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Autocatalytic Oxidization of Nanosilver and Its Application to Spectral Analysis

SUBJECT AREAS:
NANOSENSORS
SENSORS

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The stable yellow nanosilver (AgNP) and blue nanosilver (AgNPB) sols were prepared by the NaBH_4 procedure. The new nanocatalytic reaction of AgNP-NaCl- H_2O_2 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 oxidization of Ag on AgNP surface by H_2O_2 was observed firstly and the AgNP/AgCl nanoparticles were characterized. The $[\text{Ag}^+]$ from AgNP is different to the Ag^+ from AgNO_3 that adsorb on the AgNP surface. An autocatalytic oxidization 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 H_2O_2 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 properties^{1–5}. Based on the optical properties of nanoparticles, some new types of optical sensors and optoelectronic devices have been developed^{6–9}. And the research of nanocatalysis and its application has become the important research directions in catalytic synthesis and nanoanalysis^{10–16}. Among the nanocatalysis, the reports were mainly about nanogold catalysis and nano titanium dioxide photocatalysis^{17–19}. Recently, some new nanocatalytic analytical methods were established^{20–25}, based on the catalysis of nanogold on the Cu(II)-glucose, HAuCl_4 -ascorbic, HAuCl_4 -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 nanosilver^{26,27}, the catalysis of nanosilver has been observed. Nanosilver modified by aptamer exhibited strong catalysis of the Cu_2O particle reaction of Fehling reagent-glucose, and it has been used to determine trace melamine by RRS technique²⁸. Up to date, the autocatalytic oxidization of AgNP and its application in trace H_2O_2 analysis have not been reported.

The content of H_2O_2 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 H_2O_2 content is also very important in biochemical reactions, clinical test, food safety, and other fields^{20–32}. At present, the spectral methods for H_2O_2 content are mainly including chemiluminescence, fluorescence, spectrophotometry, etc^{33–35}. 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, Hg^{2+} , H_2O_2 , HCl and so on^{36–41}. 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 etc^{28,43–45}. However, there is no report about the research and application of AgNP-NaCl- H_2O_2 autonanocatalytic system yet. In this paper, the reaction mechanism of AgNP-NaCl- H_2O_2 was studied by SPR, RRS^{46–48}, SERS and SEM techniques. Thus, two simple, rapid and sensitive spectral methods have been developed to determine H_2O_2 .

Results

Scanning electron microscope. Stable AgNP sol was prepared by NaBH_4 reduction of AgNO_3 in the presence of citrate. The SEM shows that they are spherical, with average size of 10 ± 2 nm (Fig. 1a). In AgNP-NaCl- H_2O_2

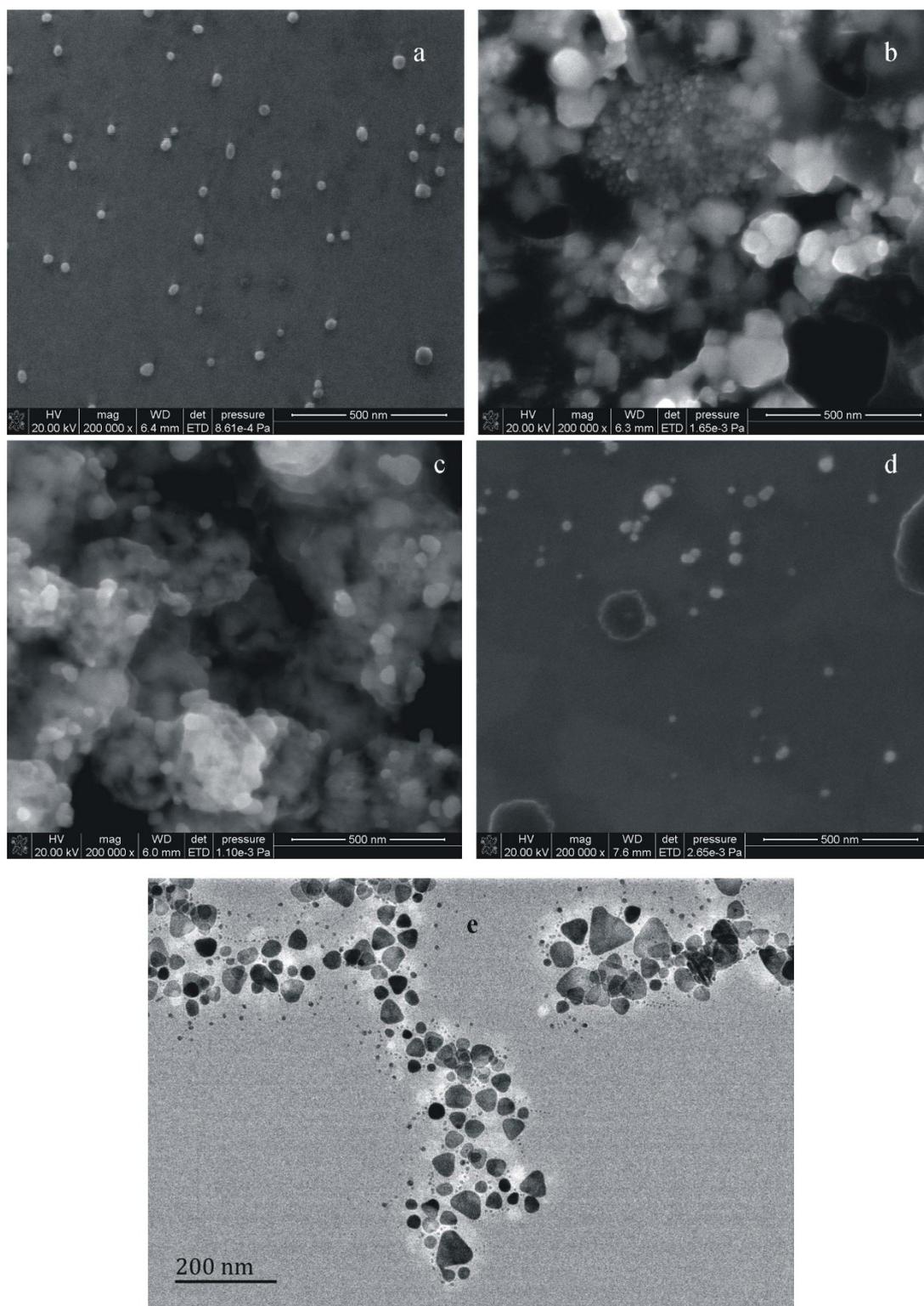


Figure 1 | SEM (a–d) and TEM (e) of AgNP. (a): 9.25×10^{-5} mol/L AgNP; (b): 9.25×10^{-5} mol/L AgNP- 2.0×10^{-3} mol/L NaCl- 20×10^{-5} mol/L H_2O_2 ; (c): 9.25×10^{-5} mol/L AgNP- 2.0×10^{-3} mol/L H_2SO_4 - 2.0×10^{-3} mol/L NaCl- 3.75×10^{-5} mol/L $FeSO_4$ - 1.5×10^{-5} mol/L H_2O_2 ; (d): 5.0×10^{-5} mol/L AgNPB; (e): 5.0×10^{-5} mol/L AgNPB.

system, there is an autocatalytic oxidation reaction on the surface of AgNP to generate large $Ag_n/AgCl$ particles with an average size of 60 ± 15 nm (Fig. 1b). In AgNP- H_2SO_4 -NaCl- $FeSO_4$ - H_2O_2 system, on one hand the autocatalytic oxidation reaction of AgNP generate Ag^+ on the surface, on the other hand surface atoms of AgNP also can generate Ag^+ by the Fenton oxidation reaction, so the large $Ag_n/AgCl$ 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.

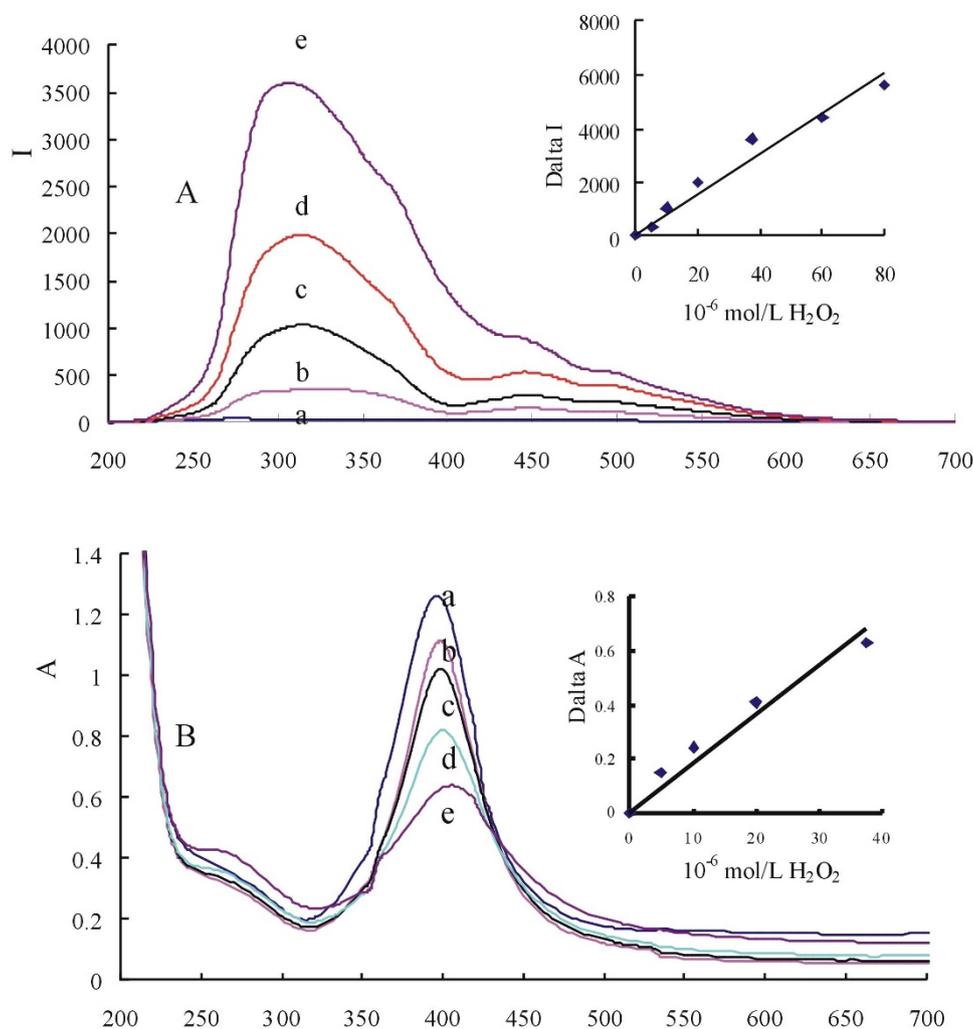


Figure 2 | RRS (A) and SPR (B) spectra of AgNP-NaCl-H₂O₂ system. (a): 9.25×10^{-5} mol/L AgNP – 2.0×10^{-3} mol/L NaCl; (b): $a-5.0 \times 10^{-6}$ mol/L H₂O₂; (c): $a-1.0 \times 10^{-5}$ mol/L H₂O₂; (d): $a-2.0 \times 10^{-5}$ mol/L H₂O₂; (e): $a-5.0 \times 10^{-5}$ mol/L H₂O₂.

RRS spectra. In 2.0×10^{-3} mol/L NaCl medium, AgNPs are stable and its RRS signal is very weak (Fig. 2A). With addition of H₂O₂, AgNP catalyze H₂O₂ 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 H₂SO₄, 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 H₂O₂, the Fenton reaction (FeSO₄-H₂O₂) also produced HO· that oxidize AgNP to form [Ag⁺] and AgNP/[AgCl] particles. With H₂O₂ concentration increase its peak enhanced linearly due to more particles forming.

With addition of different concentration of AgNO₃ to the system of 2.0×10^{-3} 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 AgNO₃ concentration in the range of $12.5-100 \times 10^{-6}$ mol/L with the regression equation of $\Delta I_{335 \text{ nm}} = 53.3c_{\text{Ag}^+} - 93$. For the system of 2.0×10^{-3} mol/L NaCl-0.035% sodium citrate- 2.0×10^{-3} mol/L H₂SO₄- 3.75×10^{-5} mol/L FeSO₄-AgNO₃, AgCl particles exhibited strong scattering signal at 335 nm (Fig. 3S). The increased intensity $\Delta I_{335 \text{ nm}}$ was linear to AgNO₃ concentration in the range of $12.5-100 \times 10^{-6}$ 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-H₂O₂ 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-H₂O₂ 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 AgNO₃. Compare to RRS spectra of NaCl-sodium citrate-AgNO₃ 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 theory⁴⁹ 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 nm⁵⁰, which is out-of-plane dipole SPR absorption peak⁵¹. In the systems of NaCl and NaCl-H₂SO₄-FeSO₄, 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 H₂O₂ concentration increased and can be chosen to determine H₂O₂. The AgNO₃-NaCl and AgNO₃-NaCl-H₂SO₄-FeSO₄ systems were examined by spectrophotometry. With addition of different AgNO₃ concentration to the two systems of 2.0×10^{-3} mol/L NaCl-0.035% sodium citrate and 2.0×10^{-3} mol/L NaCl-0.035% sodium citrate – 2.0×10^{-3} mol/L H₂SO₄ – 3.75×10^{-5} mol/L FeSO₄, the produced AgCl particles exhibited weak SPR peak at

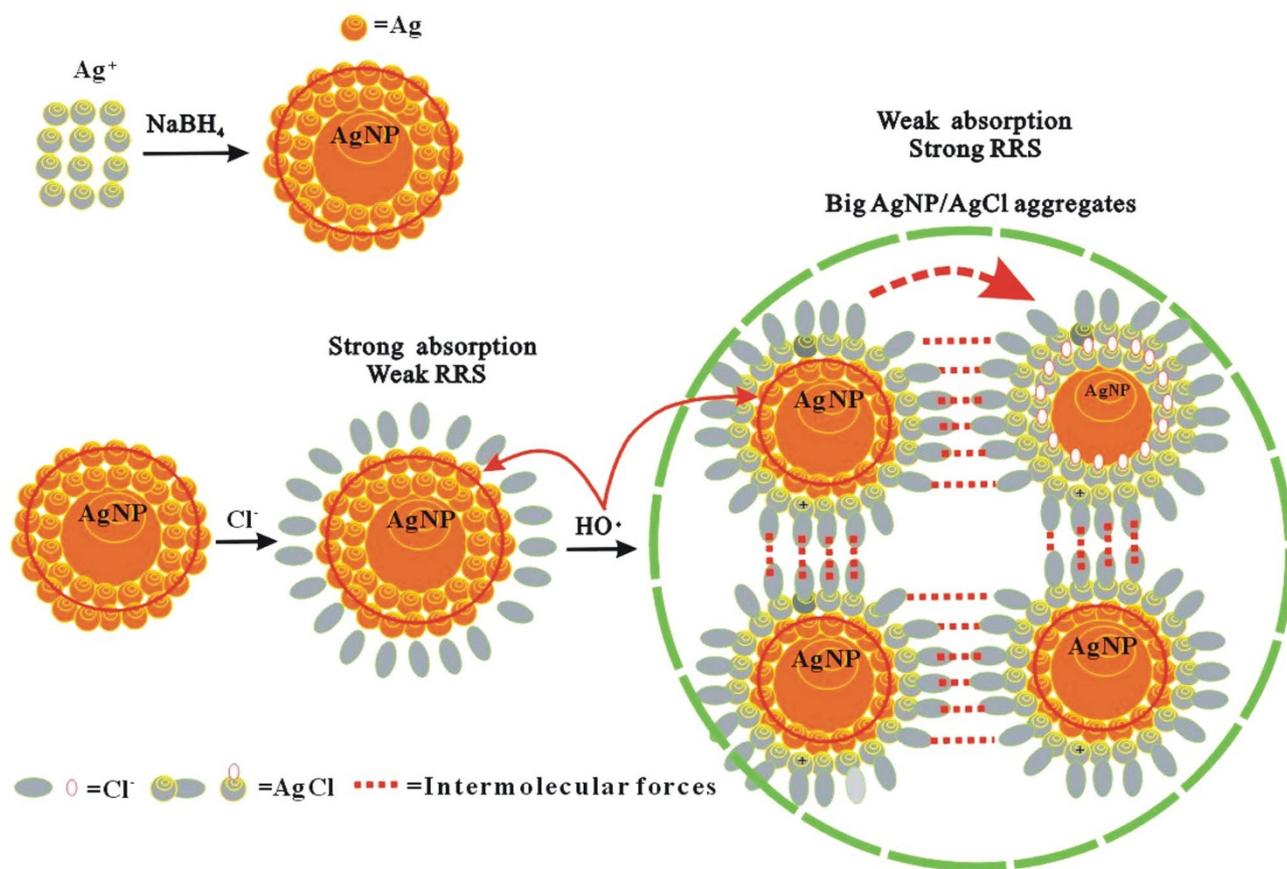


Figure 3 | Principle of autocatalytic oxidation of AgNP to detect H_2O_2 .

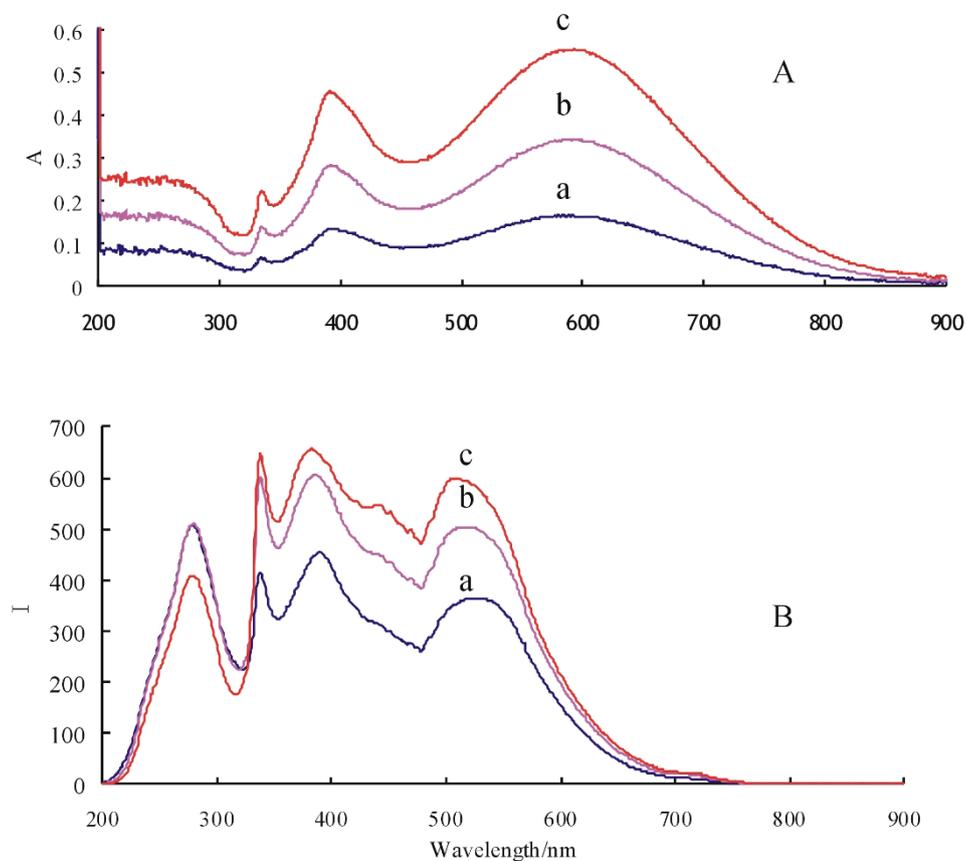


Figure 4 | SPR spectra (A) and RRS spectra (B) of AgNPB. (a): 2.5×10^{-5} mol/L AgNPB; (b): 5.0×10^{-5} mol/L AgNPB; (c): 7.5×10^{-5} mol/L AgNPB.



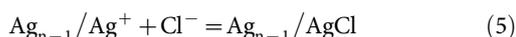
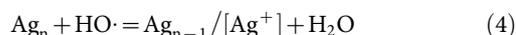
285 nm (Fig. 6S,7S). The absorbance increased slowly with the AgNO₃ concentration increased in the range of 12.5–100 × 10⁻⁶ mol/L because AgCl particles have weak absorption. In the medium of 5.0 × 10⁻⁴ mol/L NaCl, AgNPB has two SPR absorption peaks at 330 nm and 530 nm (Fig. 8S). The absorbance at 530 nm decreased linearly with the H₂O₂ concentration increased in the range of 2–8 × 10⁻⁵ 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 probe⁵², 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 × 10⁻⁵ mol/L AgNP and 9.25 × 10⁻⁵ 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.

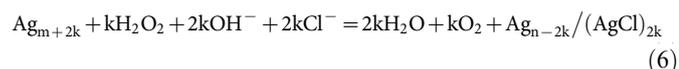
Discussion

Mechanism of autocatalytic oxidization of AgNP. Stable 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 weaker. When H₂O₂ increased, the RRS intensity increased linearly due to more big AgNP/AgCl aggregates forming, and the SPR absorption decreased linearly due to much less small nanosilver forming. Thus, two new SPR absorption and RRS methods were established to determine H₂O₂.

According to the generation mechanism of HO· and the autocatalytic oxidation mechanism of AgNP^{53,54} (AgNP = Ag_n = Ag_m + 2k), the main reactions of AgNP-NaCl-H₂O₂ system are as follows,



In the presence of NaCl, the reducing ability of Ag was enhanced and made the reaction of H₂O₂ oxidize AgNP to form Ag_{m-2k}/[AgCl]_{2k} complex particles become easily, as the result of the formation of AgCl particle with low solubility. The total reaction is as follow,



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^{54,55}. 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^{56,57}. 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 Δ*I* and H₂O₂ concentration was drawn. The linear range of AgNP-NaCl system was 2.0 × 10⁻⁸–8.0 × 10⁻⁵ mol/L, with a regression equation of Δ*I* = 71.4c-1.6, a correlation coefficient of 0.9852, and a detection limit of 8 × 10⁻⁹ mol/L. A 5.0 × 10⁻⁷ mol/L, 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-H₂SO₄-FeSO₄ system was 1.0 × 10⁻⁷–2.5 × 10⁻⁵ mol/L, with a detection limit of 2 × 10⁻⁸ mol/L. In the RRS analytical system, the AgNP-NaCl is most sensitive, simple, stabile 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 SO₄²⁻, 70 times of Ca(II) and Mg(II), 50 times of Cu²⁺, Mo⁶⁺, I⁻, triethanolamine, Co²⁺, NO₂⁻, 10 times of Mn²⁺, Br⁻, 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 λ_{ex} and emission wavelength λ_{em} (λ_{ex}-λ_{em} = Δλ = 0) and the RRS intensity. A Model TU-1901 double beams 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 (Kedao Company, Shanghai, China), and a model magnetic stirrer (Zhongda Instrumental Plant, Jiangsu, China) were used.

A 1.0 × 10⁻³ mol/L AgNO₃ solution, 1% (W/V) sodium citrate solution, 0.05 mol/L NaCl solution, and 1.0 × 10⁻³ mol/L FeSO₄ solution were used. A 0.05% (W/V) NaBH₄ was prepared freshly. A 0.100 mol/L H₂O₂ standard solution was prepared as follows: 1.02 mL H₂O₂ (30%) was diluted to 100 mL with water, it was standardized by KMnO₄ procedure, and was diluted to 5.00 × 10⁻⁴ mol/L before use.

A 1.85 × 10⁻⁴ mol/L AgNP was prepared as follows: 9.25 mL 1.0 × 10⁻³ mol/L AgNO₃ and 3.5 mL 1% trisodium citrate were added into a conical flask with stirring and diluted to 40 mL with water, then 4 mL 0.05% NaBH₄ was added slowly with about 15 min, the mixture was diluted to 50 mL, and it can be used after 24 h to make the NaBH₄ decomposing completely. The preparation of AgNP sols was repeated five times, the SPR peak is at 395 nm with an average absorption value of 2.50 ± 0.10, and the sols were stabile within 20 days (Fig.20S). A 1.0 × 10⁻⁴ mol/L AgNPB was prepared as follows: 40 mL of water, 500 μL 1.0 × 10⁻² mol/L AgNO₃, 1.5 mL 6.0 × 10⁻² mol/L sodium citrate, 120 μL 30% H₂O₂, and 200 μL 0.1 mol/L NaBH₄ were added into a triangle flask in turn with constantly stirring for 15 min. Then heat to



boil for 5 min to get rid of the excess H_2O_2 and 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 1.85×10^{-4} mol/L AgNP solution, 80 μL 0.05 mol/L NaCl (or adding 80 μL 5.0×10^{-2} mol/L H_2SO_4 , 75 μL 1.0×10^{-3} mol/L FeSO_4), 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 (I) was recorded by a fluorescence spectrophotometer with synchronous scanning ($\lambda_{\text{ex}} - \lambda_{\text{em}} = \Delta\lambda = 0$). A blank (I_0) without H_2O_2 was recorded and the value of $\Delta I = I - I_0$ was calculated.

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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.

Additional information

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