Resonance Rayleigh Scattering and SERS Spectral Detection of Trace Hg(II) Based on the Gold Nanocatalysis

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Abstract: Mercury (Hg) is a heavy metal pollutant, there is an urgent need to develop simple and sensitive methods for Hg(II) in water. In this article, a simple and sensitive resonance Rayleigh scattering (RRS) method was developed for determination of 0.008–1.33 µmol/L Hg, with a detection limit of 0.003 µmol/L, based on the Hg(II) regulation of gold nanoenzyme catalysis on the HAuCl4·H2O2 to form gold nanoparticles (AuNPs) with an RRS peak at 370 nm. Upon addition of molecular probes of Victoria blue B (VBB), the surface-enhanced Raman scattering (SERS) peak linearly decreased at 1612 cm⁻¹ with the Hg(II) concentration increasing in the range of 0.013–0.5 µmol/L. With its good selectivity and good accuracy, the RRS method is expected to be a promising candidate for determining mercury ions in water samples.

Keywords: mercury ion; gold nanoparticle; nanocatalysis; resonance Rayleigh scattering; SERS

1. Introduction

Nanomaterials not only have unique optical, electrical, and magnetic properties, but also have bio-enzyme activity [1,2]. They are known as mimic nanoenzymes, and also called di-functional molecules or multifunctional molecules. Since Fe3O4 nanoparticles have been found to have intrinsic peroxidase-like activity [3], nanoenzyme have become interesting to people. They have vast application prospects with advantages of easy production process, good stability and recycling, low-cost of storage and transport, and high adaptability of heat, acid, and alkali [1–11]. It is a new study filed, that is, how to organically combine nanoenzyme catalysis with its physical and chemical properties to create more novel functions. In analytical chemistry, nanoenzymes have been used in absorption, fluorescence, and chemiluminescence analysis [3–13]. Gold nanoparticles have peroxidase activity that catalyze the colored redox reaction of 3,3′,5,5′-tetramethylbenzidine (TMB)-H2O2 [12]. Combining glucose peroxidase and gold nanoenzyme, a 18–1100 µmol/L glucose can be detected spectrophotometrically, with a detection limit of 4 µmol/L. Li et al. [13] constructed CdTe dots and gold nanoparticles into the SiO2 microball surface respectively to obtain a nanoenzyme that catalytically oxidized to form oxidant, and a 1.32 µmol/L glucose can be determined by fluorescence method.
Mercury is a highly toxic heavy metal element which is very widely distributed in nature. Therefore, the monitoring of Hg\(^{2+}\) becomes very important. At present, several methods have been reported to determine Hg\(^{2+}\), such as atomic fluorescence spectroscopy (AFS), atomic absorption spectrometry (AAS), and inductively coupled plasma mass spectrometry (ICP-MS) [14–16]. Although these methods have high selectivity and sensitivity for Hg\(^{2+}\) detection, however, these methods have a number of weaknesses such as expensive instruments, long analysis period, need for professional operators, and so on. It is of great significance to develop a simple, rapid, and low-cost method for mercury detection.

In recent years, some new methods for the detection of Hg\(^{2+}\) have been reported such as aptamer and functionalized gold nanoparticle biosensors [17–19]. Resonance Rayleigh scattering (RRS) method is a simple and sensitive spectral analysis technique. It has been used for the analysis of proteins, nucleic acids, metal ions, and so on [20–24]. Early studies of our group have developed sensitive and selective nanogold catalysis, immunonanogold catalysis, and peptide modified-nanogold catalysis methods [25–31], including the silver nitrate-hydroquinone [28] and HAuCl\(_4\)-ascorbic acid reactions [29]. The above nanoenzyme catalytic RRS methods were all based on the aggregations of nanoparticles that presented unstable analytical systems and complicated operations. In this study, we have observed that AuNPs have strong catalysis on the redox reaction of HAuCl\(_4\)-H\(_2\)O\(_2\), while Hg\(^{2+}\) exhibits strong inhibition on this nanocatalytic reaction, and the nanoreaction product of formed AuNPs demonstrated RRS effect and SERS activity in the presence of Victoria blue B (VBB) probes. Thus, two simple, rapid, low cost, high sensitivity, and good selectivity RRS and SERS methods were established for detection of Hg\(^{2+}\).

2. Results and Discussion

2.1. Principle

Nano-catalysis is an important way to amplify analysis signal. It has significance in developing a new nano-catalysis reaction. From the experiment, we found that, in hydrochloric acid medium, the reaction of H\(_2\)O\(_2\)-HAuCl\(_4\) was relatively slow. While nanocatalyst of AuNP was added, a large number of HAuCl\(_4\) adsorbed on the AuNP surface, and H\(_2\)O\(_2\) was also adsorbed on the surface that there had many free electrons, which can enhance the redox electron-transfer between H\(_2\)O\(_2\)-HAuCl\(_4\). Thus, it enhanced the reduction of Au\(^{3+}\) to form elemental gold, and led to the gold nanoparticles forming greatly. The formed gold nanoparticles have strong SERS and RRS signal. Therefore, the nanogold catalytic reaction can be used to establish SERS and RRS detection methods for AuNPs (Figure 1).

\[
\begin{align*}
\text{Au}^{3+} + \text{AuNP} &= \text{AuNP-Au}^{3+} \text{ (adsorb)} \\
\text{H}_2\text{O}_2 + \text{AuNP-Au}^{3+} &= \text{Au}^{3+}\text{-AuNP-H}_2\text{O}_2 \text{ (adsorb)} \\
\text{Au}^{3+}\text{-AuNP-H}_2\text{O}_2 &= \text{Au}^{7+}\text{-AuNP-H}_2\text{O}_2 + \text{O}_2 \\
\text{Au}^{+}\text{-AuNP-H}_2\text{O}_2 &= \text{AuNP + Au + O}_2 \\
\text{nAu} &= (\text{Au})_n \text{ = AuNPs}
\end{align*}
\]

It is known that Au and Hg have stronger affinities to form Au-amalgam than other metals such as Ag, Pb, and Cu. Thus, the stable AuNP-Hg\(^{2+}\) would form in the presence of Hg\(^{2+}\). Similarly, in the analytical system, the formed AuNP-HgCl\(_4\) can adsorb on the surface of AuNP, which greatly inhibits the red electron-transfer, and decreases the AuNP catalytic reaction. With the Hg\(^{2+}\) connection increased, the catalytic reaction rate slowed, and the RRS and SERS intensity decreased (Figure 1). Hereby, a RRS and SERS method was established for selective determination of Hg\(^{2+}\).
When Hg^2+ catalytic reaction can be used to establish SERS and RRS detection methods (Figure 1). Hereby, professional analytical system, the formed nanogold catalysis, immunonanogold catalysis, aptamer such as aptamer and functionalized gold nanoparticle biosensors were all based on the aggregations of nano-AuNP. Therefore, the monitoring of Hg^2+ was weakened. The RRS intensity at 370 nm decreased linearly with the Hg^2+ concentration increased (Figure 3), and was selected for the determination of Hg(II). In addition, the RRS spectra of the Hg^2+–HNP–HAuCl4–H2O2 system were recorded at room temperature. Results (Figure S2) show that the RRS signals were very weak and constant when Hg^2+ concentration increased up to 12 µmol/L. This indicated that Hg^2+ ions could strongly adsorb on the AuNP_b surfaces and there are no aggregations in the system.

2.2. RRS Spectra

In HCl medium, nanocatalyst of AuNP_b, AuNP_c, and AgNP could catalyze H2O2 to reduced HAuCl4 to form AuNPs with three RRS peaks at 280, 370, and 550 nm. When nanocatalyst AuNP increased, the RRS intensity at 370 nm enhanced linearly (Figure 2 and Figure S1). The catalytic activity of AuNP_b was higher than AuNP_c, due to the smaller particle size, and the larger specific surface area. When Hg^2+ was adsorbed on the surface of AuNP_b to form AuNP_b–HgCl2−, the catalytic activity of AuNP_b was weakened. The RRS intensity at 370 nm decreased linearly with the Hg^2+ concentration increased (Figure 3), and was selected for the determination of Hg(II). In addition, the RRS spectra of the Hg^2+–AuNP_c–HAuCl4–H2O2 system were recorded at room temperature. Results (Figure S2) show that the RRS signals were very weak and constant when Hg^2+ concentration increased up to 12 µmol/L. This indicated that Hg^2+ ions could strongly adsorb on the AuNP_b surfaces and there are no aggregations in the system.

**Figure 1.** Resonance Rayleigh scattering (RRS)/surface-enhanced Raman scattering (SERS) detection of trace Hg^2+ based on the inhibition of gold nanoparticles (AuNP) catalysis.

**Figure 2.** RRS spectra of the AuNP_b-HAuCl4-H2O2 nanocatalytic system. (a) 4.48 µmol/L HAuCl4 + 0.67 mmol/L HCl + 3.33 mmol/L H2O2; (b) a + 0.018 ng/mL AuNP_b; (c) a + 0.095 ng/mL AuNP_b; (d) a + 1.9 ng/mL AuNP_b; (e) a + 5.7 ng/mL AuNP_b; (f) a + 7.6 ng/mL AuNP_b; (g) a + 1.9 ng/mL AuNP_b; (h) a + 5.7 ng/mL AuNP_b; (i) a + 7.6 ng/mL AuNP_b.
When Hg was tested as a SERS probe, but its Raman intensity was very weak. When Hg(II) (Figure S5). Rhodamine 6G was tested as a SERS probe, but its Raman intensity was very weak. When Hg(II) (Figure 4). Among them, the SERS peak at 1372 cm\(^{-1}\) was the most sensitive. As the AuNP\(_b\) increase, the intensity of SERS at 1612 cm\(^{-1}\) linearly increased (Figure S4). Using safranin T as SERS probe, it displayed SERS peaks at the Raman shifts of 349, 612, 1240, 1372, 1551, and 1639 cm\(^{-1}\). Among them, the SERS peak at 1372 cm\(^{-1}\) was the most sensitive. With the AuNP\(_b\) increased, the intensity of SERS at 1372 cm\(^{-1}\) linearly increased (Figure S5). Rhodamine 6G was tested as a SERS probe, but its Raman intensity was very weak. When Hg\(^{2+}\) adsorbed on the surface of AuNP\(_b\), the nanocatalytic activity weakened, the peak at 1612 cm\(^{-1}\) decreased linearly, and the AuNP\(_b\) catalytic system was chosen for quantitative analysis of Hg(II) (Figure 4).

2.3. SERS Spectra

SERS is a sensitive molecular spectral technique [31–33], and has been used in trace analysis. Recently, it was selected to study some nanocatalysis reactions [32,33], with good results. In this article, it was used to examine the Hg(II)-AuNP\(_b\)-H\(_2\)O\(_2\)-HAuCl\(_4\)-molecular probe system. When RhS was used as SERS probe, it could adsorb on the generated gold nanoparticle surfaces that exhibited strong SERS peaks at the Raman shifts of 618, 732, 1199, 1277, 1356, 1507, 1527, and 1645 cm\(^{-1}\). Among them, the SERS peak at 1645 cm\(^{-1}\) was most sensitive and was selected for use. With the AuNP\(_b\) increase, the intensity of SERS at 1645 cm\(^{-1}\) increased linearly (Figure S3). Using VBB as a SERS probe, it displayed SERS peaks at the Raman shifts of 795, 1167, 1200, 1364, 1394, and 1612 cm\(^{-1}\). Among them, the SERS peak at 1612 cm\(^{-1}\) was the most sensitive. As the AuNP\(_b\) increased, the intensity of SERS at 1612 cm\(^{-1}\) linearly increased (Figure S4). Using safranin T as SERS probe, it displayed SERS peaks at the Raman shifts of 349, 612, 1240, 1372, 1551, and 1639 cm\(^{-1}\). Among them, the SERS peak at 1372 cm\(^{-1}\) was the most sensitive. With the AuNP\(_b\) increased, the intensity of SERS at 1372 cm\(^{-1}\) linearly increased (Figure S5). Rhodamine 6G was tested as a SERS probe, but its Raman intensity was very weak. When Hg\(^{2+}\) adsorbed on the surface of AuNP\(_b\), the nanocatalytic activity weakened, the peak at 1612 cm\(^{-1}\) decreased linearly, and the AuNP\(_b\) catalytic system was chosen for quantitative analysis of Hg(II) (Figure 4).
When AuNP with the nanocatalyst increase (Figure S9). However, when Hg (Figure 5b). For the HAuCl$_2$ peak increased (Figure S8). AgNP exhibited the nanocatalysis on the reaction, the SPR peak increased with nanocatalyst of AuNP. There were few gold nanoparticles in reaction solution. When nanocatalyst of AuNP was used as nanocatalyst, it had a SPR peak at 590 nm. The generated gold nanoparticles were reduced at 570 nm. With AuNP, the color changed from colorless to red (Figure S6) and the SPR peak value $A_{570\,nm}$ increased (Figure S7). When AuNP$_c$ was used as nanocatalyst, it had a SPR peak at 590 nm. As AuNP$_c$ increased, the SPR peak increased (Figure S8). AgNP exhibited the nanocatalysis on the reaction, the SPR peak increased with the nanocatalyst increase (Figure S9). However, when Hg$^{2+}$ was added to the AuNP$_b$, the intensity at 560 nm of the nanocatalytic system decreased linearly (Figure S10), and the peak was chosen for the detection of Hg, with lowest-cost. Furthermore, it can be detected by lake-eye.

2.4. Absorption Spectra

AuNP$_b$ exhibited a surface plasmon resonance (SPR) peak at 510 nm, it catalyzed H$_2$O$_2$ reduced HAuCl$_4$ to form gold nanoparticles with a SPR peak at 570 nm. With AuNP$_b$ increased, the color changed from colorless to red (Figure S6) and the SPR peak value $A_{570\,nm}$ increased (Figure S7). When AuNP$_c$ was used as nanocatalyst, it had a SPR peak at 590 nm. As AuNP$_c$ increased, the SPR peak increased (Figure S8). AgNP exhibited the nanocatalysis on the reaction, the SPR peak increased with the nanocatalyst increase (Figure S9). However, when Hg$^{2+}$ was added to the AuNP$_b$, the intensity at 560 nm of the nanocatalytic system decreased linearly (Figure S10), and the peak was chosen for the detection of Hg, with lowest-cost. Furthermore, it can be detected by lake-eye.

2.5. Scanning Electron Microscopy (SEM)

The AuNP$_b$, AuNP$_c$, and Ag NPs were in spherical shape in size of 5, 10, and 9 nm respectively (Figure S11). For the HAuCl$_4$-H$_2$O$_2$ system, the reaction rate was slow in the absence of AuNP$_b$, and there were few gold nanoparticles in reaction solution. When nanocatalyst of AuNP$_b$ was added, a plenty of irregular gold nanoparticles were generated (Figure 5a). As Hg$^{2+}$ was added, it inhibited the nanocatalytic reaction of AuNP$_b$-H$_2$O$_2$-HAuCl$_4$. The generated gold nanoparticles were reduced (Figure 5b).
The effect of HCl concentration on the AuNP-H₂O₂-HAuCl₄ catalytic reaction was considered. The amount of HCl had great influences on the generated nanogold. When the concentration was 0.67 mmol/L, the ΔI value was the largest, and the color was pink with λ₅₀₆ nm of 3506, and the blank was colorless with λ₃₇₀ nm of 506. When HCl concentration continued to increase, a large number of hydrogen ions in the solution limited the redox of H₂O₂-HAuCl₄. Therefore, the concentration of 0.67 mmol/L HCl was selected in this experiment (Figure S12). We also considered the effect of the HAuCl₄ concentration on the catalytic reaction, and found that the ΔI value was the largest when the concentration was 4.48 µmol/L (Figure S13). When HAuCl₄ concentration increased continuously the SERS value held constant due to forming the largest AuNPs. The effect of H₂O₂ concentration on ΔI was studied and the best concentration was 3.33 mmol/L (Figure S14). The effect of the temperature on the catalytic reaction was investigated. The ΔI value increased with a temperature increase in the range of 30–60 °C due to an increase in the number of formed AuNPs. When the temperature was 60 °C, the ΔI value was the largest due to formed largest AuNPs, and the blank formed small nanogolds with a pale pink color. When reaction temperature was higher than 60 °C, the ΔI value decreased due to the blank increasing significantly. Thus, 60 °C was chosen (Figure S15). We also investigated the heating time and 15 min was selected (Figure S16). We found that when the heating time exceeded 15 min, the blank generated nanogold and the RRS intensity increased. Even when the heating time was 25 min, the blank solution presented a reddish color that meant a large amount of nanogold was produced. Moreover, after heating, the system was immediately cooled in an ice bath to stop the reaction. Effect of RhS, VBB, and safranine T concentration on the SERS intensity was investigated, and 7, 13.2, and 6.7 µmol/L were selected respectively (Figures S17–S19).

### 2.7. Effect of Foreign Substances

According to the procedure, the effect of foreign substances on the determination of 1.5 × 10⁻⁷ mol/L Hg²⁺ was tested, when the relative error was within ±10%. The results indicated that 8.3 × 10⁻⁵ mol/L Cu²⁺; 3.3 × 10⁻⁵ mol/L I⁻ and Cd²⁺; 6.7 × 10⁻⁶ mol/L Zn²⁺ and Bi³⁺; 3.3 × 10⁻⁶ mol/L Pb²⁺; 2.0 × 10⁻⁶ mol/L S²⁻; Pd²⁺ and Pt²⁺; 1.7 × 10⁻⁶ mol/L Co³⁺; and Cr³⁺ and Ni²⁺ did not interfere with the determination. It indicated that this method had a good selectivity due to stronger intermolecular forces between Au and Hg than the other Au metals.
2.8. Working Curve

Under optimal conditions, the relationship between the nanocatalyst concentration of AuNP\textsubscript{b}, AuNP\textsubscript{c}, and AgNPs and their corresponding $\Delta I_{370 \text{ nm}}$ were obtained (Table 1, Figures S20–S22). The results showed that the AuNP\textsubscript{b} is the strongest catalyst with maximum slope, and it was chosen for use. For the AuNP\textsubscript{c}–H\textsubscript{AuCl\textsubscript{4}}–H\textsubscript{2}O nanocatalytic system, using RhS, VBB, and safranine T as molecular probes respectively, their SERS intensities were recorded. The experimental results indicated that VBB was the most sensitive SERS probe (Figures S23–S25). For the Hg$^{2+}$ analytical system, the RRS, SERS, and Abs methods were studied (Figures S26–S28). From Table 1, we can see that the RRS is most sensitive and was chosen for detection of Hg. The RRS method was compared with the reported methods for determination of Hg$^{2+}$ [34–37], this method is more simple, and the reagent is very easy to obtain, with high sensitivity and good selectivity.

| Analyte  | Method | Regression Equation | Linear Range ($\mu$L) | Coefficient | Detection Limit ($\mu$L) |
|----------|--------|---------------------|------------------------|-------------|------------------------|
| AuNP\textsubscript{b} | RRS    | $\Delta I_{370 \text{ nm}} = 131.3C + 300$ | 0.025–25 | 0.9951 | 0.008 |
| AuNP\textsubscript{c} | RRS    | $\Delta I_{370 \text{ nm}} = 51.5C + 267$ | 0.05–75 | 0.9941 | 0.02 |
| AgNP     | RRS    | $\Delta I_{370 \text{ nm}} = 23.4C + 73$ | 0.5–50 | 0.9971 | 0.2 |
| AuNP\textsubscript{b} | SERS\textsuperscript{a} | $\Delta I_{1645 \text{ cm}^{-1}} = 2.28C + 72$ | 0.5–50 | 0.9786 | 0.2 |
| AuNP\textsubscript{b} | SERS\textsuperscript{b} | $\Delta I_{1612 \text{ cm}^{-1}} = 5.94C + 86$ | 0.2–50 | 0.9942 | 0.1 |
| AuNP\textsubscript{b} | SERS\textsuperscript{c} | $\Delta I_{1372 \text{ cm}^{-1}} = 1.47C - 9.1$ | 0.6–50 | 0.9879 | 0.3 |
| Hg$^{2+}$ | RRS    | $\Delta I_{370 \text{ nm}} = 3650C + 111$ | 0.008–1.33 | 0.9958 | 0.003 |
| Hg$^{2+}$ | SERS\textsuperscript{b} | $\Delta I_{1612 \text{ cm}^{-1}} = 326C + 6.4$ | 0.013–0.5 | 0.9932 | 0.03 |
| Hg$^{2+}$ | Abs    | $\Delta A_{600 \text{ nm}} = 0.083C + 0.0087$ | 0.5–2.33 | 0.9876 | 0.2 |

\textsuperscript{a} RhS; \textsuperscript{b} VBB; \textsuperscript{c} safranine T.

2.9. Analysis of Samples

Three water samples—including tap, river, and pond—were collected from Guangxi Normal University, and filtrated according to the reference [35]. The following operations were according to the procedure to detect Hg$^{2+}$. The obtained results were accorded with the cold atomic absorption spectrometry (AAS) (Table S1). The average values ($n = 5$) for the water samples after adding a certain amount of Hg$^{2+}$ were determined. The recovery was in the range of 97–102%, and the relative standard deviation (RSD) was in the range of 4.5–5.2%. This indicated the method is accuracy and reliable.

3. Materials and Methods

3.1. Apparatus

A DXR smart Raman spectrophotometer (Thermo Fisher, Waltham, MA, USA) with a power of 2.5 mW, laser wavelength of 633 nm, and slit width of 50 mm; a Cary Eclipse fluorescence spectrophotometer (Varian, Santa Clara, CA, USA); a model of TU-1901 double-beam UV—visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China); a C-MAG HS7 magnetic stirrer with heating (IKA, Staufen, Germany), and a constant temperature magnetic stirrer (Kewei Yongxing Instrument Co., Ltd., Beijing, China) were used. A FEI Quanta 200 FEG Field emission scanning electron microscope (FEI, Hillsboro, OR, USA) was recorded the SEM of nanoparticles, the sample preparation was as follows: put 1.5 mL of the reaction solution of the procedure into a 2 mL centrifuge tube and centrifuge for 20 min ($150 \times 100 \text{ r/min}$), discard the supernatant and add water to 1.5 mL, then dispers for 30 min with ultrasonication. After centrifuging again, add 1 mL water, and disperse for 30 min. Place 2 $\mu$L of the sample solution by pipette dripping on silicon slices and dry naturally for use.
3.2. Reagents

A 1% HAuCl₄·4H₂O (National Medicine Group Chemical Reagent Co., Ltd., Shanghai, China), 1% trisodium citrate, 10 mmol/L sodium borohydride, 0.01 mol/L HCl solution and 0.3% H₂O₂ (0.1 mol/L) were prepared. Victoria blue B solution: 0.025 g VBB was dissolved in 5.0 mL ethyl alcohol before diluting to 50.0 mL with water, and the concentration was 1.0 × 10⁻³ mol/L. It was stepwise diluted to 1.0 × 10⁻⁵ mol/L before use. A 5.23 × 10⁻⁵ mol/L RhS and 5.0 × 10⁻⁵ mol/L safranine T solution were prepared. Preparation of gold nano sol (AuNP₄): At room temperature, 40 mL of water was added into a conical flask, 0.5 mL 1.0% HAuCl₄ and 3.5 mL 1.0% trisodium citrate were added into the flask in order by stirring. Then, 4.0 mL 0.05% NaBH₄ was added slowly. The mixture was stirred for 10 min, to obtain a concentration of 58 μg/mL 5 nm AuNP₄. Preparation of AuNP₆: 50 mL of water was added into a conical flask, heated to boiling. Then, 0.5 mL 1% HAuCl₄ and 3.5 mL 1% trisodium citrate were added rapidly into the boiling water successively. After boiling for 10 min while stirring, the color went from colorless to wine red. The mixture was stirred continuously to room temperature, and then diluted to 50.0 mL to obtain about 10 nm of AuNP₆, a certain amount of Hg²⁺ were added, the catalysis was greatly inhibited and the SPR effect decreased. Thus, two new RRS and SERS methods were developed for determination of Hg²⁺, with simplicity, high sensitivity, and good selectivity.

3.3. Procedure

In a 5 mL marked test tube, 100 μL 0.57 μg/mL AuNP₄, and a certain amount of Hg²⁺ were added and diluted to 200 μL, then left to rest for about 20 min. 80 μL 0.1% HAuCl₄ (84 μmol/L), 100 μL 0.01 mol/L HCl, and 50 μL 0.3% (0.1 mol/L) H₂O₂ were added sequentially, diluted to 1.5 mL and mixed well. Then the mixture heated for 15 min in a 60 °C water bath and cooled with tap water. The RRS spectra were recorded by means of synchronous scanning excited wavelength λex and emission wavelength λem (λex - λem = Δλ = 0) on fluorescence spectrophotometer, with a photomultiplier tube (PMT) voltage of 400 v, and both excited and emission slit widths were 5 nm, emission filter = 1% T attenuator. The reaction solution RRS intensity at 370 nm I₃₇⁰ nm and the blank solution without Hg²⁺ (I₃₇⁰ nm) were recorded. The value of ΔI₃₇⁰ nm = I₃₇⁰ nm - (I₃₇⁰ nm) was calculated. For the SERS detection, a 200 μL 1.0 × 10⁻⁵ mol/L VBB was added in the reaction solution, mixed well, and transferred to a 1 cm quartz cell. Its SERS spectra were recorded by the Raman spectrophotometer. The SERS intensity at 1612 cm⁻¹ (I) and the blank value (I₀) without Hg²⁺ were recorded. The value of ΔI = I - I₀ was calculated.

4. Conclusions

The gold nanoreaction of HAuCl₄·H₂O₂ is slow. Upon addition of nanocatalyst of AuNP₄, the nanoreaction enhanced greatly to form gold nanoparticles with strong RRS, SERS and SPR absorption effects. When analyte of Hg²⁺ was added, the catalysis was greatly inhibited and the SPR effect decreased. Thus, two new RRS and SERS methods were developed for determination of Hg²⁺, with simplicity, high sensitivity, and good selectivity.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-4991/7/5/114/s1.

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