Electronic Supporting Information (ESI) for

## High sensitive SERS sensor for mercury ions based on the catalytic reaction of mercury ions decorated Ag nanoparticles

Guohua Qi,<sup>a</sup> Cuicui Fu,<sup>a</sup> Gang Chen,<sup>a,b</sup> Shuping Xu,<sup>a</sup> and Weiqing Xu<sup>a\*</sup>

a. State Key laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry,

Jilin University, 2699 Qianjin Ave., Changchun, The People's Republic of China. Email: xuwq@jlu.edu.cn

b. College of Chemistry, Jilin University, 2699 Qianjin Ave., Changchun, The People's Republic of China.

## 1. Preparation of Ag NPs

All the glassware were cleaned by the deionized water and dried to use. Ag NPs was synthesized using Lee's method as described previously.<sup>S1</sup> AgNO<sub>3</sub> (0.027g) was dissolved in 150 mL of deionized water under vigorously stirring and heating. When the solution got to boil, a sodium citrate aqueous solution (3.0 mL, 1wt%) was quickly added. The solution kept near boiling for 40 min. Then it was cooled to room temperature and stored in dark for further use. The obtained Ag sol has the maximum absorption peak at 418 nm.



Figure S1. UV-vis absorbance spectrum and the size distribution of Ag NPs.

## 2. Optimization of reaction conditions

The pH and Ag NP volume were optimized for the catalytic reaction. It should be noted that, when we carried out the mercury ion detection, we should keep these conditions involving the amount of Ag NPs, reaction time, pH, temperature in same to insure that these conditions provide the constant contributions to SERS signal in each trial.

The SERS signal is also determined by the amount of Ag NPs. The strongest enhanced Ag NPs can bring the highest detection sensitivity of mercury ions. So, we need to optimize the strongest enhanced Ag NPs by changing Ag NP concentration while the mercury ions concentration is unchanged. To find the effect of volume of the Ag NPs for the reaction solution, the volume of the Ag NPs (3.0nM) was changed from 20 to 200  $\mu$ L and other conditions (reaction time=35 min, t=50 °C, [Hg<sup>2+</sup>]=1.0×10<sup>-6</sup> M, pH=6.0) kept invariable. We recorded the SERS spectra of DAP obtained under different adding volumes of Ag colloid and plotted the peak intensities at 997 cm<sup>-1</sup> vs. adding volumes in Figure S2 (a).

In order to study pH for the reaction, we used the citrate buffer (0.1 M) with the pH values from 4.0 to 6.5. Hg<sup>2+-</sup>Ag NPs were added into 0.1 mL of 2.0 mM OPD. Other conditions remain unchanged as Ag NP volume =100  $\mu$ L, [Hg<sup>2+</sup>] =1.0×10<sup>-6</sup> M, temperature=50 °C and reaction time=35 min. We recorded the SERS spectra of DAP obtained under different pH values and plotted the peak intensities at 997 cm<sup>-1</sup> vs. pH in Figure S2 (b).



Figure S2. (a) The plot of SERS intensities at 997 cm<sup>-1</sup> of produced DAP obtained by adding different volumes of Ag NPs in same volume OPD solutions. (b) The SERS

intensities at 997 cm<sup>-1</sup> of produced DAP obtained under different pH values.

3. Effect of excitation wavelengths.



Figure S3 SERS spectra of the produced DAP by different laser lines while  $[Hg^{2+}] = 1.0 \times 10^{-6} \text{ M}.$ 

The Raman spectra under 633 nm and 785 nm were carried out by a confocal Raman system (LabRAM ARAMIS, HORIBA Jobin Yvon, USA). Raman spectra under a 532 nm laser were recorded by a portable BWTEK Raman spectrometer. The reaction solutions were dropped on the  $1 \text{cm} \times 1 \text{cm}$  silicon pellet to form a spot with a diameter of 1.5 µm for Raman measurements.



4. Comparison of SERS of DAP in solution or casting film.

Figure S4 The monitoring of the reaction solution when the droplet was drying under a microscope. SERS spectra of the produced DAP from above five time points while  $[Hg^{2+}] = 1.0 \times 10^{-5}$  M. Images 1-5 correspond to the drying time of 0, 2, 4, 6 and 8 min.

By SERS monitoring the drying process of the reaction solution, we can find the totally dried sample gives the highest SERS signals.

5. Reproducibility of SERS detection.



Figure S5 (a) SERS spectra from randomly selected 25 points. (b) The intensities of two different peaks at 25 points on the same sample while  $[Hg^{2+}] = 1.0 \times 10^{-5}$  M.

Reproducibility is an important factor for SERS detection. In order to prove the reproducibility, we have randomly selected 25 point on the same sample to compare the SERS signal of the product DAP. Two peaks at 997 and 1265 cm<sup>-1</sup> were chosen to evaluate their reproducibilities and we found that the relative standard deviations (RSD) of Raman signals are calculated as 9.2% and 7.9%, which can meet standard in which the RSD is less than 20 % of SERS detection.

6. SERS enhancement activity of Hg<sup>2+</sup>-Ag NPs.



Figure S6 (a) and (b) SERS spectra of DAP with and without the Hg<sup>2+</sup>-Ag NPs measured in solution. The pure DAP solution without Hg<sup>2+</sup>-Ag NPs was achieved by centrifuging the reaction solution (while Hg<sup>2+</sup>= $1.0 \times 10^{-6}$  M) at a speed of 10000 rpm. The precipitates were Hg<sup>2+</sup>-Ag NPs and the suspension solution was used for Raman measurement (b).

To convince the SERS enhancement activity of  $Hg^{2+}$ -Ag NPs, we compared two SERS detection results with and without  $Hg^{2+}$ -Ag NPs (separated by centrifugation) as shown in Fig. S6. It can be found that if the  $Hg^{2+}$ -Ag NPs were removed from the reaction system, we can't obtain the SERS signal of DAP at all, which proves the  $Hg^{2+}$ -Ag NPs play a role of the SERS activity.

7. The UV-vis spectra of DAP under different condition.



Figure S7 (a)-(c) UV-vis spectra of the produced DAP solution, obtained by mixing the OPD solutions (100 $\mu$ L, 0.2 M) with Hg<sup>2+</sup> (100  $\mu$ L, 1.0  $\mu$ M), Ag NPs (100  $\mu$ L, 3.0nM), Hg<sup>2+</sup>-Ag NPs (100 $\mu$ L, containing 1.0  $\mu$ M of Hg<sup>2+</sup> and 3.0 nM of Ag NPs), respectively, for 35 min and then removing Ag NPs or Hg<sup>2+</sup>-Ag NPs by centrifugation.

As Scheme 1 a and b shown, we employed this  $Hg^{2+}$ -Ag NPs catalyzed redox reaction between OPD and dissolved oxygen to trace mercury ions (B in Scheme 1). This  $Hg^{2+}$ -Ag NPs play as a catalyst. If we replaced the  $Hg^{2+}$ -Ag NPs by individual mercury ions or Ag NPs, the catalytic reaction would slow down. Fig. S7 are UV-vis spectra of the reaction solutions after removing Ag NPs or  $Hg^{2+}$ -Ag NPs, obtained by mixing the OPD solutions (100µL, 0.2 M) with  $Hg^{2+}$  (100 µL, 1.0 µM), Ag NPs (100 µL, 3.0 nM),  $Hg^{2+}$ -Ag NPs(100µL, containing 1.0 µM of  $Hg^{2+}$  and 3 nM of Ag NPs), respectively, for 35 min. The redox is caused slightly between OPD solution and dissolved oxygen in the presence of mercury ions in solution (Fig. S7, curve a). When the only Ag NPs are added in solution of OPD, the UV-vis spectrum maximum absorbance intensity is slightly stronger than the OPD solution that is added with  $Hg^{2+}$ (curve b). While  $Hg^{2+}$ -Ag NPs are added in the solution, it is seen that the UV- vis maximum absorbance intensity is increased more significantly than others (curve c). It reveals that the Hg<sup>2+</sup>-Ag NPs have excellent catalytic activity <sup>[S2]</sup>.

## Reference

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- [S2]. L. Yan, Z. Chen, Z. Zhang, C. Qu, L. Chen, D. Shen, Analyst, 2013, 138, 4280.