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Journal Name

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Ultrasensitive Detection and Co-stability of Mercury(II) Ions Based on Amalgam Formation with Tween 20-Stabilized Silver Nanoparticles

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Zhi Guo[a,b], Guiqiu Chen[*,a,b], Guangming Zeng[*,a,b], Zhongwu Li[a,b], Anwei Chen[c], Ming Yan[a,b], Lingzhi Liu[a,b], Daoyou Huang[d]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, P.R. China.

[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, P.R. China.

[c] College of Resources and Environment, Hunan Agricultural University, Changsha 410128, P.R. China.

[d] Key laboratory for Agro-ecological Processes in Subtropical Region, Institution of Subtropical Agriculture, Chinese Academy of Science, Changsha 410125, P.R. China.

[*]Corresponding Author. Phone: +86 731 88822829. Fax: +86 731 88823701. E-mail: gqchen@hnu.edu.cn (G.C.); zgming@hnu.edu.cn (G.Z.).

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EXPERIMENTAL SECTION

Synthesis of Bare AgNPs. A 59.5 ml solution containing 0.23 mM $NaBH_4$ was prepared in double distilled water and was stirred vigorously in ice bath. Upon addition of 0.48 ml, 23.5 mM $AgNO_3$ under stirring, the colour of solution turned yellow, indicating the formation of the AgNPs. After 3 h of additional stirring at room temperature, the soluble byproducts were removed by centrifugal ultrafiltration (molecular weight cutoff of 8000), and the AgNPs were washed with double distilled water.

References

(1) B. M. W. Fong, T. S. Siu, J. S. K. Lee, and S. J. Tam, *Anal. Toxicol.*, 2007, **31**, 281–287.

(2) S. Gil, I. Lavilla, and C. Bendicho, *Anal. Chem.*, 2006, **78**, 6260−6264.

(3) A. Ono, and H. Togashi, *Angew. Chem., Int. Ed.*, 2004, **43**, 4300–4302.

(4) M. Hollenstein, C. Hipolito, C. Lam, D. Dietrich, and D. M. Perrin, *Angew. Chem.*, 2008, **47**, 4346−4350.

(5) M. Li, Q Y. Wang, X. D. Shi, L. A. Hornak, and N. Q. Wu, *Anal. Chem.*, 2011, **83**, 7061–7065.

(6) L. Deng, X. Y. Ouyang, J. Y. Jin, C. Ma, Y. Jiang, J. Zheng, J. S. Li, Y. H. Li, W. H. Tan, and R. H. Yang, *Anal. Chem.*, 2013, **85**, 8594–8600.

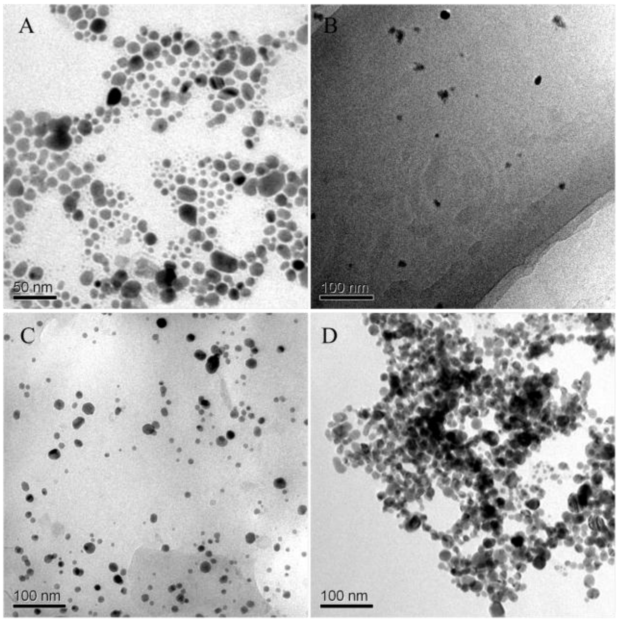


Figure S1. TEM of (A) Citrate-AgNPs. (B) Bare AgNPs. (C) Tween-20 AgNPs. (D) Ag/Hg amalgam.

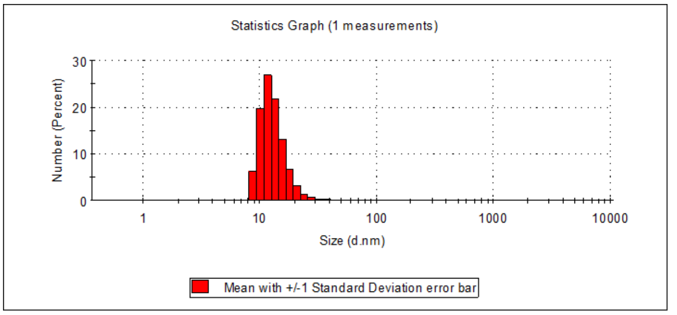


Figure S2. Size distribution of bare AgNPs.

Temperature (°C):	25.0	Zeta Runs:	30
Count Rate (kcps):	0.0	Measurement Position (mm):	2.00
Cell Description:	Clear disposable zeta cell	Attenuator:	10

			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-14.6	Peak 1:	-14.6	100.0	16.3
Zeta Deviation (mV):	16.3	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.865	Peak 3:	0.00	0.0	0.00

Result quality : See result quality report

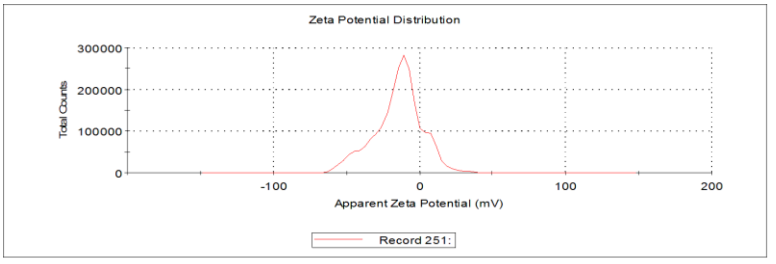
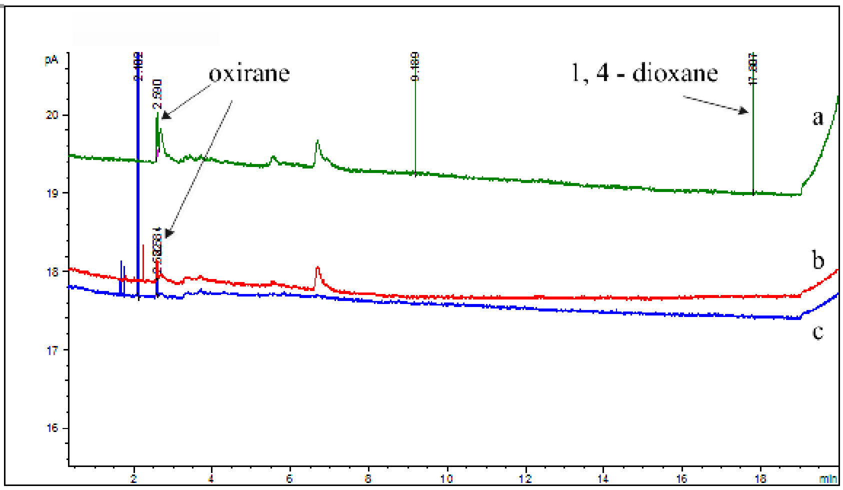


Figure S3. DLS zeta potential distribution of Tween 20-AgNPs (-14.6 mV).



sample	subject	area	height	width
a	oxirane	1.3	0.63	0.0294
	1,4-dioxane	10.3	70	5.0471E-3
b	oxirane	0.441	0.27	0.0241
	1,4-dioxane	2	2	2
c	oxirane	0.311	0.24	0.0214
	1,4-dioxane	2	2	2

Figure S4. Gas chromatography analysis of (a) standard sample of Tween 20, (b) dialysis solution of Tween 20-AgNPs with 100 nM Hg^{2+}, (c) dialysis solution of Tween 20-AgNPs without Hg^{2+}.

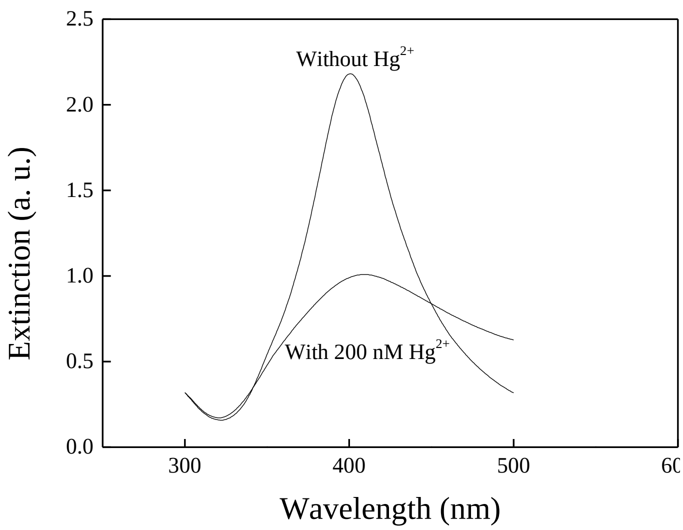


Figure S5. Extinction spectra of solutions with and without the addition of 200 nM Hg^{2+}

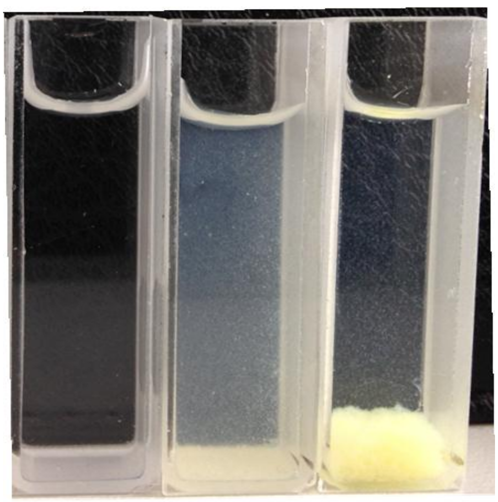


Figure S6. Reduction of Hg^{2+} (0, 5.0, 10.0 μM from left to right) at room temperature using citrate ions in the absence of Tween 20 AgNPs.

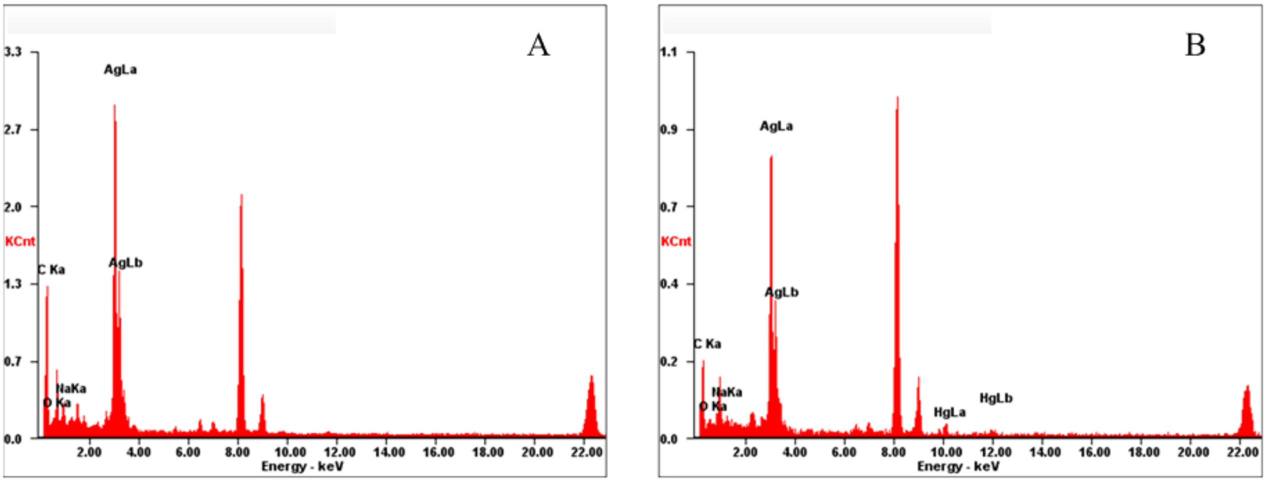


Figure S7. EDX spectroscopy analysis of (A) Tween 20-AgNPs and (B) Ag/Hg amalgam formed in the presence of 100 nM Hg^{2+}.

Table S1. Elemental analysis results of Tween 20-AgNPs obtained by EDX spectra

element	weight percentage	atom percentage
C K	21.20	68.80
O K	1.10	2.60
Na K	0.30	0.60
Ag L	77.40	28.00

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Table S2. Elemental analysis results of Ag/Hg amalgam obtained by EDX spectra

element	weight percentage	atom percentage
C K	21.20	68.80
O K	1.10	2.60
Na K	0.30	0.60
Ag L	77.40	28.00
Hg L	6.40	1.60

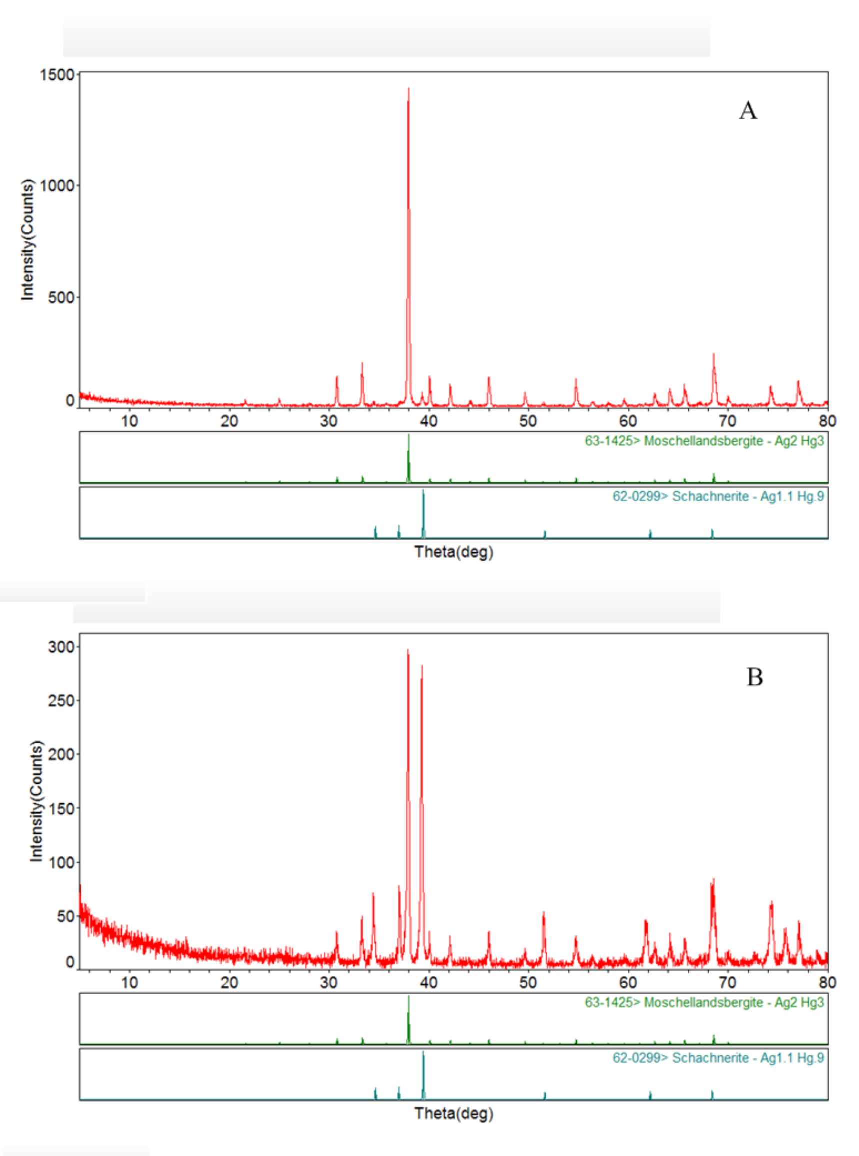

Figure S8. XRD analysis of Ag/Hg amalgam in the presence of (A) 50.0 nM and (B) 500.0 nM Hg^{2+}.

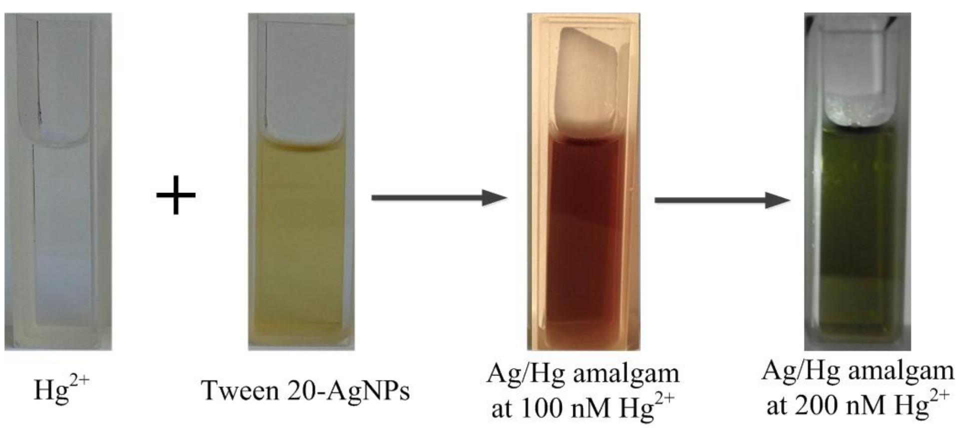

Figure S9. Photographs of working solutions containing Tween 20-AgNPs after adding 100 and 200 nM Hg^{2+}.

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Table S3. Comparison of Assay Methods for Monitoring Mercury

detection methods	linear range (nM)	detection limit (nM)	reference
ICP−MS	10.0−500.0	0.65	1
AAS/cold vapor	*a*	0.5	2
T−Hg^{2+}−T/FRET	40.0−100.0	40.0	3
T−Hg^{2+}−T/DNAzyme	*a*	100.0	4
T−Hg^{2+}−T/QDs	2.0−60.0	2.0	5
silver amalgamation	10.0−8000.0	2.6	6
silver amalgamation	0.5−120.0	0.31	this work

[a]No reported results.

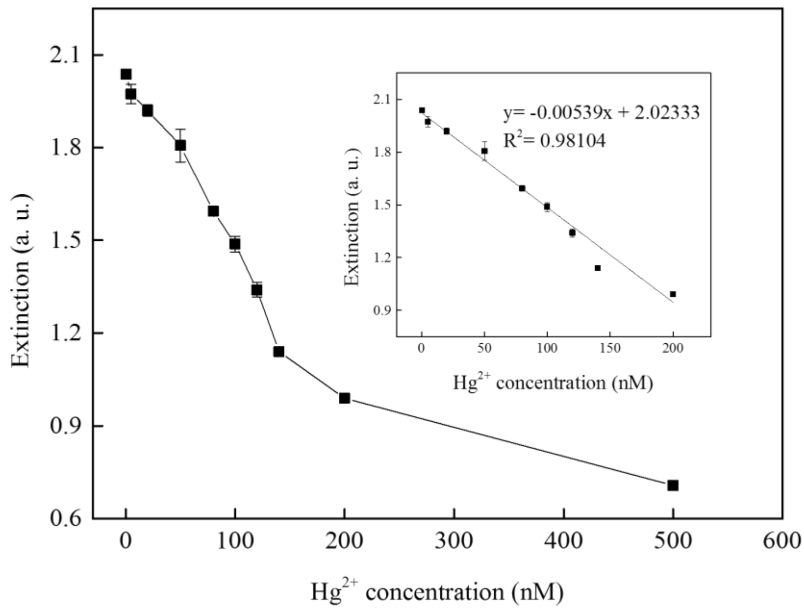

Figure S10. The calibration curve of UV-Vis absorbance intensity against Hg^{2+} concentration in buffer samples. Inset shows the response linearity of the assay with Hg^{2+} concentrations at 0.5, 5.0, 20.0, 50.0, 80.0, 100.0, 120.0 and 200.0 nM.

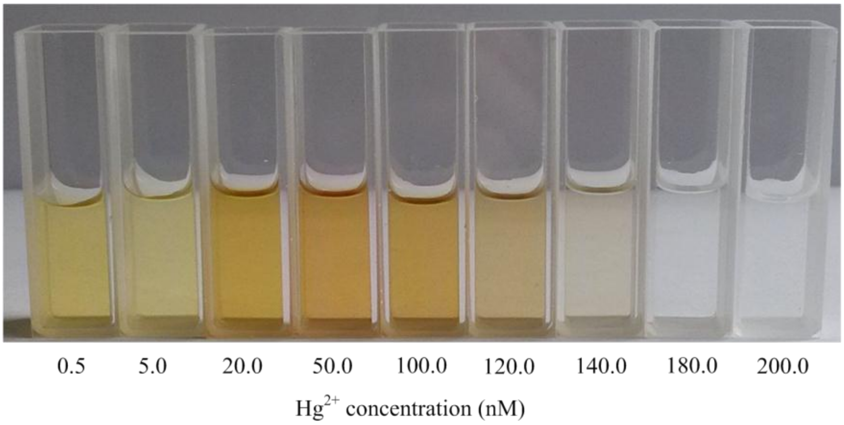

Figure S11. Photographs of working solutions containing Tween 20-AgNPs after adding various concentrations of Hg^{2+} in buffer.

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Table S4. Determination of Hg^{2+} (nM) in Water Samples Using the Proposed Method and AFS

sample	added	proposed method mean[a] ±SD[b]	AFS mean ±SD
tap water 1	0	*c*	*c*
tap water 2	20.0	20.03 ±0.13	20.02 ±0.07
tap water 3	50.0	49.99 ±0.17	50.02 ±0.22
tap water 4	100.0	103.98 ±0.36	101.98 ±0.20
spring water 1	0	<0.1	*c*
spring water 2	20.0	20.02 ±0.19	20.03 ±0.08
spring water 3	50.0	50.10 ±0.22	50.05±0.14
spring water 4	100.0	101.17 ±0.23	101.39 ±0.16
lake water 1	0	<0.1	<0.1
lake water 2	20.0	20.04 ±0.21	20.06 ±0.08
lake water 3	50.0	49.97 ±0.37	50.03 ±0.35
lake water 4	100.0	101.26 ±0.46	103.51 ±0.12

[a]Mean of three determinations. [b]SD, standard deviation. [c]No Hg^{2+} concentration could be detected.