

Electronic supplementary information for Localized surface plasmon resonance light-scattering detection of Hg(II) with 3-aminopropyltriethoxysilane -assisted synthesis of highly stabilized Ag nanoclusters

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EXPERIMENTAL SECTION

Reagents. All chemicals used are of at least analytical grade. 3-aminopropyltriethoxysilane (APTES), silver nitrate (AgNO₃) and polyethyleneimine (PEI) (Mw = 600, 99%) were purchased from Aladdin (Shanghai, China). Methanol (CH₃OH) and formaldehyde (HCHO) were purchased from bodi chemical Co., LTD (Tianjin, China) and Sinopharm chemical reagent Co., LTD (Shanghai, China), respectively. All solutions were freshly prepared before use.

Apparatus. The morphologies of the prepared samples were examined using JEM-100SX electron microscope (Nicolet, Japan). Fourier Transform Infra-Red (FTIR) spectra were taken with a Spectrum One FTIR spectrophotometer (Perkin-Elmer, America) at room temperature. **Element analysis was performed with inductively coupled plasma atomic emission spectrometry (ICP-AES) (Perkin-Elmer, America).** The UV-vis absorption measurements were performed on ZF-I Three-operating UV analyzer (Gucun Electricity Light Instrumental Factory, China). The LSPR scattering were obtained by scanning simultaneously the excitation and emission monochromators of the spectrofluorometer from 300 to 700 nm with the same starting wavelength and same scanning speed by RF-540 fluorophotometer (Tokyo, Japan).

Synthesis of the Ag NCs. PEI-capped Ag NCs were synthesized according to a recently reported method with modification. Typically, 44 μmol AgNO₃ and 11 μmol APTES were dissolved in 3 ml methanol and stirred 2 h in the dark. PEI (1 ml, 0.0073 g/mL) was added and homogenized by stirring for 2 min. Then, 56 μL of formaldehyde solution (38%) was added under vigorous stirring for 4 h in the dark. A series of control experiments (different ratio of APTES / Ag)

were performed to demonstrate the influence of APTES on the synthesis Ag NCs.

Measurement procedure. A typical Hg^{2+} detection procedure was conducted as follows. Hg^{2+} solution at different concentration was obtained by a serial dilution of the stock solution. The as-prepared Ag NCs solutions were diluted 20 times for Hg^{2+} detection. Then 5 μl of different concentrations of Hg^{2+} solution was added to 3 mL of the diluted Ag NCs. The LSPR scattering signals of the solution were obtained by fluorophotometer.

Real Samples. Tap and lake water samples were collected from Hubei University in China. In the LSPR scanning, the tap water were diluted 5 times with pure water before detection to eliminate the background, whereas the lake water was filtrated with funnel and diluted 10 times. In the element analysis by ICP-AES, each sample was filtered using a 0.45 μm PTFE filter, and adjusted to approximately pH 5 by adding NaOH/ HNO_3 .

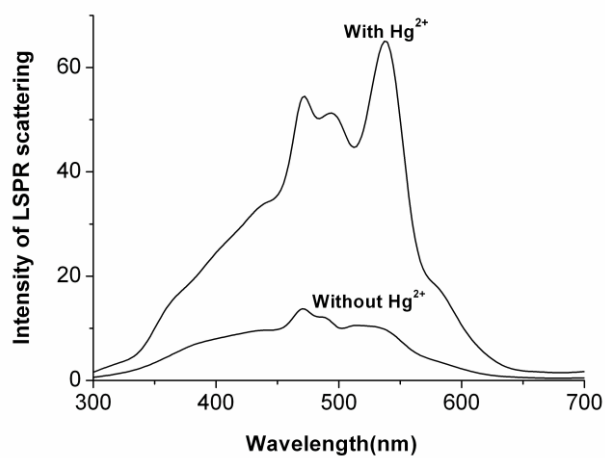


Figure S1. LSPR scattering spectra of the PEI capped-Ag NCs in the present and in the absence of Hg²⁺. APTES/Ag= 4:1.

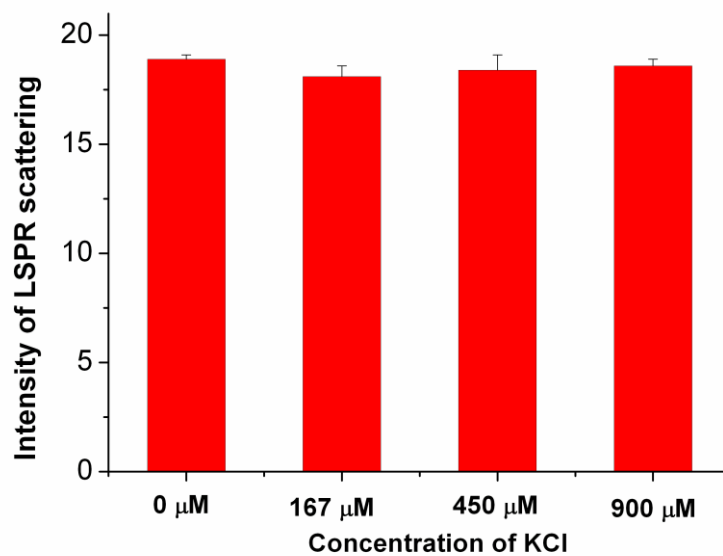


Figure S2. LSPR scattering intensity of Ag NCs measured at 530 nm for different concentrations of KCl. *APTES/Ag*= 4:1.

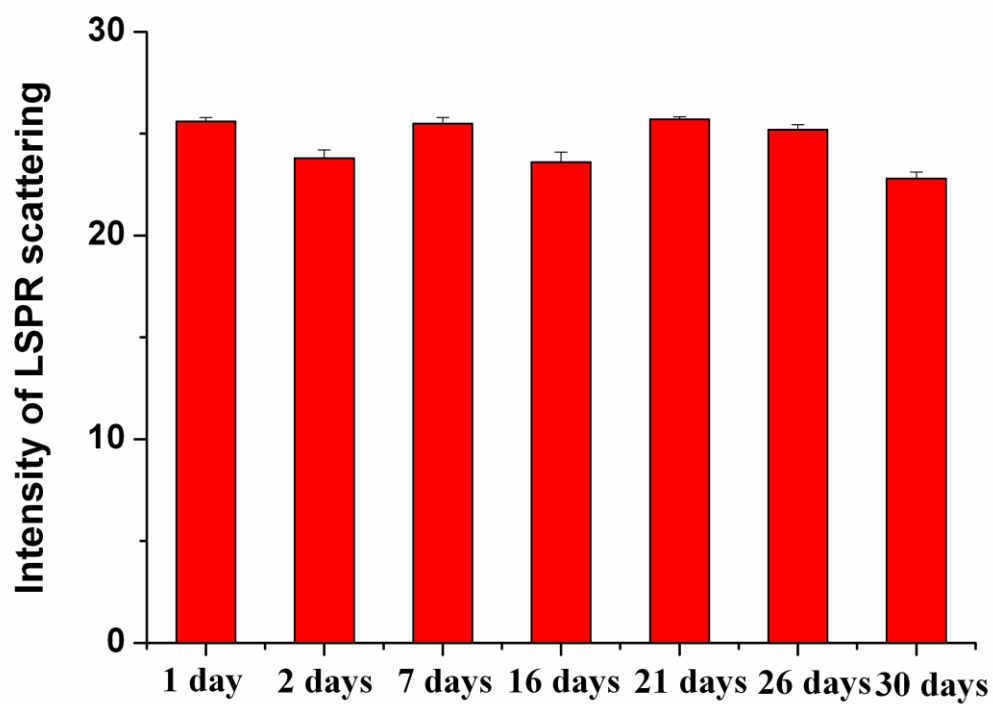


Figure S3. The long-term stability of the Ag NCs after diluting 20 times in water. APTES/Ag= 4:1.

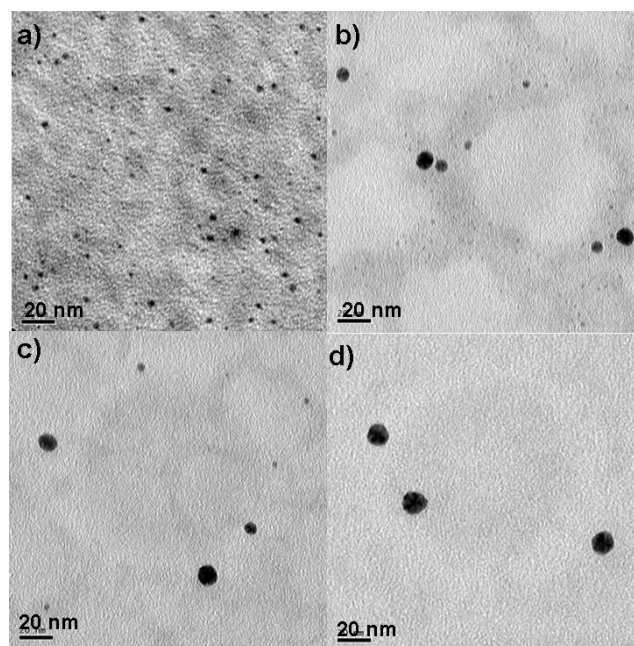


Figure S4. TEM images of the as-prepared Ag NCs in the absence (a) and presence (b, c, d) of Hg²⁺ ions. Hg²⁺ ions from b to d: 33 μM, 167 μM, 1.5 mM. **APTES/Ag= 4:1.**

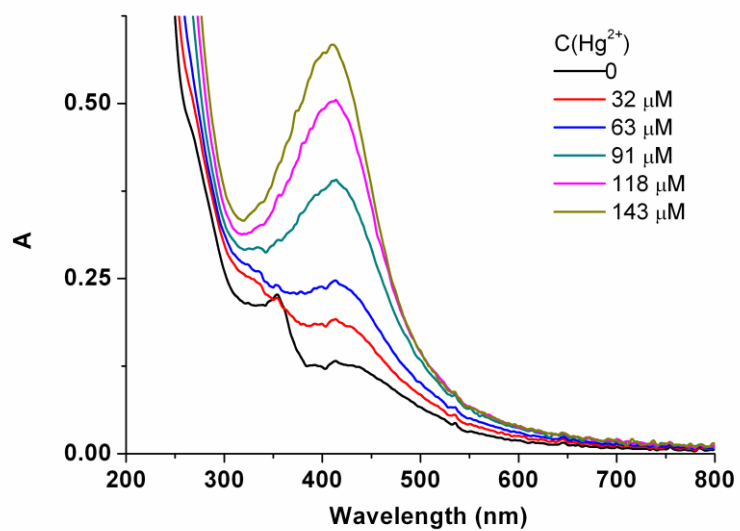


Figure S5. Absorption spectra of the as-prepared Ag NCs in the absence and presence of different concentrations of Hg^{2+} APTES/Ag= 4:1.

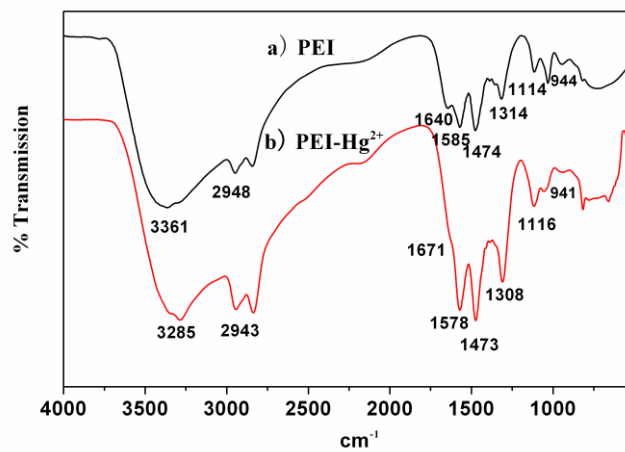


Figure S6. FTIR spectra of the PEI and PEI-Hg.

Table S1 Determination of Hg in water sample using the proposed method and ICP-AES method

Samples	Spiked (mM)	Proposed method		ICP-AES method	
		Measured(mM)	Recovery (%)	Measured(mM)	Recovery (%)
Pure water	0.167	0.162±0.007	97.0±4.2	0.165±0.003	98.8±1.8
Tap water	0.167	0.161±0.009	96.4±5.4	0.168±0.008	100.5±4.8
Lake water	0.167	0.163±0.004	97.6±2.4	0.166±0.007	99.4±2.4

Table S2 Comparison between proposed methods with some other methods for Hg²⁺

Method	LOD(ngL ⁻¹)	Reference
HPLC-CVGAFS	457	[1]
HPLC-ICPMS	5.2	[2]
ETAAS	60	[3]
LSPR	20	this method

[1] R Badugu, J R Lakowicz, C D Geddes. *Talanta* , 2005, 65, 762 -768.

[2] R. M. Blanco, M. T. Villanueva, J.E. Sánchez Uría, A. Sanz-Medel, *Anal. Chim. Acta* 2000, 419, 137-144.

[3] I López-García, R. E. Rivas, M. Hernández-Córdoba, *Anal. Chim. Acta* 2012, 743, 69- 74.