## **Supplementary Information**

## Microwave-facilitated rapid synthesis of gold nanoclusters with tunable optical property for sensing ions and fluorescent ink

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## **EXPERIMENTAL SECTION**

**Chemicals.** Tetrachloroauric acid trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Glutathione in the reduced form (GSH) was purchased from Sangon Biotech Ltd. (Shanghai, China). All other compounds were commercially available and used without further purification. Ultrapure water (18.2 M $\Omega$  cm) was used throughout the experiment.

Synthesis of luminescent GS-AuNCs with varying emissions. In a typical procedure, freshly prepared aqueous solutions of GSH (10 mL, 7.5 mM) and HAuCl<sub>4</sub> (10 mL, 5 mM) were mixed under gentle stirring for 5 min, followed by being transferred into the specific microwave vessel and sealed. The reaction temperature was set at 90 °C, which took 2 min to reach from room temperature. Afterwards, the irradiation time varied from 10 min to 6 h, generating a series of GS-AuNCs emitting faint red to intense orange luminescence. After cooling down, the solutions were stored at 4 °C for at least 24 h before further treatment. The final products were then precipitated out of the solutions by adding ethanol and NaCl (1 M), dispersed in 20 mL HEPES-NaOH buffer (10 mM, pH = 7.4), and kept at 4 °C or under ambient conditions ( $18 \pm 2$  °C), respectively.

**Calibration curve for the detection of Cu<sup>2+</sup> (or Ag<sup>+</sup>) ion by AuNCs-3h.** In HEPES buffer (10 mM, pH = 7.4) and the absorbance of AuNCs-3h at 410 nm was 0.006, the calibration for the detection of Cu<sup>2+</sup> (or Ag<sup>+</sup>) ion was performed by the addition of Cu<sup>2+</sup> (or Ag<sup>+</sup>) at different concentrations to the solution. The volume of the sensing solution was set to be 1 mL. The widths of excitation and emission slit were both 10 nm.

**Detection of Ag<sup>+</sup> ion in lake water by AuNCs-3h.** The lake water was collected from our campus. After simple filtration by membrane (0.22  $\mu$ m), the water was assayed for Ag<sup>+</sup> ion within 24 h.

**Characterization.** The microwave reaction was conducted with a MDS-6G microwave digestion system (Sineo, China). UV-vis optical spectra were recorded with a Lambda 25 UV-vis spectrophotometer (PerkinElmer). Steady state photoluminescence (PL) spectra were recorded with a Hitachi F-4600 fluorescence spectrophotometer, and time-resolved PL lifetimes were measured by time-correlated single photo counting (TCSPC) on a Horiba JY Fluorolog-3-Tou spectrofluorometer with 410 and 605 nm as the excitation and emission

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wavelength, individually. Transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectrometer (EDX) and high-resolution TEM images of NCs were obtained on a JEOL-2100F TEM instrument operating at 200 kV. The size distributions and zeta potential of these clusters were examined on a Malvern Zetasizer instrument. The product yield with Au atom basis was calculated from inductively coupled plasma-optical emission spectrometry (ICP-OES) result by an Optima 7300DV (PerkinElmer). Matrixassisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed with a Bruker Autoflex Speed mass spectrometer. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldidene] malononitrile (DCTB) was used as the matrix for MALDI. X-ray photoelectron spectroscopy (XPS) study was performed on an ESCALAB 250 spectrometer (VG Scientific). Thermogravimetric analysis (TGA) was performed on a TGA Q5000IR analyzer under N<sub>2</sub> atmosphere. X-ray powder diffraction (XRD) pattern was obtained using a D/Max-yA rotating-anode X-ray diffractometer (Rigaku). The elemental contents of C, H, N, O, and S in the nanoclusters were measured on a Vario EL III elemental analyzer system (Germany). Agarose gel electrophoresis was run by 2% agarose gel in 0.5×TBE buffer (Tris, 44.5 mM; EDTA, 1 mM; and boric acid, 44.5 mM, pH 8.0) for 45 min at 10 V/cm at 4 °C.

## SUPPLEMENTARY FIGURES



**Fig. 1** Photoemission spectra of GS-AuNCs prepared (a) during elongated time, (b) under higher microwave power, and (c) at different microwave temperature. For figure (a), the microwave temperature and power are 90 °C and 300 W, for figure (b), the microwave temperature is 90 °C, and for figure (c), the microwave power and time are 300 W and 1 h. Other conditions for the syntheses include that solution pH is 2 and GSH/Au molar ratio is 1.5.

Note: The quantum yields were measured to be 3.0%, 4.4%, and 3.5% for AuNCs by 4 h, 5 h, and 6 h of reaction, and the quantum yield for AuNCs prepared at 600 W for 3 h was 3.1%.



**Fig. S2** Photoemission spectra of the GS-AuNCs solutions (a) after storage at 4 °C for 60 days and (b) after storage at ambient temperature.



Fig. S3 TEM image and size histogram of the GS-AuNCs prepared for 5 h.



**Fig. S4** Powder XRD pattern of the GS-AuNCs prepared for 3 h. The sticks represent the standard diffraction angles for fcc structure of gold (JCPDS 04-0784).



**Fig. S5** Positive (left) and negative (right) MALDI-TOF mass spectra of the gold clusters prepared for 10, 90, and 180 min.



**Fig. S6** XPS spectra of purified AuNCs-3h: (a) survey scan; (b)  $Au_{4f}$ ; (c)  $S_{2p}$ . (d) TGA analysis of purified AuNCs-3h.



**Fig. S7** (a) The PL excitation spectrum using 605 nm as the emission wavelength and PL emission spectra with different excitation wavelengths for the AuNCs-3h solution. (b) The time-resolved fluorescence decay curve for the AuNCs-3h solution using 410 nm as the excitation wavelength. (c) Temperature-dependent PL emission spectra of the AuNCs-3h solution. (d) Time-dependent emission intensity at 605 nm of the AuNCs-3h solution using 410 nm as the excitation wavelength.



**Fig. S8** Time-dependent PL change of AuNCs-3h solution under continuous excitation on a fluorescence microscope.



Fig. S9 Selectivity test of the AuNCs-3h towards a variety of anions (100 µM) and metal ions (1 µM).



**Fig. S10** Effects of AuNCs with different reaction time, buffer, and concentration of AuNCs on the detection of  $Cu^{2+}$  ion. From (a), it is concluded that AuNCs (180 min) has the best sensing performance among the three AuNCs selected, which suggests increasing the size of NCs will improve the detection. From (b), it is concluded that buffer composition has no influence upon the sensing. From (c), it is concluded that the lower the concentration of AuNCs, the higher sensitivity of detection is obtained. In this sense, the optimal conditions are generalized to be AuNCs-3h, HEPES buffer, and  $A_{410nm}$  of NCs solution being 0.006.



**Fig. S11** UV-vis absorption spectra of AuNCs-3h solution in the absence and presence of (a)  $Cu^{2+}$  ion and (b) Ag<sup>+</sup> ion. (c) Time-resolved fluorescence decay curves of AuNCs-3h solution in the absence and presence of  $Cu^{2+}$  and Ag<sup>+</sup> ion, individually.



**Fig. S12** UV-vis absorption spectra of AuNCs-3h solution in the absence and presence of  $Co^{2+}$  ion,  $Ni^{2+}$  ion, and  $Hg^{2+}$  ion.

GS-AuNCs	Au-10 min	Au-20 min	Au-30 min	Au-45 min	Au-60 min	Au-90 min	Au-120 min	Au-180 min
$\lambda_{em} (nm)$	670	670	660	635	625	613	610	605
Φ(%)	0.42	0.47	0.55	0.65	0.89	1.2	1.3	2.4

Table S1 The dominant emission wavelength ( $\lambda_{em}$ ) and quantum yield ( $\Phi$ ) of the GS-AuNCs.\*

\*  $\Phi$  is based on the average of three measurements using 360, 380, and 400 nm as excitation wavelength, respectively, with quinine sulfate (in 0.5 M H<sub>2</sub>SO<sub>4</sub>) as reference (0.54).

Table S2 Hydrodiameters (HDs) of the GS-AuNCs.

GS-AuNCs	Au-10 min	Au-20 min	Au-30 min	Au-45 min	Au-60 min	Au-90 min	Au-120 min	Au-180 min
HD (nm)	$2.4\pm0.2$	$2.6\pm0.3$	$2.4\pm0.3$	$2.8\pm0.3$	$3.0\pm0.2$	$3.2\pm0.4$	$3.6 \pm 0.4$	$3.3 \pm 0.3$

Table S3 Elemental analysis of the AuNCs-3h.

Element	С	Н	Ν	0	S	Au (calculated)
Percentage	19.57	2.99	6.78	18.91	6.65	45.1
(%)						

Table S4 Determination of  $Ag^+$  ion in lake water sample. All data are based on the average of two measurements.

Detected (µM)	Spiked (µM)	Found (µM)	Recovery (%)
Undetectable	0.2	0.20	100
	0.5	0.47	94
	1.0	0.87	87

Table S5 Lifetime for the AuNCs before and after incubation with Cu<sup>2+</sup> and Ag<sup>+</sup> ions, individually.

$\tau_{average}$	$=\frac{\sum_{i=1}^{2}A_{i}\tau_{i}^{2}}{\sum_{i=1}^{2}A_{i}\tau_{i}}$				
Lifetime (µs)	$ au_1$	A <sub>1</sub>	$ au_2$	A <sub>2</sub>	$\tau_{average}$
AuNCs	3.28	0.87	14.4	0.13	7.69
AuNCs + Cu <sup>2+</sup>	1.11	1	/	/	1.11
AuNCs + Ag <sup>+</sup>	3.64	0.79	17.4	0.21	11.34

Lifetime (µs)	τ	Α	
AuNCs + Co <sup>2+</sup>	2.47	1	
AuNCs + Ni <sup>2+</sup>	2.37	1	
AuNCs + Hg <sup>2+</sup>	2.61	1	

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Table S6 Lifetime for the AuNCs before and after incubation with  $Cu^{2+}$  and  $Ag^+$  ions, individually.