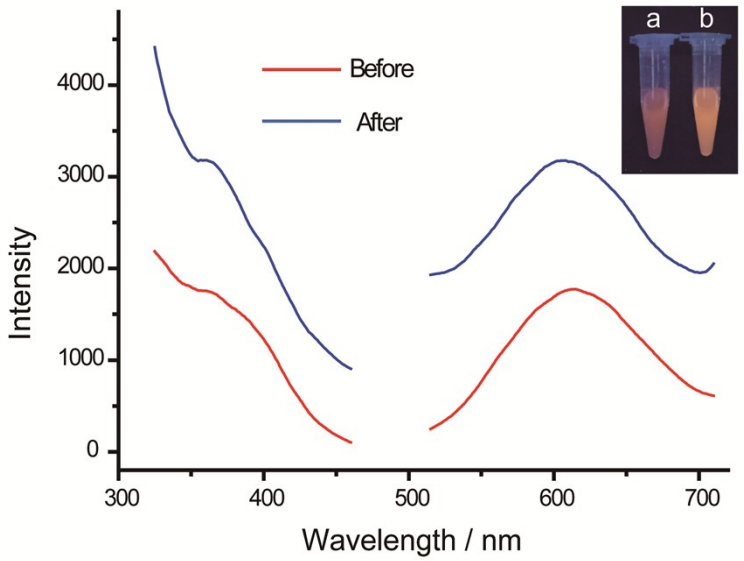

Fig. S1 Fluorescence excitation and emission spectra of glutathione stabilized Au-NCs before (red curves) and after (blue curves) the addition of Pb^{2+}. Inset: digital photographs of Au-NCs in the absence (a) and presence (b) of Pb^{2+} under 365 nm UV light.

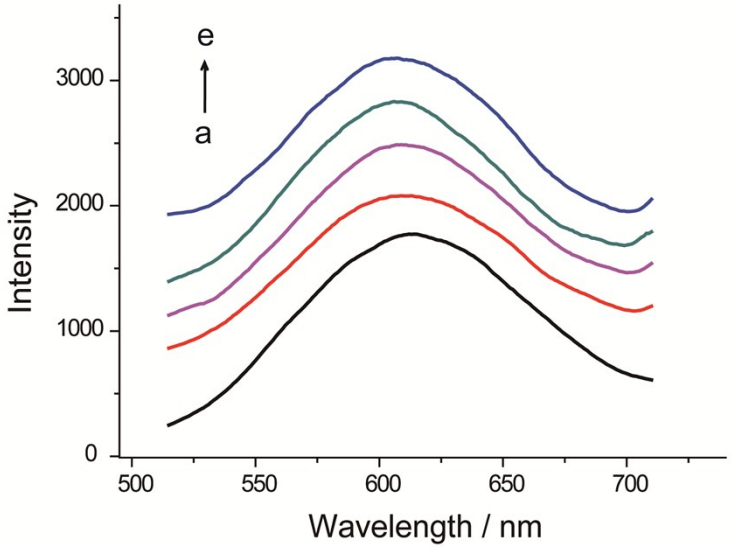

Fig. S2 Fluorescence emission spectra of Au-NCs in the presence of different concentrations of Pb^{2+} (from a to e: 0 μM, 50 μM, 100 μM, 200 μM, 300 μM)

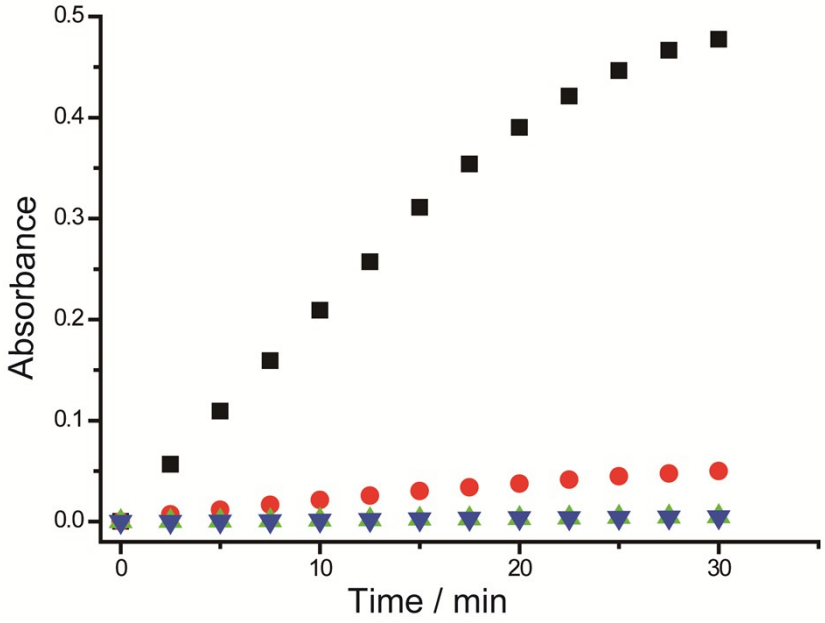

Fig. S3 The kinetic curves of TMB-H_2O_2 (▼) and TMB-H_2O_2 in the presence of Pb^{2+} (▲), Au-NCs (●), and both the Pb^{2+} and Au-NCs (■).

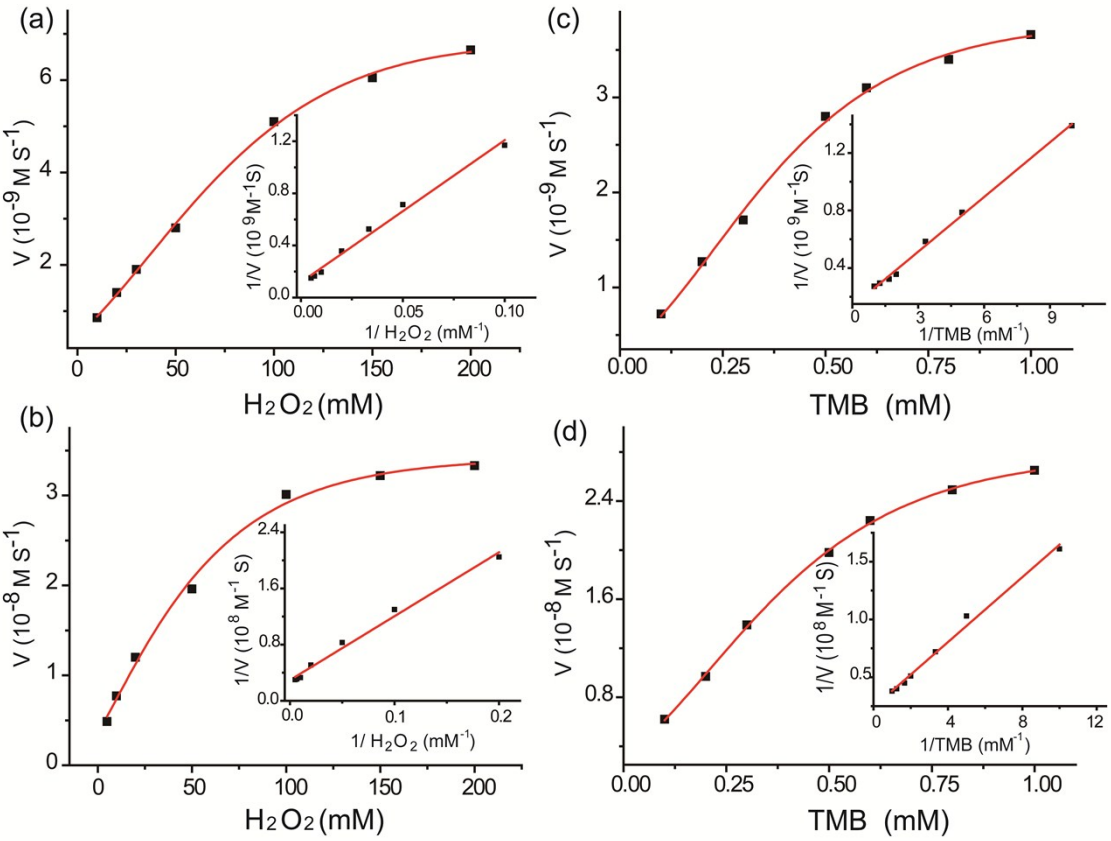

Fig. S4 Steady-state kinetic assays of the Au-NCs in the absence (a, c) and presence (b, d) of Pb^{2+}. The kinetic data were obtained by varying one substrate concentrations while keeping the other substrate concentration constant (0.5 mM TMB or 50 mM H_2O_2). Insets are the Lineweaver-Burk plots of the double reciprocal of the Michaelis-Menten equations.

Table S1 Comparison of the kinetic parameters of Au-NCs in the absence and presence of Pb^{2+}. K_m is the Michaelis-Menten constant, V_{max} is the maximal reaction rate, K_{cat} is the catalytic constant, $K_{cat} = V_{max}/[E]$, and $[E]$ is the concentration of Au-NCs.

Catalyst	Substrate	K_m / mM	V_{max} / M s^{-1}	K_{cat} / s^{-1}	K_{cat}/K_m [s^{-1} mM^{-1}]
Au-NCs	H_2O_2	92.4	8.47×10^{-9}	0.027	2.92×10^{-4}
Au-NCs in the presence of Pb^{2+}	H_2O_2	30.8	3.39×10^{-8}	0.109	3.54×10^{-3}
Au-NCs	TMB	0.96	7.52×10^{-9}	0.024	0.025
Au-NCs in the presence of Pb^{2+}	TMB	0.58	4.13×10^{-8}	0.132	0.228

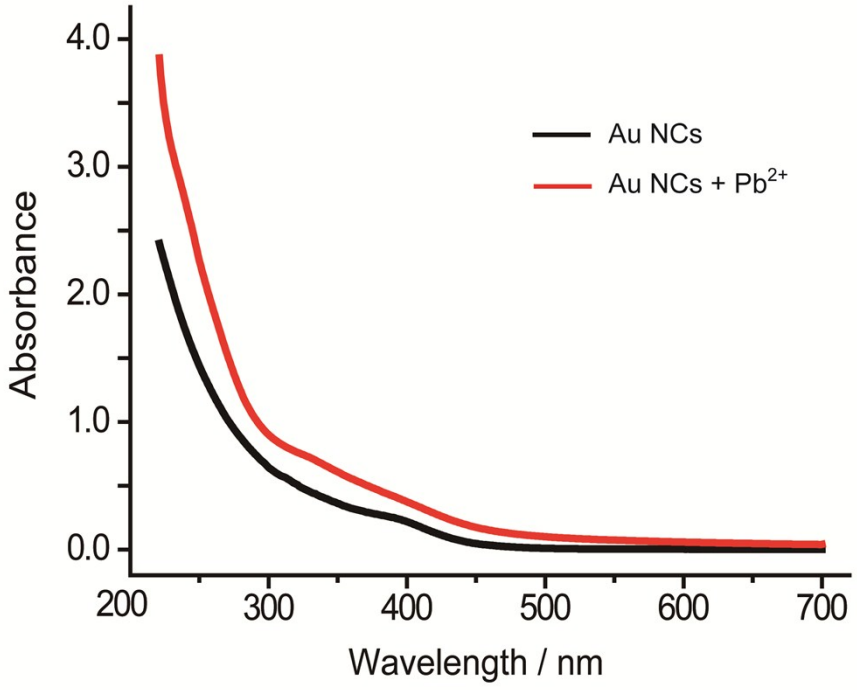

Fig. S5 UV-vis absorption spectra of Au-NCs in the absence and presence of Pb^{2+}.

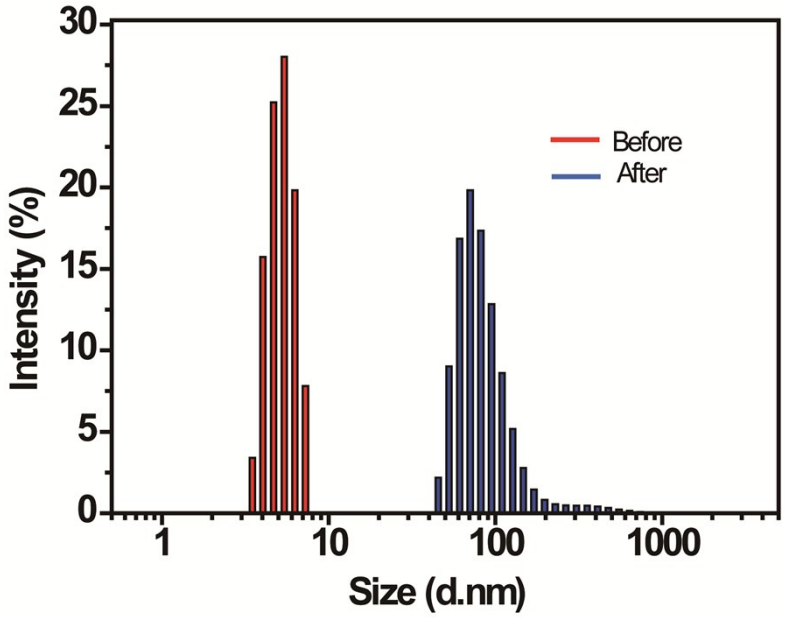

Fig. S6 The hydrodynamic size distribution of Au-NCs before (red) and after (blue) the addition of Pb^{2+}.

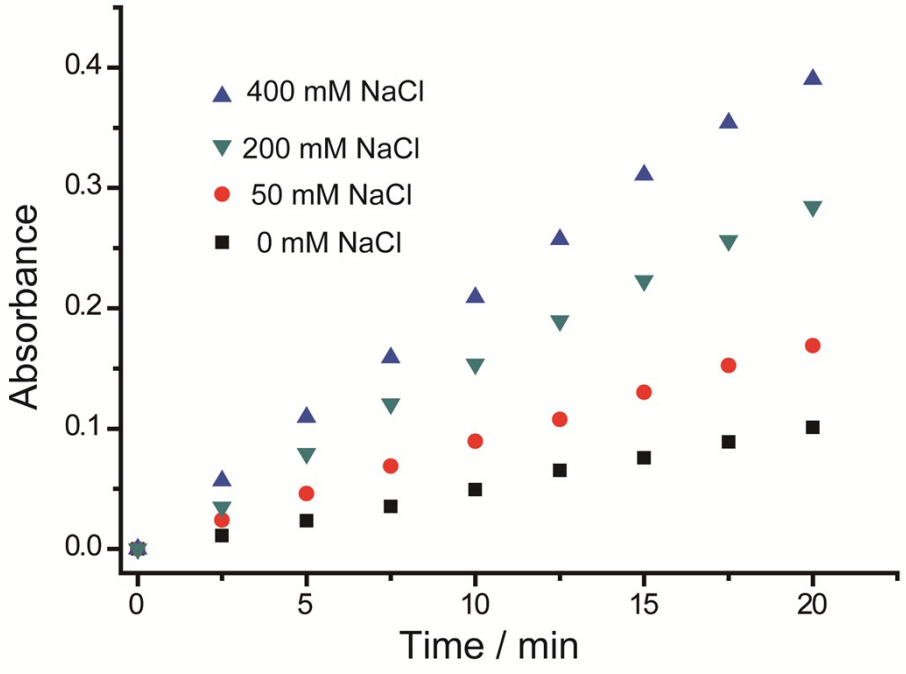

Fig. S7 Reaction kinetics of the system in the presence of different concentrations of NaCl.

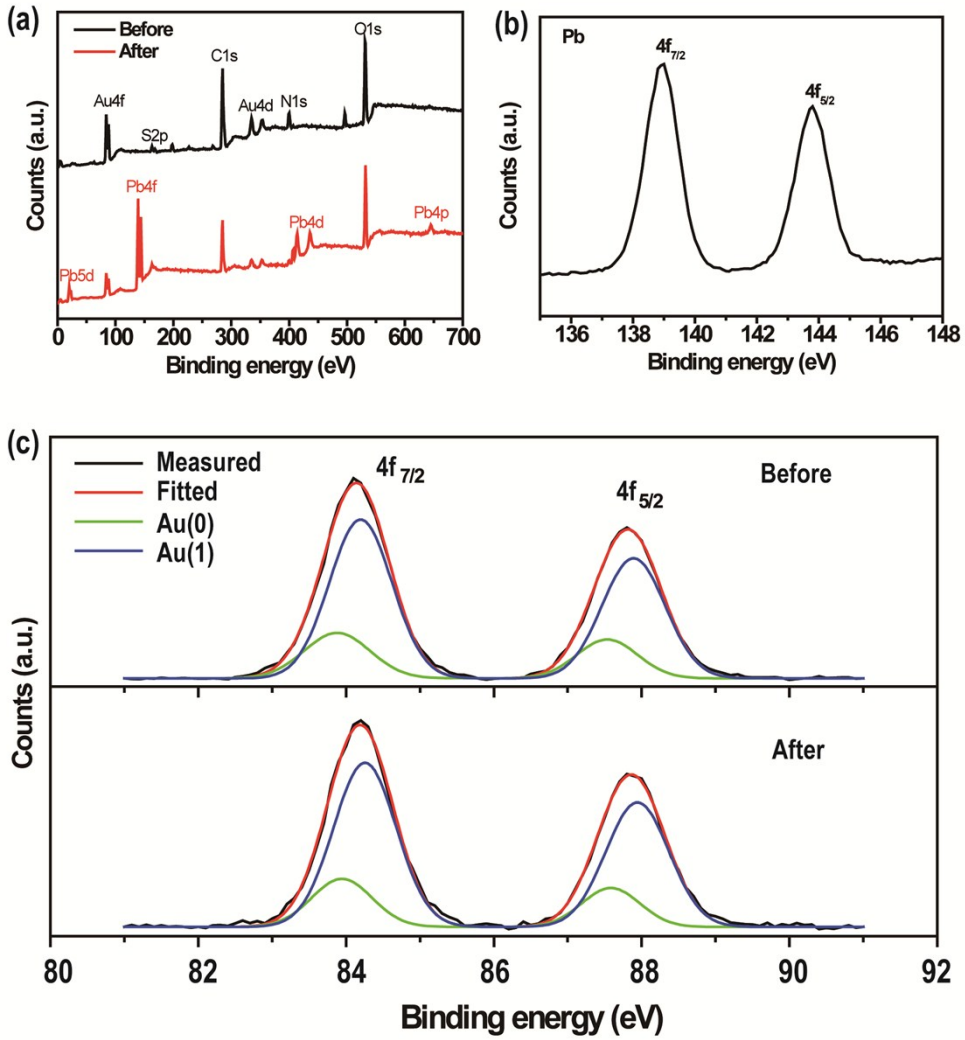

Fig.S8 XPS spectra of (a) all the surface elements of Au-NCs before and after the addition of Pb^{2+}, (b) high-resolution Pb 4f spectra of Au-NCs after the addition of Pb^{2+}, and (c) high-resolution Au 4f spectra before and after the addition of Pb^{2+}.

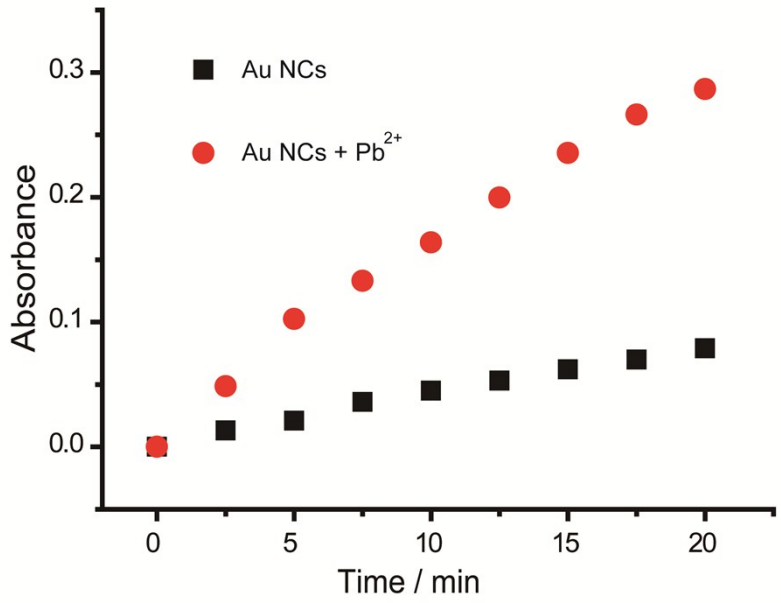

Fig. S9 The kinetic curves of Au-NCs toward ABTS (0.5 mM) oxidation in the presence of H_2O_2 (10 mM) in the absence (■) and presence (●) of Pb^{2+} (0.2 mM).

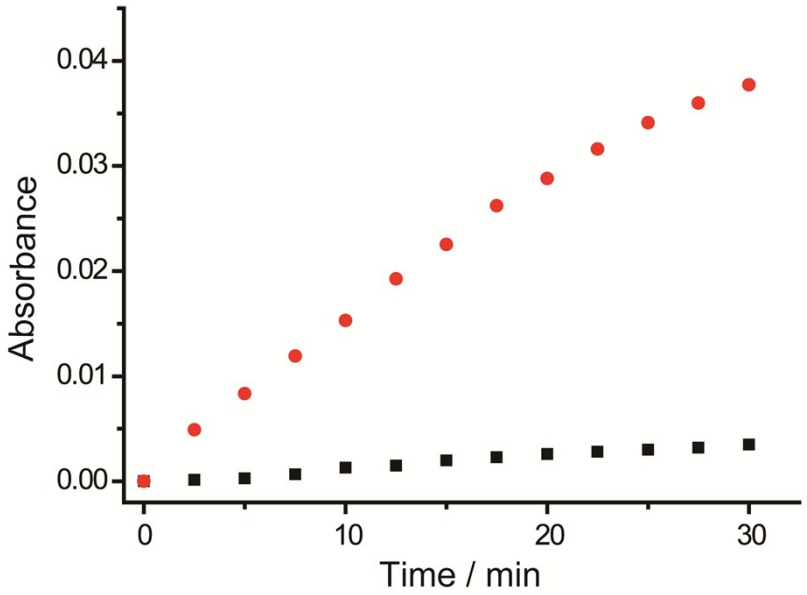

Fig. S10 Reaction kinetics of TMB-H_2O_2 system in the presence of Au(I)-thiolate complexes (■), and Au(I)-thiolate complexes with Pb^{2+} (●).

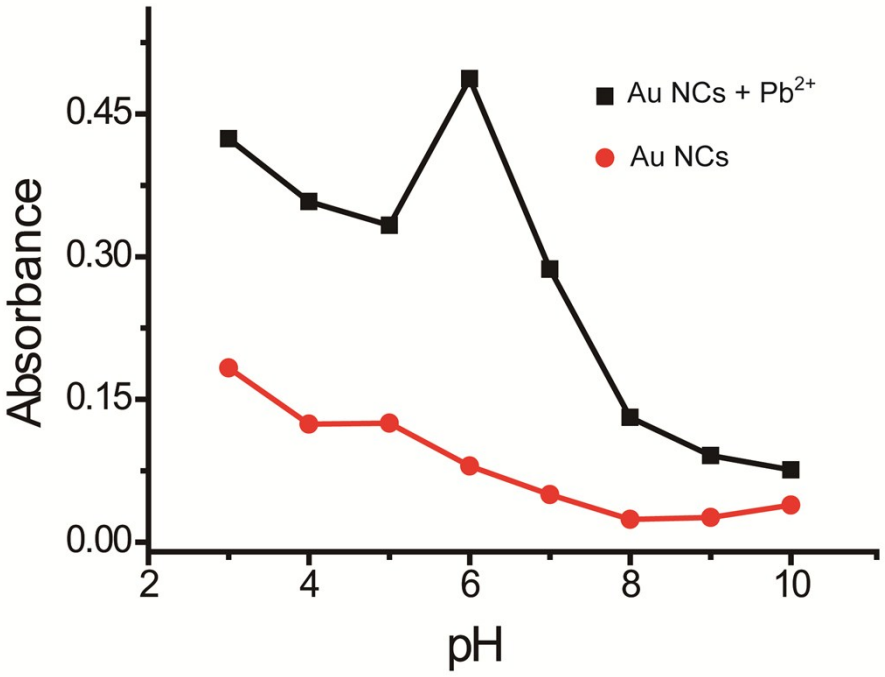

Fig. S11 Comparison the peroxidase-like activity of Au-NCs in the absence and presence of Pb^{2+} in different pH values.

Table S2 The analytical performance comparison of this work with other fluorescent methods for Pb^{2+} detection.

Sensing principle	Method	Linear range	Detection limit	References
Aggregation of Au-NCs	Colorimetric	2-250 μM	2 μM	This work
Aggregation of Au-NCs	Fluorescence enhancement	5-50 μM	5 μM	1
Ligand exchange of Au-NCs	Fluorescence quenching	5 nM-5 μM	2 nM	2
Aggregation of Au-NCs	Fluorescence quenching	10-100 nM	4.8 nM	3
Synergistic aggregation of Au(I)-glutathione	Fluorescence enhancement	0.5-40 μM	0.5 μM	4

Table S3 The analysis of Pb^{2+} concentrations in lake water by the standard addition method.

Lake water	Pb^{2+} added (μM)	Pb^{2+} found (μM)	Pb^{2+} recovery (%)
1	20	19.1	95.5
2	100	96.3	96.3
3	200	197.2	98.6

References

1. L. Ji, Y. Guo, S. Hong, Z. Wang, K. Wang, X. Chen, J. Zhang, J. Hu and R. Pei, *RSC adv.*, 2015, **5**, 36582-36586.

2. Z. Yuan, M. Peng, Y. He and E. Yeung, *Chem. Commun.*, 2011, **47**, 11981-11983.

3. C. Lee, N. Hsu, M. Wu and Y. Lin, *RSC Adv.*, 2016, **6**, 79020-79027.

4. C. Liu, J. Ling, X. Zhang, J. Peng, Q. Cao and Z. Ding, *Anal. Methods*, 2013, **5**, 5584- 5588.