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ORIGINAL PAPER

# Resonance Scattering Spectral Detection of Catalase Activity Using Au@Ag Nanoparticle as Probe and Coupling Catalase Catalytic Reaction with Fenton Reaction

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**Abstract** The $Au_{core}Ag_{shell}$ (Au@Ag) nanoparticles in size of 30 nm were prepared using 10 nm gold nanoparticles as seeds at 90°C, and were purified by high-speed centrifugation to remove the excess trisodium citrate to obtain Au@Ag nanoprobe. In the medium of pH 4.0 acetate buffer solution—7.2 μmol/L $H_2O_2$–67 μmol/L Fe(II), Au@Ag nanoparticles exhibited a resonance scattering (RS) peak at 538 nm. Upon addition of Catalase (Ct), the system produced hydroxyl radical that oxidized the Au@Ag nanoprobe to form the AuAg nanoparticles with partly bare nanogold. Those AuAg nanoparticles aggregated to large nanoclusters that led to the RS peak wavelength red-shift and its RS peak intensity enhanced. The catalase activity ($C$) is linear to the enhanced RS intensity ($\Delta I$) in the range of 6 to 2,800 U/L, with regression equation of $\Delta I$=0.168 $C$-0.2, the correlation coefficient of 0.9952, and detection limit of 2.8 U/L. This method was applied to the detection of serum samples, and the results were agreement with that of the spectrophotometry. A new catalytic mechanism of catalase was proposed with oxywater principle that was agreement with the results of resonance scattering spectroscopy, absorption spectrophotometry, transmission electron microscopy and laser scattering.

**Keywords** Catalase · Au@Ag nanoprobe · Hydroxyl radical · Resonance scattering spectral assay

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## Introduction

Catalase (Ct) is a kind of antioxidant enzyme in organism, containing iron porphyrin ring. The biological function is through the decomposition of $H_2O_2$ to oxygen to prevent the peroxide reactions in cells, reaching detoxification and protection of the based chain. Furthermore, it plays protective and alexipharmic effect on thiol enzyme, membrane protein with glutathione peroxidase (GSH-PX) [1]. The emergence of certain diseases often associated with the increased concentration of Ct, its detection is significant for the metabolism of free radicals, anti-aging, the protection of amino acids and tumor pathogenesis research [2]. In addition to, it is also an important reagent for preparation $H_2O_2$ sensor [3]. Therefore, the determination of Ct activity is of great importance [4]. Presently, several methods have been developed for the detection of Ct activity, including iodimetry, spectrophotometry, chemiluminescence (CL), electrochemistry (EC), fluorescence spectrometry (FS) and so on [5, 6]. Spectrophotometry was simple, FS method had high sensitivity. These methods are based on following principle, first the Ct catalyzing decomposition of $H_2O_2$, and then determining the residual concentration of hydrogen peroxide to detect Ct [5, 6]. Based on our knowledge, there is no report about the

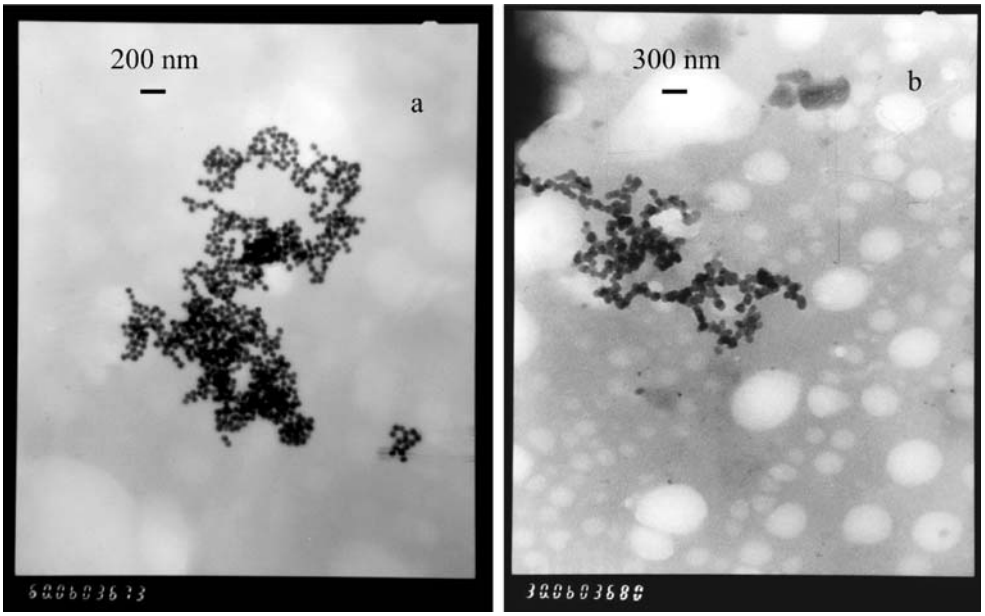



**Fig. 1** TEM of nanoparticles. **a** TEM of Au@Ag nanoparticles (Amplification times, 60,000); **b** The reacted Au@Ag nanoparticles (Amplification times, 30,000)

coupling Ct-$H_2O_2$ enzymatic catalytic reaction and $H_2O_2$-Fe(II) or horseradish peroxidase (HRP)-Au@Ag nanoparticles catalytic reaction and its application to resonance scattering (RS) analysis.

RS or resonance light scattering (RLS) was a sensitive, rapid and simple analytical technique, and was applied to nucleic acid, protein and small molecule analysis [7–15]. Enhancing their selectivity and sensitivity is necessary to analyze real sample. Catalytic reaction can be used to simply signal that is a good way to increase the selectivity and sensitivity. On the one hand, RS technique can be coupled with inorganic catalytic reaction and highly selective enzymatic catalytic reaction to determine of trace metal ions and enzyme activity [16, 17]. On the other hand, highly sensitive immunonanogold catalytic reaction can be combined with the RS effect of Au, and Ag particulates to detection of trace antigens, with good results [18, 19]. Due to nanoparticles being novel physical and chemical properties, they have been used in biochemical analysis. Recently, the application of nanoparticles to RS spectral analysis also comes to the fore [10, 20]. Based on the RS effect of nanosilver, trace sudan

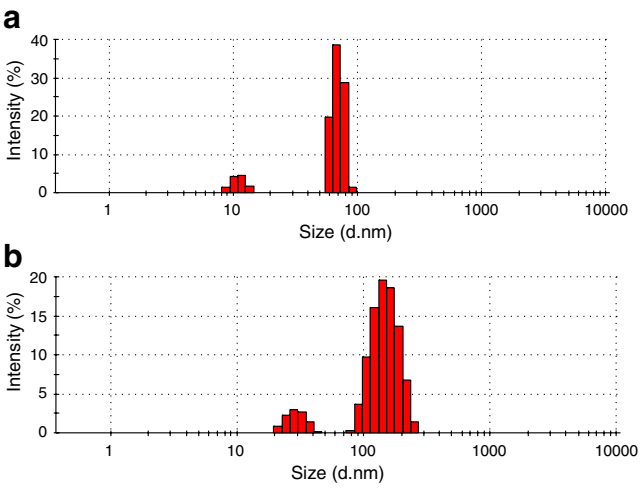



**Fig. 2** The histograms of Ct-Fe(II)-$H_2O_2$-Au@Ag system. **a** pH 4.0 HAC-NaAC-7.2 μmol/L $H_2O_2$-29.4 μmol/L Au@Ag–67 μmol/L Fe (II); **b** a–2,800 U/L Ct

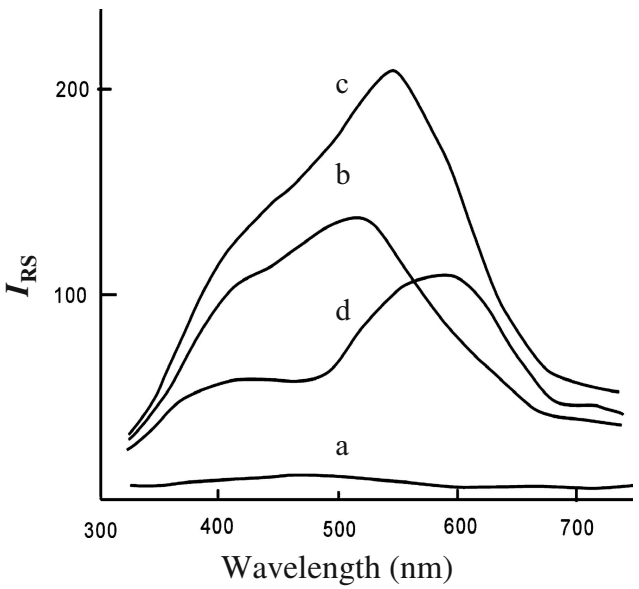



**Fig. 3** RS spectra of Ct-nanoparticle system. **a** pH 4.0 HAC-NaAC–2,800 U/L Ct; **b** pH 4.0 HAC-NaAC–29.4 μmol/L Au@Ag; **c** pH 4.0 HAC-NaAC–29.4 μmol/L Au@Ag–2,800 U/L Ct; **d** pH 4.0 HAC-NaAC–4.64 μg/mL Au–2,800 U/L Ct

I can be detected [10]. Coupled nanogold aggregation and HRP catalytic reaction, trace $H_2O_2$ have been determined by RS spectral analysis [20]. Au@Ag nanoparticle is a kind of bimetal particle which have core-shell structure, it has the physicochemical properties of $(Au)_{core}$ and the good reactivity of $(Ag)_{shell}$, the preparation of Au@Ag nanoparticle often reduced by ascorbic acid and oxy-ammonia [21, 22]. However, the study about RS spectra of Au@Ag nanoparticle and its use to detect Ct have not been reported. In this work, the new catalytic reaction of Ct-$H_2O_2$-Fe(II) - Au@Ag was studied by RS technique, and a new RS spectral method was set up for rapid determination of Ct.

## Experimental section

*Apparatus* A model Cary Eclipse fluorescence spectrophotometer (Varian Company, Palo Alto, CA) was used to record the RS spectra by means of synchronous scanning excited wavelength $\lambda_{ex}$ and emission wavelength $\lambda_{em}$ ($\lambda_{ex}$–$\lambda_{em}$ = $\lambda$ = 0) and the RS intensity. Model Sigma 3K30 high-speed refrigeration centrifuge (Sigma Company, Harz, Germany), model DK-8B thermostated water bath (Jinghong Experimental Equipment Limited Company, Shanghai, China), model SK1200H ultrasonic reactor (Kedao Ultrasonic Instrument Limited Company, Shanghai, China), model TU-1901 double beams UV-visible spectrophotometer (Beijing Purkinje General Instrument Limited Company, China), model H-600 transmission electron microscope (TEM) (Electronic Stock Limited Company, Japan), model NaNo-ZS90 particle size and Zeta potentiometer analyzer (England) were used.

*Reagents* Ct (3,500 U/mg) was purchased from Sigma Company, and 1.2 mg Ct was dissolved in 100 mL water to obtain 42 U/mL Ct (12 μg/mL). 20 μg/mL horseradish peroxidase (HRP), 20 μg/mL hemoglobin (HG), 1.0% chloroauric acid ($HAuCl_4$) (National Pharmaceutical Group Chemical Reagents Company, China), 1.0% trisodium citrate solution, $2.94\times10^{-4}$ mol/L $AgNO_3$ solution were used. A 0.2 mol/L acetic acid-sodium acetate buffer solution (pH 3.6–4.6) was prepared. $2.0\times10^{-3}$ mol/L Fe(II) solution was prepared by ferrous ammonium sulfate. $H_2O_2$ stock solution concentration was standardized by titration with potassium permanganate. The working solution of $2.16\times10^{-4}$ mol/L $H_2O_2$ was obtained by diluting the stock solution appropriately just before use. 58.0 μg/mL Au nanoparticles in size of 10 nm were prepared by using the Frens procedure [23, 24]. A 1.0 mL 1.0% trisodium citrate solution and 5.0 mL $2.94\times10^{-4}$ mol/L $AgNO_3$ solution were added to a 25-mL graduated tube containing 4.0 mL 58.0 μg/mL Au nanoparticles, mixed well, and placed the tube in a bath at 90°C for 10 min. Stop the reaction by tap-water cooling, the solutions were transferred into a 80-mL centrifuge tube, was centrifuged at 16,000 rpm for 15 min. The supernatant was removed by sampler, after that 10 mL water was added to centrifuge tube, and dispersed in an ultrasonic reactor for 15 min. Centrifuged it twice by the same way, $1.47\times10^{-4}$ mol/L Au@Ag nanoparticles, calculating as silver, were obtained and were stored in a refrigerator at 4°C. All used reagents were of analytical grade and the water was double distilled.

*Procedure* A 0.10 mL pH 4.0 HAC-NaAC buffer solution, a certain quantity of Ct, 0.10 mL $2.16\times10^{-4}$ mol/L $H_2O_2$ solution, 0.60 mL $1.47\times10^{-4}$ mol/L Au@Ag nanoparticles and 0.10 mL 2.0 mmol/L Fe(II) solution were successively added to a 5-mL graduated tube, and mixed well, 15 min later, diluted to 3.0 mL with water. The RS spectrum was recorded by means of synchronous scanning. Then, the RS peak intensity was recorded, and the $I_0$ value without Ct was recorded. The $\Delta I=I-I_0$ value was calculated.

**Table 1** Effect of protein concentration on the RS peak

| $C_{Protein}$ (μg/mL) [a] | 0 | 0.04 | 0.2 | 0.32 | 0.8 |
|---|---|---|---|---|---|
| $(\lambda_{RS})_{Ct\text{-}Au}$/nm | 530 | 540 | 545 | 560 | 589 |
| $(\lambda_{RS})_{HRP\text{-}Au}$/nm | 530 | 545 | 614 | 620 | 620 |
| $(\lambda_{RS})_{HG\text{-}Au}$/nm | 530 | 560 | 620 | 622 | 625 |
| $(\lambda_{RS})_{Ct\text{-}Au@Ag}$/nm | 526 | 530 | 535 | 540 | 541 |
| $(\lambda_{RS})_{Ct\text{-}H2O2\text{-}Fe(II)+Au@Ag}$/nm | 538 | 556 | 583 | 603 | 610 |

[a] Proteins include Ct (Catalase), HRP (horseradish peroxidase) and HG (hemoglobin)

## Results and discussion

*Principle* Due to nanogold particles being high electron density and strong absorption capacity, $Ag^+$ can be absorbed easily on the surface of nanogold particles, and the $Ag^+$ oxidation potential enhanced [24], that can be reduced easily to elemental silver and coating on the surface of nanogold particles to form Au@Ag nanoparticles. It was reported that $H_2O_2$ can be catalyzed by Ct to produce active $H_2O_2^*$ and oxywater (water oxide) $H_2O$-O that is an isomer of hydrogen peroxide [25, 26]. On the one hand, $H_2O_2^*$ reacted with $H_2O$-O to form $H_2O$ and $O_2$. On the other hand, $H_2O_2^*$ can be also catalyzed rapidly by Fe(II) (or HRP, HG) to form •OH. Under the experimental conditions, the rate of $H_2O_2$ - Fe(II) (or HRP, Hemoglobin) catalytic reaction to produce ·OH was slow. The result indicated that Au@Ag nanoparticles can't be oxidized by the $H_2O_2$-Fe(II) (or HRP, HG), and $H_2O_2$-Ct

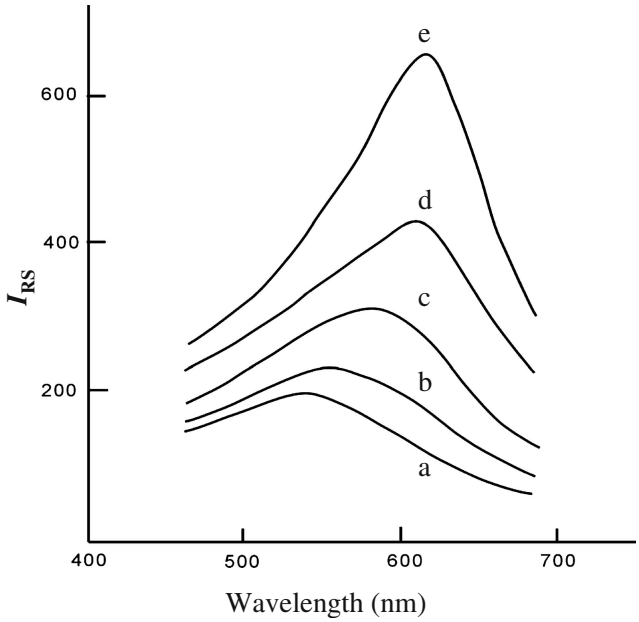



**Fig. 4** RS spectra of Ct-$H_2O_2$-Fe(II)-Au@Ag system. **a** pH 4.0 HAC-NaAC–7.2 μmol/L $H_2O_2$–67 μmol/L Fe(II)–29.4 μmol/L Au@Ag; **b** a–140 U/L Ct; **c** a–700 U/L Ct; **d** a–1,120 U/L Ct; **e** a–2,800 U/L Ct

reactions, but can be oxidized by Ct-Fe(II) (or HRP, HG)-$H_2O_2$. That is, the system generated a large number of strong oxidizer ·OH [27] that oxidize nanosilver to silver ion. When ·OH touch Au@Ag nanoparticles, the thin Ag part of Au@Ag nanoparticles has higher activity that was oxidized by ·OH preferentially to generate AuAg nano-

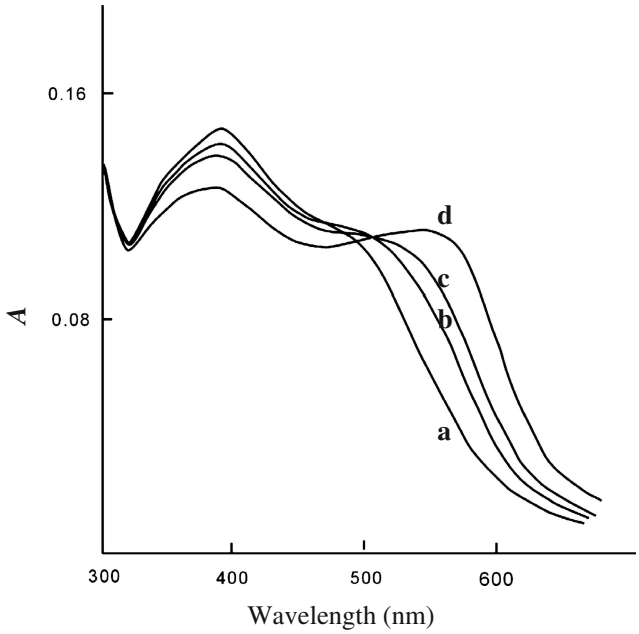



**Fig. 5** Absorption spectra of Ct-$H_2O_2$-Fe(II)-Au@Ag system. **a** pH 4.0 HAC-NaAC–7.2 μmol/L $H_2O_2$–29.4 μmol/L Au@Ag – 67 μmol/L Fe(II); **b** a–700 U/L Ct; **c** a–1,400 U/L Ct; **d** a–2,800 U/L Ct

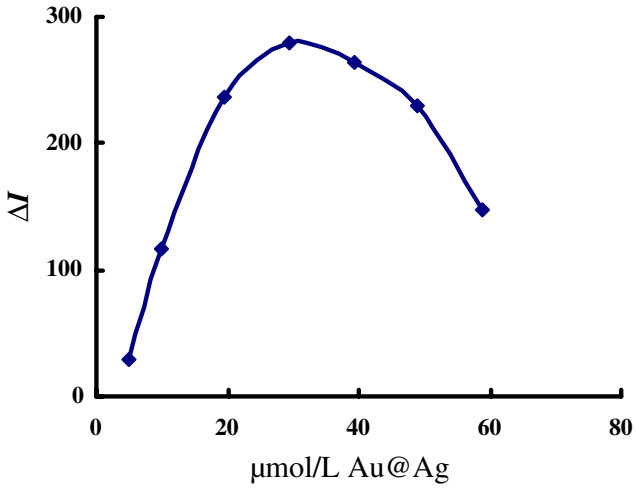



**Fig. 6** Effect of Au@Ag concentration. pH 4.0 HAC-NaAC–1,800 U/L Ct–7.2 μmol/L $H_2O_2$–67 μmol/L Fe(II)

paticles with partly bare nanogold. Under the action of Ct and salts, those AuAg nanopaticles aggregations led to red shift of the RS peak and enhancement of RS peak. On those grounds, a new RS method for Ct detection was set up. The main reactions containing Ct catalytic reaction and Fenton reaction were as follows,

$$Ct + H_2O_2 = Ct{\cdot}H_2O_2$$

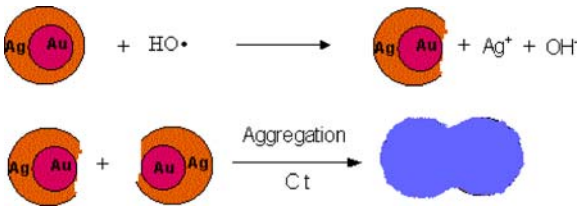
$$Ct{\cdot}H_2O_2 + H_2O_2 = Ct{\cdot}H_2O\text{-}O + H_2O_2^{*}$$

$$Ct{\cdot}H_2O\text{-}O + H_2O_2^{*} = Ct + H_2O + H_2O + O_2$$

$$H_2O_2^{*} + Fe(II) = Fe(II){\cdot}H_2O_2^{*} \quad \text{(fast)}$$

$$Fe(II){\cdot}H_2O_2^{*} = Fe(II) + HO{\cdot} \quad \text{(fast)}$$

$$H_2O_2 \quad Fe(II) \quad HO{\cdot} \quad \text{(slow)}$$




The total reaction follows,

$$H_2O_2 + (Au)_n(Ag)_mCt - Fe(II) \ \text{couplingcatalysis} (Au)_n(Ag)_{m-k} + k\,Ag^{+} + O_2 + OH^{-}$$

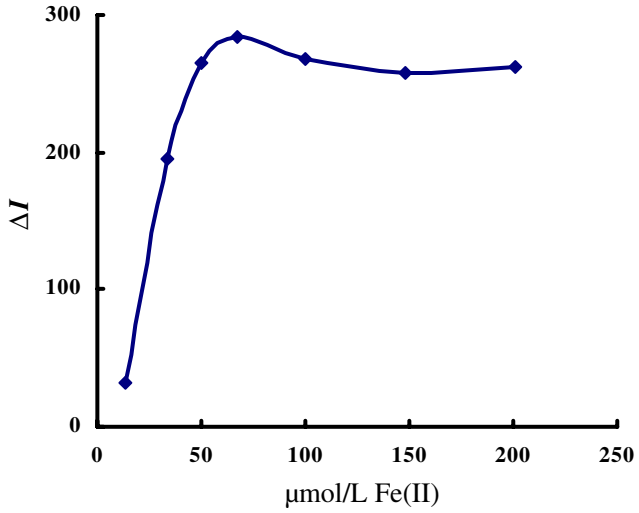



**Fig. 7** Effect of Fe(II) concentration. pH 4.0 HAC-NaAC–1,800 U/L Ct–7.2 μmol/L $H_2O_2$–29.4 μmol/L Au@Ag

*Characterization of nanoparticles* Au@Ag nanoparticles and the reacted Au@Ag nanoparticles were observed by TEM (Fig. 1). The 30 nm Au@Ag nanoparticles was in spherical (Fig. 1a), the reacted Au@Ag nanoparticles aggregated to form large particles in mean size of 75 nm (Fig. 1b). Laser scattering images of Fe(II)-$H_2O_2$-Au@Ag system as Fig. 2, the average diameter was 69 nm (Fig. 2a), bigger than the 30 nm Au@Ag nanoparticles because the adding of Fe(II) to the system led to slight aggregation. Upon addition of Ct, the average diameter was 115 nm (Fig. 2b), due to the shell of Au@Ag nanoparticles being oxidized by ·OH to generate the AuAg nanopaticles with partly bare nanogold that aggregated by Ct and salts.

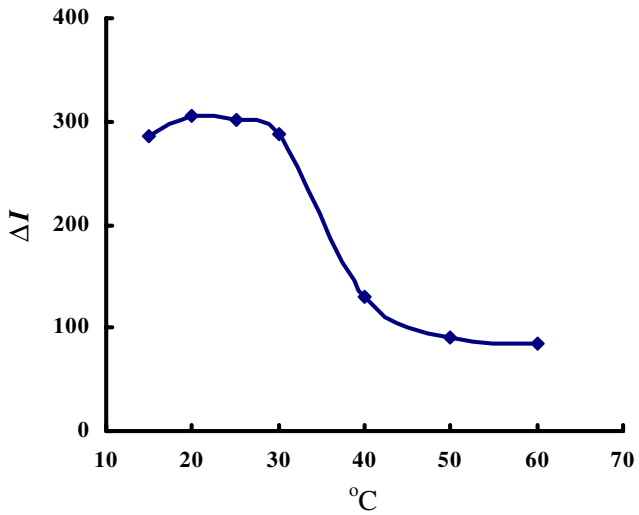



**Fig. 8** Effect of temperature. pH 4.0 HAC-NaAC–1,800 U/L Ct–7.2 μmol/L $H_2O_2$–29.4 μmol/L Au@Ag–67 μmol/L Fe(II)

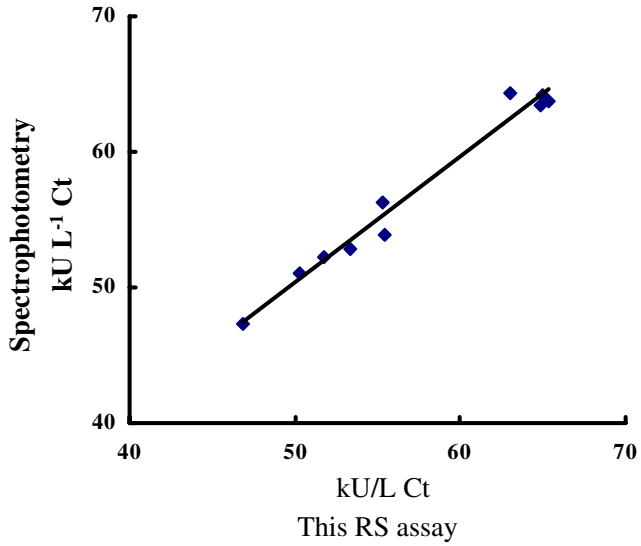



**Fig. 9** Linear regress analysis

*Resonance scattering spectra* Good water soluble Ct and 10 nm nanogold exhibited weak scattering signals (Fig. 3a). Au@Ag nanoparticles exhibited a RS peak at 526 nm (Fig. 3b). Upon addition of Ct, the color did not change, the RS peak increased (Fig. 3c). Table 1 indicated that the RS peak max red-shit of Ct-Au, HRP-Au, HG-Au, Ct-Au@Ag and Ct-$H_2O_2$-Fe(II)-Au@Ag system was 59 nm, 90 nm, 95 nm, 15 nm and 72 nm, respectively. This indicated that Ct caused Au@Ag nanoparticles RS peak red-shit slightly. However, Ct caused nanogold aggregation strongly and the color in blue-violet, the RS intensities enhanced greatly and RS peak exhibited strong red-shift (Fig. 3d). The effect of HRP and HG on the nanogold aggregation is similar to the Ct due to the three proteins being porphyrin ring. Furthermore, the RS peak of both Ct-$H_2O_2$-Au@Ag system and the Ct-Au@Ag system with weak red shift and the both RS enhancements were consistent. In other words, Ct can not catalyze $H_2O_2$ producing •OH to oxidize Au@Ag nanoparticles. Under the experimental condition, the RS peak and the RS intensities of the Fe(II) (or HRP, HG)-$H_2O_2$-Au@Ag system changed a little, it means that little ·OH produced.

**Table 2** Analytical features for detection of Ct

| System | Linear range (U/L Ct) | Regress equation | Relative coefficient | DL (U/L Ct) |
|---|---|---|---|---|
| Fe(II)-$H_2O_2$-Au@Ag | 6–2,800 | $\Delta I$=0.168 $C$–0.2 | 0.9983 | 2.8 |
| HRP-$H_2O_2$-Au@Ag | 7–3,500 | $\Delta I$=0.085 $C$+7.6 | 0.9985 | 5 |
| HG-$H_2O_2$-Au@Ag | 14–4,200 | $\Delta I$=0.0475 $C$+8.8 | 0.9962 | 7 |

Upon addition of Ct, the Ct-Fe(II)-$H_2O_2$-Au@Ag system appeared red shift and the RS intensities enhanced greatly (Fig. 4). In addition to, the Ct-Fe(II)-$H_2O_2$-Au@Ag system was more sensitive for Ct detection when comparing to the Ct-Fe(II)-$H_2O_2$-nanosilver system. In this work, Ct-Fe(II)-$H_2O_2$-Au@Ag was selected, and the RS peak value was used for quantitative analysis.

*Absorption spectra* Absorption spectra of Ct-$H_2O_2$-Fe(II)-Au@Ag system was showed in Fig. 5. Au@Ag nanoparticles exhibited a surface plasma resonance (SPR) absorption peak at 393 nm for nanosilver, and a weak surface plasma resonance absorption peak at about 500 nm for nanogold (Fig. 5a). Upon addition of Ct, the peak at 393 nm decreased, but did not disappear. This demonstrated that there is the shell of nanosilver. On the other hand, the SPR peak for the nanogold core appeared considerably with red-shift (Fig. 5d), and the system was in blue-violet color that indicated that nanogold core aggregated by Ct.

*Optimal conditions* The effect of pH 3.8–5.0 HAc-NaAc buffer solution was tested. The pH had little influence on the blank system, but had great influence on the Ct catalytic system. The pH value was between 3.8 and 4.4, the $\Delta I$ was higher. When the pH was higher than 4.5, the $\Delta I$ was lower. A pH 4.0 HAc-NaAc was chosen. In the range of 0–5 μmol/L $H_2O_2$, the $\Delta I$ increased along with the concentration. When the concentration was 7.2 μmol/L, the $\Delta I$ was maximal, and was chosen for use. Figure 6 showed that 29.4 μmol/L Au@Ag, giving maximal $\Delta I$, was chosen for use. Fe(II), HRP, and HG were commonly used catalysts for the •OH reaction. Effect of their concentration on the $\Delta I$ was considered respectively. The results showed that 67 μmol/L Fe(II) (Fig. 7), 0.020 μg/mL HRP, and 0.022 μg/mL HG, giving maximal $\Delta I$, were chosen. Figure 8 indicated that the $\Delta I$ changed weakly when the temperature was in the range of 15–25°C. When the temperature was higher than 30°C, the $\Delta I$ was become low. Thus, room temperature was chosen. Effect of reaction time was tested. The results showed that 5 min later, the $\Delta I$ was stable within 40 min. 15 min was chosen as the optimal reacted time.

*Linear range* According to the procedure, the $\Delta I$ at different concentration of Ct was recorded, and was used to plot working curve. The Fe(II), HRP and HG system's analytical features such as linear range and detection limit (DL) were listed in Table 2. Results showed that the Fe(II) system was most sensitive, and the catalyst was easy to obtain and cheapest, and was chosen for the detection of Ct.

*Effect of foreign substances* Under the chosen conditions, influence of foreign substances on the detection of 1,120 U/L Ct (0.32 μg/mL) was examined, with a relative error of ±5%. Results indicated that 80 μg/mL $Zn^{2+}$, 50 μg/mL $Mg^{2+}$, *L*-Lysine, and nicotin, 40 μg/mL $Ca^{2+}$, 30 μg/mL $Al^{3+}$, 20 μg/mL $Cu^{2+}$, and BSA, 15 μg/mL $Co^{2+}$, 10 μg/mL $Mn^{2+}$, sucrose, *L*-glutamic acid, HSA, and *L*-tyrosine, 5 μg/mL niacin, glucose, and carbamide, 3 μg/mL *L*-cystine did not interfered with the determination, and this assay has good selectivity.

*Analytical application* Ten healthy serum samples were collected from Guilin No. 5 People's Hospital. 80 μL sera were used to detect activity using this catalytic RS assay and $H_2O_2$-KI-starch spectrophotometry. Results were showed in Fig. 9, this RS assay results were agreement with the spectrophotometry, and normal results 51.55± 16.4 kU/L Ct [28]. The linear regress analysis of both assay results revealed a correlation coefficient, slope, and intercept of 0.989, 0.929, and 3.9 kU/L, respectively. A known amount of Ct was added to the sample, and the recovery of 93.4–100.6% was obtained.

## Conclusions

The thin Ag shell of Au@Ag nanoparticles can be oxidized to AuAg nanoparticles with partly bare Au core by HO· that come from the coupled catalytic reaction of Ct-Fe(II)-$H_2O_2$. Under the action of Ct and salt, the 10 nm nanogold particles, and the AuAg nanoparticles aggregated to large nanogold clusters and AuAg nanoparticles clusters in blue-violet color respectively. In which the RS peak of Ct-Fe(II)-$H_2O_2$-Au@Ag nanoparticles system led to enhancement and red-shit, and the enhanced RS peak intensity is linear to the catalase activity in the range of 6–2,800 U/L, with detection limit of 2.8 U/L. This coupled catalytic RS method was applied to the detection of sera samples, with sensitivity, selectivity, simplicity and rapidity. The coupled catalytic mechanism was also studied by the RS spectroscopy, absorption spectrophotometry, transmission electron microscopy and laser scattering.

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