Autocatalytic Oxidation of Nanosilver and Its Application to Spectral Analysis

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The stable yellow nanosilver (AgNP) and blue nanosilver (AgNPB) sols were prepared by the NaBH₄ procedure. The new nanocatalytic reaction of AgNP-NaCl-H₂O₂ was investigated by surface plasmon resonance (SPR) absorption, resonance Rayleigh scattering (RRS), surface-enhanced Raman scattering (SERS) and scanning electron microscope (SEM) techniques. The autocatalytic oxidation of Ag on AgNP surface by H₂O₂ was observed firstly and the AgNP/AgCl nanoparticles were characterized. The [Ag⁺] from AgNP is different to the Ag⁺ from AgNO₃ that adsorb on the AgNP surface. An autocatalytic oxidation mechanism was proposed to explain experimental phenomena. The relationship between the SPR absorption peaks and the RRS peaks of AgNPB was studied, and three characteristic RRS peaks called as out-of-plane quadrupole, out-of-plane dipole and in-plane dipole RRS peaks were observed firstly. Using AgNP as nanoprobe, a simple, sensitive and selective RRS method was developed for assay of H₂O₂ in the range of 2.0 × 10⁻⁸-8.0 × 10⁻⁵ mol/L.

Nanoparticles have become research hot-spot in subjects such as physics, chemistry and materials due to their unique physical and chemical properties1–5. Based on the optical properties of nanoparticles, some new types of optical sensors and optoelectronic devices have been developed6–9. And the research of nanocatalysis and its application has become the important research directions in catalytic synthesis and nanoanalysis10–16. Among the nanocatalysis, the reports were mainly about nanogold catalysis and nano titanium dioxide photocatalysis17–19. Recently, some new nanocatalytic analytical methods were established20–25, based on the catalysis of nanogold on the Cu(II)-glucose, HAuCl₄-ascorbic, HAuCl₄-citrate, Te(IV)-Sn(II), phosphomolybdic acid-formic acid and Ag(I)-hydroquinone particle reactions. It is rare report about nanosilver catalytic reaction. In synthesis of triangular nanosilver26,27, the catalysis of nanosilver has been observed. Nanosilver modified by aptamer exhibited strong catalysis of the Cu₂O particle reaction of Fehling reagent-glucose, and it has been used to determine trace melamine by RRS technique28. Up to date, the autocatalytic oxidation of AgNP and its application in trace H₂O₂ analysis have not been reported.

The content of H₂O₂ is closely related to the photochemical reactions, oxidation-reduction reactions in natural water bodies. It is one of the important factors to affect the transfer, transformation, and ecological effect of chemical substances in water, and it is also one of the main reasons in the formation of acid rain29. In addition, the detection of H₂O₂ content is also very important in biochemical reactions, clinical test, food safety, and other fields30–32. At present, the spectral methods for H₂O₂ content are mainly including chemiluminescence, fluorescence, spectrophotometry, etc33–35. Among them, spectrophotometry is commonly used for its simple operation and low-cost. Recently, stable metal nanoparticles, especially nanogold and nanosilver, are interesting to analyst. The spectral probe, based on nanogold color and RRS, have been used for determination of tumor markers, Hg²⁺, H₂O₂, HCl and so on36–41. Compare to nanogold, AgNP has the advantage of low cost, and its aggregates do not interfere to the absorbance measurement since its absorption is very weak. In addition, stable AgNP can be prepared by modern synthesis procedure and it has become novel spectral probe due to its strong SPR absorption, strong RRS and SERS effects of its aggregates42. It has been utilized to colorimetric chiral recognition of enantiomers, detection of DNA and melamine etc43–45. However, there is no report about the research and application of AgNP-NaCl-H₂O₂ autonanocatalytic system yet. In this paper, the reaction mechanism of AgNP-NaCl-H₂O₂ was studied by SPR, RRS46–48, SERS and SEM techniques. Thus, two simple, rapid and sensitive spectral methods have been developed to determine H₂O₂.

Results

Scanning electron microscope. Stabile AgNP sol was prepared by NaBH₄ reduction of AgNO₃ in the presence of citrate. The SEM shows that they are spherical, with average size of 10 ± 2 nm (Fig. 1a). In AgNP-NaCl-H₂O₂
system, there is an autocatalytic oxidation reaction on the surface of AgNP to generate large Ag\textsubscript{n}/AgCl particles with an average size of 60 ± 15 nm (Fig. 1b). In AgNP-H\textsubscript{2}SO\textsubscript{4}-NaCl-FeSO\textsubscript{4}-H\textsubscript{2}O\textsubscript{2} system, on one hand the autocatalytic oxidation reaction of AgNP generate Ag\textsuperscript{+} on the surface, on the other hand surface atoms of AgNP also can generate Ag\textsuperscript{+} by the Fenton oxidation reaction, so the large Ag\textsubscript{n}/AgCl particles with an average size of 75 ± 16 nm was formed (Fig. 1c).

SEM of AgNPB system shows that they are nearly spherical, with particle size between 6–100 nm and an average size of 40 ± 8 nm (Fig. 1d). The shape of AgNPB can not be observed satisfactorily by SEM, and the TEM of AgNPB system was done. Figure 2e indicated that there triangle nanosilver particles in the system, with the side length between 30–90 nm and an average side length of 45 ± 10 nm, in addition to the nearly spherical particles.
In 2.0 \times 10^{-3} \text{ mol/L NaCl medium}, AgNPs are stable and its RRS signal is very weak (Fig. 2A). With addition of H$_2$O$_2$, AgNP catalyze H$_2$O$_2$ to produce HO$^-$ and oxidize Ag atoms on the surface of AgNP to produce [Ag$^+$]. The [Ag$^+$] combined with Cl$^-$ to form [AgCl] with strong hydrophobicity and then lead to form larger AgNP/AgCl aggregates that obviously enhanced the RRS intensity at 330 nm, 460 nm and 500 nm. The most sensitive RRS peak at 330 nm was selected to use in this paper. In existence of Fe(II) and H$_2$SO$_4$, the system had four RRS peaks at 290 nm, 360 nm, 455 nm and 500 nm (Fig. 1S). Fe(II) can hydrolyze and cause weak aggregation of AgNPs, and the blank increased. When adding H$_2$O$_2$, the Fenton reaction (FeSO$_4$-H$_2$O$_2$) also produced HO$^-$ that oxidize AgNP to form [Ag$^+$] and AgNP/[AgCl] particles. With H$_2$O$_2$ concentration increase its peak enhanced linearly due to more particles forming.

With addition of different concentration of AgNO$_3$ to the system of 2.0 \times 10^{-3} \text{ mol/L NaCl-0.035\% sodium citrate}, AgCl particles were generated and exhibited strong scattering signal at 335 nm (Fig. 2S). The increased intensity $\Delta I_{335 \text{ nm}}$ was linear to AgNO$_3$ concentration in the range of 12.5-100 \times 10^{-6} \text{ mol/L} with the regression equation of $\Delta I_{335 \text{ nm}} = 53.3c_{\text{Ag}^+} - 93$. For the system of 2.0 \times 10^{-3} \text{ mol/L NaCl-0.035\% sodium citrate-2.0 \times 10^{-5} \text{ mol/L H}_2\text{SO}_4}$, AgCl particles exhibited strong scattering signal at 335 nm (Fig. 3S). The increased intensity $\Delta I_{335 \text{ nm}}$ was linear to AgNO$_3$ concentration in the range of 12.5-100 \times 10^{-6} \text{ mol/L} with the regression equation of $\Delta I_{335 \text{ nm}} = 51.0c_{\text{Ag}^+} + 116$. This suggests that RRS signal’s enhancement of AgNP-NaCl-H$_2$O$_2$ system is the result of the formation of AgCl particles. When adding different concentration of Ag$^+$ to the AgNP-NaCl-sodium citrate system, the RRS spectrum (Fig. 4S) is different with that of AgNP-NaCl-H$_2$O$_2$ and the former is weaker. It also suggests that [Ag$^+$] which produced by AgNP surface oxidation is different with that adsorption on the surface of the AgNP by adding AgNO$_3$. Compare to RRS spectra of NaCl-sodium citrate-AgNO$_3$ system, the RRS intensity of AgNP-NaCl-sodium citrate system is greatly reduced and has a valley at 395 nm, as the result of the strongest absorption of AgNPs at 395 nm.

**SPR absorption spectra.** Mie theory$^{49}$ pointed out that, spherical nanoparticles have only one SPR absorption peak. Spherical AgNP with diameter of 20–30 nm has the strongest SPR peak near 400 nm$^{50}$, which is out-of-plane dipole SPR absorption peak$^{51}$. In the systems of NaCl and NaCl-H$_2$SO$_4$-FeSO$_4$, both have an AgNP SPR absorption peak at 395 nm (Fig. 2B, Fig. 5S). The absorbance at 395 nm of the two systems decreased linearly with the H$_2$O$_2$ concentration increased and can be chosen to determine H$_2$O$_2$. The AgNO$_3$-NaCl and AgNO$_3$-NaCl-H$_2$SO$_4$-FeSO$_4$ systems were examined by spectrophotometry. With addition of different AgNO$_3$ concentration to the two systems of 2.0 \times 10^{-3} \text{ mol/L NaCl-0.035\% sodium citrate and 2.0 \times 10^{-3} \text{ mol/L NaCl-0.035\% sodium citrate-2.0 \times 10^{-5} \text{ mol/L H}_2\text{SO}_4}$, the produced AgCl particles exhibited weak SPR peak at
Figure 3 | Principle of autocatalytic oxidization of AgNP to detect H₂O₂.

Figure 4 | SPR spectra (A) and RRS spectra (B) of AgNPB. (a): 2.5 × 10⁻⁵ mol/L AgNPB; (b): 5.0 × 10⁻⁵ mol/L AgNPB; (c): 7.5 × 10⁻⁵ mol/L AgNPB.
285 nm (Fig. 6S,7S). The absorbance increased slowly with the 
AgNO3 concentration increased in the range of 12.5-100 × 10^-6 mol/L because AgCl particles have weak absorption. In the medium of 5.0 × 10^-2 mol/L NaCl, AgNPB has two SPR absorption peaks at 330 nm and 530 nm (Fig. 8S). The absorbance at 530 nm decreased linearly with the H2O2 concentration increased in the range of 2-8 × 10^-3 mol/L H2O2 that can be used to determine H2O2.

SERS spectra of AgNP-NaCl-H2O2 system. SERS technology is very sensitive for the detection of nano-aggregate, and it is very important to choose a suitable molecular probe. Reportedly cationic dye rhodamine 6G was used as a sensitive SERS probe, but it can interact with AgNP to form aggregate and cannot be used in the analysis of AgNP-NaCl system. Victoria blue B (VBB), used as a SERS probe, had very weak Raman signals in the two systems of 9.25 × 10^-3 mol/L AgNP and 9.25 × 10^-3 mol/L AgNP-2.0 × 10^-3 mol/L NaCl. With addition of H2O2, SERS signals enhanced due to the formation of AgCl and Ag/AgCl aggregate and the system exhibited Raman peaks at 224 cm^-1, 307 cm^-1, 351 cm^-1, 564 cm^-1, 608 cm^-1, 772 cm^-1, 1127 cm^-1, 1179 cm^-1, 1309 cm^-1, 1359 cm^-1, 1508 cm^-1, 1571 cm^-1, 1647 cm^-1 (Fig. 9S). This demonstrated that there are AgNP/AgCl aggregates in the system.

Discussion

Mechanism of autocatalytic oxidation of AgNP. Stabile AgNP in size of 10 nm was prepared conveniently by NaBH4 reduction of Ag+. When NaCl was added, Cl- can be adsorbed on the surface of AgNP, and the signals of SPR absorption and RRS are still very weak that indicated no aggregation in the system. After adding H2O2, small AgNP can catalyze H2O2 to produce free radicals HO· with strong oxidation ability, which can oxidize Ag atoms on the surface of AgNP to produce [Ag+] that is different with the Ag+ from AgNO3. The [Ag+] combined with Cl- to form [AgCl] molecules which had strong hydrophobic property and then lead to form large AgNP/AgCl aggregates that enhanced the scattering signal. Small size HO· can penetrate the gap of [AgCl] molecules to further oxidize Ag atoms on inner layer of AgNP (Fig. 3), and made AgNP become smaller and its SPR absorption peaks at 330 nm and 530 nm (Fig. 8S). The absorbance increased slowly with the detection of Ag2+ concentration was drawn. The linear range of AgNP-NaCl system was 2.0 × 10^-6-8.0 × 10^-5 mol/L with a regression equation of ΔI = 71.4c-1.6, a correlation coefficient of 0.9852, and a detection limit of 5 × 10^-6 mol/L. A 5.0 × 10^-6 mol/L and 20 × 10^-6 mol/L H2O2 were determined five times, and the related standard deviations (RSD) were 4.1%, 3.7% and 3.8% respectively, this showed that the RRS method has good accuracy. The linear range of AgNP-NaCl-H2O2-FeSO4 system was 1.0 × 10^-2-2.5 × 10^-3 mol/L, with a detection limit of 2 × 10^-5 mol/L. In the RRS analytical system, the AgNP-NaCl is most sensitive, simple, stable and low blank (Table 1S), and it was chosen to detect H2O2 concentration. The SPR methods of the two systems also can be used to determine H2O2 with low-cost, though they were not as sensitive as RRS methods. According to the procedure, a standard solution containing 20 × 10^-6 mol/L H2O2 and various coexistent compounds were examined, with a relative error of less than ±10%. A 100 times of ClO4- and SO4^2-, 70 times of Ca(II) and Mg(II), 50 times of Cu^2+, MoO4^2-, Br-, triethanolamine, Co3+, NO3-, 10 times of Mn^2+, Cr, citric acid, and 2.5 mg/L HSA did not interfere with the determination. This indicated that the method has good selectivity.

Methods

Apparatus and reagents. A Model F-7000 fluorescence spectrophotometer (Hitachi Company, Japan) was used to record the RRS spectra by means of synchronous scanning excitation wavelength λex and emission wavelength λem (λex=λem = λx=0) and the RRS intensity. A Model TU-1901 double beam spectrophotometer (Puxi Tongyong Apparatus Limited Company, Beijing) was used to record the SPR spectra and the SPR intensity. A model JSM-6380LV scanning electron microscope (Electronic Stock Limited Company, Japan), a model of JEM-2100F field emission transmission electron microscope (Electronic Stock Limited Company, Japan), a model DXR smart Raman spectrometer (Thermo Fisher Scientific Co., Ltd., USA), a model SK8200LH ultrasonic reactor (Keda Company, Shanghai, China), and a model magnetic stirrer (Zhongda Instrumental Plant, Jiangsu, China) were used.

Analytical features

The scattering signal of AgNP-NaCl-H2O2 system was used to determine H2O2 concentration, and the working curve between ΔI and H2O2 concentration was drawn. The linear range of AgNP-NaCl system was 2.0 × 10^-6-8.0 × 10^-5 mol/L, with a regression equation of ΔI = 71.4c-1.6, a correlation coefficient of 0.9852, and a detection limit of 5 × 10^-6 mol/L. A 5.0 × 10^-6 mol/L and 20 × 10^-6 mol/L H2O2 were determined five times, and the related standard deviations (RSD) were 4.1%, 3.7% and 3.8% respectively, this showed that the RRS method has good accuracy. The linear range of AgNP-NaCl-H2O2-FeSO4 system was 1.0 × 10^-2-2.5 × 10^-3 mol/L, with a detection limit of 2 × 10^-5 mol/L. In the RRS analytical system, the AgNP-NaCl is most sensitive, simple, stable and low blank (Table 1S), and it was chosen to detect H2O2 concentration. The SPR methods of the two systems also can be used to determine H2O2 with low-cost, though they were not as sensitive as RRS methods. According to the procedure, a standard solution containing 20 × 10^-6 mol/L H2O2 and various coexistent compounds were examined, with a relative error of less than ±10%. A 100 times of ClO4- and SO4^2-, 70 times of Ca(II) and Mg(II), 50 times of Cu^2+, MoO4^2-, Br-, triethanolamine, Co3+, NO3-, 10 times of Mn^2+, Cr, citric acid, and 2.5 mg/L HSA did not interfere with the determination. This indicated that the method has good selectivity.

Relationship between the SPR absorption peaks and the RRS peaks of AgNPB. AgNPBs exhibited special optical property that have one sharp out-of-plane quadrupole SPR absorption peak at 330 nm (Fig. 4A), one out-of-plane dipole peak at 390 nm, and one broad in-plane dipole peak at 580 nm. The absorbance of the three peaks was linearly increased with AgNPB concentration increased. The study of RRS spectra of nanoparticles in liquid phase shown that, their RRS peaks are closely related with the emission intensity of light source and the SPR absorption peaks. The light source of model F-7000 Hitachi fluorescence spectrometer has the strongest emission wavelength at 280 nm that cause a scattering peak at 280 nm, and the emission intensity weaken as the increase of the wavelength. AgNPB has a sharp scattering peak at 330 nm which is corresponding to the out-of-plane quadrupole SPR absorption peak (Fig. 4B) that was called as out-of-plane quadrupole RRS peak. AgNPB has a strong RRS peak at 390 nm that was ascribed to out-of-plane dipole SPR absorption, was called as out-of-plane dipole RRS peak. Besides, the in-plane dipole peak at 530 nm is violet-shift 50 nm compare to its SPR absorption peak because the light source has strong emission at 530 nm. Though the RRS intensity of the three peaks increased with AgNPB concentration increased, they had no linear relationship since the sols exist in multiple scattering.

Analytical features

Under the selected conditions (Fig. 10S–19S), the RRS intensity at 330 nm (I) of different H2O2 concentration was recorded, and the working curve between ΔI and H2O2 concentration was drawn. The linear range of AgNP-NaCl system was 2.0 × 10^-6-8.0 × 10^-5 mol/L with a regression equation of ΔI = 71.4c-1.6, a correlation coefficient of 0.9852, and a detection limit of 5 × 10^-6 mol/L. A 5.0 × 10^-6 mol/L and 20 × 10^-6 mol/L H2O2 were determined five times, and the related standard deviations (RSD) were 4.1%, 3.7% and 3.8% respectively, this showed that the RRS method has good accuracy. The linear range of AgNP-NaCl-H2O2-FeSO4 system was 1.0 × 10^-2-2.5 × 10^-3 mol/L, with a detection limit of 2 × 10^-5 mol/L. In the RRS analytical system, the AgNP-NaCl is most sensitive, simple, stable and low blank (Table 1S), and it was chosen to detect H2O2 concentration. The SPR methods of the two systems also can be used to determine H2O2 with low-cost, though they were not as sensitive as RRS methods. According to the procedure, a standard solution containing 20 × 10^-6 mol/L H2O2 and various coexistent compounds were examined, with a relative error of less than ±10%. A 100 times of ClO4- and SO4^2-, 70 times of Ca(II) and Mg(II), 50 times of Cu^2+, MoO4^2-, Br-, triethanolamine, Co3+, NO3-, 10 times of Mn^2+, Cr, citric acid, and 2.5 mg/L HSA did not interfere with the determination. This indicated that the method has good selectivity.
boil for 5 min to get rid of the excess $H_2O_2$. The solution was diluted to 50 mL. All reagents were of analytical grade and the water was highly pure sub-boiling water.

**Procedure.** A 1.0 mL $1.85 \times 10^{-3}$ mol/L AgNP solution, 80 mL 0.05 mol/L NaCl (or adding 80 mL 5.0 $\times$ 10⁻² mol/L $H_2SO_4$; 75 mL 1.0 $\times$ 10⁻² mol/L FeSO₄), and a certain amount of $H_2O_2$ solution were added into a 5 mL calibrated tube in turn, then diluted to 2 mL and mixed well. The RRS intensity at 330 nm ($\Delta I$) was recorded by a fluorescence spectrophotometer with synchronous scanning ($\lambda_{em} - \lambda_{ex} = 0$). A blank ($\Delta I_b$) without $H_2O_2$ was recorded and the value of $\Delta I = \Delta I - \Delta I_b$ was calculated.

1. Ke, J. et al. Dopant-induced modification of active site structure and surface bonding mode for high-performance nanocatalysts: CO oxidation on capping-free (110)-oriented CeO₂−x(In = La-Lu) nanowires. J. Am. Chem. Soc. 135, 15191–15200 (2013).
2. Zhang, S. et al. In-situ studies of nanocatalysis. Acc. Chem. Res. 46, 1731–1739 (2013).
3. Dutta, S. et al. Silver nanoparticle decorated reduced graphene oxide (rGO) nanosheet: a platform for SERS based low-level detection of uranyl ion. ACS Appl. Mater. Interfaces 5, 8724–8732 (2013).
4. Veerakumar, P., Ramdass, A. & Rajagopal, S. Ruthenium nanocatalysis on redox reactions. J. Nanosci. Nanotechnol. 13, 4761–4766 (2013).
5. Borys, N. J., Shafran, E. & Lupton, J. M. Surface plasmon delocalization in silver nanoparticle aggregates revealed by subdiffraction supercontinuum hot spots. Sci. Rep. 2, 2090 (2012).
6. Chen, P. et al. Single-molecule fluorescence imaging of nanocatalytic processes. Chem. Soc. Rev. 39, 4560–4570 (2010).
7. Wen, G. Q., Liang, A. H. & Jiang, Z. L. Functional nucleic acid nanoparticle-based resonance scattering spectral probe. Plasmonics 8, 899–911 (2013).
8. Zhu, Z. et al. Manipulation of collective optical activity in one-dimensional plasmonic assembly. ACS Nano 6, 2326–2332 (2012).
9. Negreiros, F. R. et al. A first-principles theoretical approach to heterogeneous nanocatalysis. Nanoscale 4, 1208–1219 (2012).
10. Fibri, A. et al. Nanocatalysts for Suzuki cross-coupling reactions. Chem. Soc. Rev. 40, 5181–5203 (2011).
11. Chang, L. L., Erathodiyil, N. & Ying, J. Y. Nanostructured catalysts for organic transformations. Acc. Chem. Res. 46, 1825–1837 (2013).
12. Roldan C. Metal nanoparticle catalysts beginning to shape-up. Acc. Chem. Res. 46, 1682–1691 (2013).
13. Li, L. et al. Selective synthesis of Cu₂O nanoparticles as shape-dependent catalysts for oxidative arylation of phenylacetylene. Chemistry 18, 10491–6 (2012).
14. Hardinge, C. S. & Jaggard, B. R. Nanocatalysis and prospects of green chemistry. ChemSusChem. 5, 65–75 (2012).
15. Yao, D. M., Wen, G. Q. & Jiang, Z. L. A highly sensitive and selective resonance Rayleigh scattering method for bisphenol A based on the aptamer-nanogold catalysis of $H_2O_2$. China Particle reaction. RSC Adv. 3, 13353–13356 (2013).
16. Cao, C. et al. Dual enlargement of gold nanoparticles: from mechanism to scometronmetric detection of pathogenic bacteria. Small 7, 1701–1708 (2011).
17. Mohamed, M. B. et al. Growth mechanism of anisotropic gold nanocrystals via microwave synthesis: formation of oleodainme by gold nanocatalysis. ACS Nano 4, 2768–72 (2010).
18. Huang, Ge. Catal Control and manipulation of gold nanocatalysis: effects of metal oxide support thickness and composition. J. Am. Chem. Soc. 131, 538–548 (2009).
19. Pan, F. & Huo, R. T. Influence of Coupling Agents modification on environmental Pollution Control Theory and Technology, the Natural Science Foundation of China (No. 12267004, 21370017, 21367005, 21365011), the Research Funds of Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, the Natural Science Foundation of Guangxi (No. 2013GXNSFAA19003, 2013GXNSFAA019046), and the Research Funds of Guangxi Education Department (No. 2013YB234, 2013YB035).

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Author contributions
G.Q.W. and Y.H.L. performed the experiment and measurement analysis. G.Q.W. and Z.L.J. prepared Fig. 1–4. A.H.L. and Z.L.J. contributed to the discussion and measurement analysis. All authors contributed to the preparation of the manuscript and reviewed the manuscript.

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