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A facile SERS strategy to detect glucose utilizing tandem enzyme activities of Au@Ag nanoparticles

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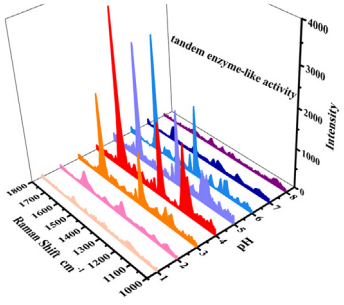
HIGHLIGHTS

- Au@Ag NPs was successfully synthesized, which can be used as SERS substrate.
- Au@Ag NPs exhibits bienzymatic activity, so Au@Ag NPs can be described as a "tandem nanoenzyme".
- A new SERS strategy with the detection limit of 5×10^{-10} mol L^{-1} for glucose was developed.

GRAPHICAL ABSTRACT

A simple seed-mediated method to synthesize Au@Ag nanoparticles (NPs) as a multifunctional biosensor for the label-free detection of hydrogen peroxide (H_2O_2) and glucose by SERS. We have developed a new SERS strategy for analysis of glucose with a detection limit of 5×10^{-10} mol L^{-1}, suggesting that Au@Ag NPs have the potential for biosensor, immunoassay and medical treatment.



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ABSTRACT

Surface-Enhanced Raman Scattering (SERS) is a powerful analysis technology, attracting more and more attention due to its high sensitivity and selectivity. Herein, we report a simple seed-mediated method to synthesize Au@Ag nanoparticles (NPs) as a multifunctional biosensor for the label-free detection of hydrogen peroxide (H_2O_2) and glucose by SERS. Au@Ag NPs, as an ultrasensitive SERS substrate, show the dual activities (peroxidase-like and GOx-like activities). Under the condition of pH 4.0 NaAc buffer solution, the glucose and H_2O can be catalyzed by Au@Ag NPs to produce glucose acid and H_2O_2, and then H_2O_2 can oxidize 3,3′,5,5′-tetramethylbenzidine (TMB) to form a blue oxidation product oxidic TMB (oxTMB) which exhibits strong SERS signals at 1188, 1330, 1605 cm^{-1}. Thus, we have developed a new SERS strategy for analysis of glucose with a detection limit of 5×10^{-10} mol L^{-1}, suggesting that Au@Ag NPs have the potential for biosensor, immunoassay and medical treatment.

1. Introduction

It is an undenied fact that Surface-enhanced Raman Spectroscopy (SERS) is a promising tool for the study of catalytic behaviors with its ultrahigh surface sensitivity down to single molecule [1–3]. Among the three most commonly used SERS substrates (Ag, Au, and Cu), the surface plasmon efficiency of Ag is greater than Au and Cu [4]. Another advantage of Ag over Au is that the SPR of Ag nanostructures can be tuned to any wavelength in the visible region of the spectrum. However, synthesis of Ag NPs in a controlled manner has been a challenging task for a long time

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period. In 2016, Tian's group [5] reported a seed-mediated method for the synthesis of Au-seed Ag-growth nanoparticles of controllable diameter (50–150 nm) as effective SERS substrates. The process verified that Ag NPs exhibited at least two orders of magnitude greater SERS enhancement than Au NPs. On the one hand, the method solved the uncontrolled problem of Ag substrates; on the other hand, it provided a new idea to synthesize excellent SERS substrates.

Natural enzymes are of great significance for the fields of environment [6], biology [7], medicine [8] and industry [9], because of their high catalytic efficiency and wide range of application. With the development of nanotechnology, artificial nanozymes are widely used to take the place of natural enzymes, simultaneously breaking the limitation of environmental conditions, such as temperature [10], acid-base property [11] and stability [12]. Therefore, artificial nanozymes and comparison of their catalytic activities have become the hottest areas these years. For instance, Hu et al. [13] assembled glucose oxidase (GOx) and lactate oxidase (LOx) onto AuNPs@MIL-101 to form AuNPs@MIL-101@GOx and AuNPs@MIL-101@LOx integrative nanozymes for in vitro detection of glucose and lactate via SERS. Moreover, the integrative nanozymes were further explored for monitoring slight variation of glucose and lactate in living brains, which are associated with ischemic stroke.

Over the past years, the reported enzyme-like activities included the peroxidase-like activity, superoxide dismutase-like activity, catalase-like activity, and so on. For example, Qu and coworkers [14] firstly demonstrated that carboxyl-modified graphene oxide (GO-COOH) exhibited intrinsic peroxidase-like activities, which could catalyze the oxidation of a typical peroxidase substrate of 3,3′,5,5′-tetramethylbenzidine (TMB) with the addition of H_2O_2. Lu [15] synthesized yolk-shell nanostructured Fe_3O_4@C nanoparticles with an intrinsic peroxidase-like activity that could quickly catalyze the enzyme substrate in the presence of H_2O_2 and produce a blue color. However, there were relatively few reports about glucose oxidase (GOx)-like activities. In 2004, Rossi et al. [16] firstly discovered that the "naked" gold nanoparticles (Au NPs) synthesized without protectors or stabilizers had GOx-like activities. Nowadays, it has become an undenied fact that gold nanoparticles (Au NPs) without protectors have glucose oxidase (GOx)-like activities, but the use of protectors which may inhibit GOx-like activities influence the application of Au NPs. Yao et al. [17] developed a SERS strategy for analysis of glucose based on the Nanosilver-H_2O_2-TMB system. Ag nanoparticles not only showed strong SERS activities, but also showed high peroxidase-like activities. Recently, Han's group [18] reported the GOx-like activities of Au@BSA NPs with different sizes, and found a two-step analytical approach that Au@BSA NPs and glucose was incubated in air and then the product H_2O_2 was detected by the oxidation of TMB. Interestingly, Au@BSA NPs showed the dual enzyme-like activities (GOx-like and peroxidase-like activities) at the same pH. So, Au@BSA can be described as "tandem nanozyme".

So far, there is no paper about SERS quantitative study for glucose based on the new and sensitive SERS two-step reaction to form oxTMB molecular probe.

In this work, we discovered that multifunctional Au@Ag NPs not only showed enhanced peroxidase-like activities, but also showed glucose oxidase (GOx)-like activities. So, Au@Ag NPs could be described as "tandem nanozyme", too. Au@Ag NPs with controlled sized were synthesized through a facile seed-mediated method, and then used in the two-step analytical approach to verify tandem enzyme-like activities. The two-step approach was as followed: Firstly, the glucose and H_2O were catalyzed by Au@Ag NPs to produce glucose acid and H_2O_2. Secondly, colorless TMB could be catalyzed by Au@Ag NPs to produce blue oxTMB in the existence of H_2O_2, then the Au@Ag NPs were surrounded with the generated oxide oxTMB whose molecules exhibit three SERS peaks at Raman shifts of 1188, 1330, 1605 cm-1. oxTMB showed the highest SERS activities on the occasion of 633 nm excitation wavelengths. Thus, one-pot enzyme-free strategy based on sole nanozyme Au@Ag NPs greatly promoted the catalytic process and products, and analyze the amount of glucose by Surface-enhanced Raman spectroscopy.

2. Experimental section

2.1. Materials and reagents

Sodium citrate, ascorbic acid, silver nitrate and chloroauric acid ($HAuCl_4$) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 3,3′,5,5′-tetramethylbenzidine (TMB), 30% hydrogen peroxide (H_2O_2), glucose and different buffers: glycine-HCl buffer (pH 1.0–2.0), acetate buffer (pH 3.0–5.0), and phosphate buffer (pH 6.0–8.0) were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China). All chemicals were used without further purification.

2.2. Apparatus

Scanning electron microscopy (SEM, Hitachi S4800) was employed to characterize the morphology and microstructures of the samples. Absorption spectra were obtained on a UV-2600 spectrophotometer (Shimadzu, Japan). Raman spectroscopy (LabRam HR Evolution) were recorded to obtain Surface-Enhance Raman Spectroscopy activities.

2.3. Synthesis of Au@Ag NPs

Fig. S1 (Supporting Information) illustrated the procedure to prepare Au@Ag nanoparticles by seed growth method. Au seeds of 16 nm were prepared according to the Frens' method. In short, two solutions were prepared: $HAuCl_4$ (0.01 wt%, solution I) and sodium citrate (1 wt%, solution II). Brought 50 mL solution I to the boil, and then quickly added 0.50 mL solution II. In about 25 s, the boiling solution would turn faintly blue, and the blue would suddenly turn bright red after approximately 70 s. In addition, the solution was boiled for 15 min to complete the reduction of Au NPs.

$AgNO_3$ was reduced on the surface of Au seed by ascorbic acid, at the same time using sodium citrate as stabilizer. Firstly, added 20 mL of water to a 100 mL round-bottomed flask. Secondly, 1 mL 16 nm Au seeds solution, 1 mL 1 wt% sodium citrate and 3 mL 20 mmol L^{-1} ascorbic acid were added. Stirred the mixture at room temperature for 5 min. Then the sols were heated in a water bath at 40 °C for 15 min. After that, 800 μL 10 mmol L^{-1} $AgNO_3$ was dripped into the mixture at a rate of 0.08 mL/min while vigorously stirring the three mixtures and keeping the temperature at 40 °C. After adding $AgNO_3$, the sols were held in a water bath at 40 °C for another 30 min. In this way, we got Au seed Ag-growth NPs with size of 50 nm. In order to synthesize Ag NP with other sizes, the amount of ascorbic acid and $AgNO_3$ seed was correspondingly increased or decreased.

2.4. Catalytic activities of Au@Ag NPs

The peroxides-like activity of Au@Ag NPs was performed according to the following procedures: At first, 5 μL of Au@Ag NPs were added to 30 μL of NaAc buffer (pH 4.0) solution containing 10 μL TMB and 10 μL H_2O_2 (30%). After the mixture was incubated in a 60 °C water bath for 10 min, Au@Ag NPs were then quickly transferred to a capillary tube and measured by SERS at 633 nm under optimal conditions. In the experiment of the effect

of pH on the catalytic activities of Au@Ag NPs, buffer solutions with different pH values (2.0–8.0) were used. In order to study the effect of temperature on peroxides-like activities, experiments were carried out from 20 °C to 80 °C in the 20 °C interval under the same conditions.

The tandem enzyme-like activities of Au@Ag NPs was performed according to the following procedures: At first, 5 μL of Au@Ag NPs were added to 30 μL of NaAc buffer (pH 4.0) solution containing 10 μL TMB and 10 μL 0.5 mol·L^{-1} Glucose. After the mixture was incubated in a 60 °C water bath for 10 min, Au@Ag NPs were then quickly transferred to a capillary tube and measured Raman spectra at 633 nm under optimal conditions. In the experiment of the effect of pH on the catalytic activities of Au@Ag NPs, buffer solutions with different pH (2.0–8.0) values were used. In order to study the effect of temperature on the peroxides-like activity, experiments were carried out from 20 °C to 80 °C in the 20 °C interval under the same conditions.

3. Results and discussion

3.1. Morphology characterization of Au@Ag NPs

Morphologies of Au@Ag NPs were observed by scanning electron microscope (SEM) (Fig. 1a-d). As shown in Fig. 1, the prepared Au@Ag NPs were nearly spherical and highly monodispersed. Each nanoparticle was an average diameter of 50 nm. In order to further study the chemical composition of Au@Ag NPs, the Au@Ag NPs were detected by EDS spectrum.

EDS spectrum can effectively analyze the content of the element contained in samples, Fig. 1e shows that the material is composed of two elements, Au and Ag, of which Au accounts for about 5.68% and Ag accounts for about 94.32%. The desired diameter of gold seed was about 16 nm, and the thickness of silver shell was about 34 nm. The content of gold and silver elements with the desired composition were similar with Ref. [6].

3.2. Discovery and comparison of the catalytic activities of Au@Ag NPs

Au@Ag NPs are able to oxidize TMB to a blue-colored product oxidized-TMB (oxTMB) in the presence of H_2O_2 (Fig. S2, Supporting Information). To verity the peroxidase-like activities of the as-prepared Au@Ag NPs, the catalytic reactions with hydrogen peroxide (H_2O_2), NaAc buffer, and 3,3′,5,5′-tetramethylbenzidine (TMB) as the substrates have been assayed.

As shown in Fig. S3 (Supporting Information), there was an obvious absorption peak at 650 nm that originates from the oxidation of TMB, proving that Au@Ag NPs had intrinsic peroxidase-like activities. At the same time, the Nanoparticle-TMB-H_2O_2 reaction system turns blue, owing to produce an oxidic product, while no color reactions occurred in the control systems. Furthermore, the nanoparticles revealed a dominant advantage in catalytic behaviors. They gave a 400% response, comparing with the case in the absence of Au@Ag NPs. From the above, it proved that Au@Ag NPs showed their excellent peroxidase-like activities in the Nanoparticle-TMB-H_2O_2 reaction system.

To verify the GOx-like activity of Au@Ag NPs, a reaction system consisting of Au@Ag NPs, TMB, and glucose was incubated in the air (Fig. S4, Supporting Information). As shown in Fig. 2b, in the reaction solution containing Au@Ag NPs, oxTMB has an obvious absorption peak at 650 nm, which proves that Au@Ag NPs have significant GOx-like activity. In this reaction system, H_2O_2 is not added, so the peroxidase-like reaction starts from the GOx-like reaction to produce H_2O_2. The whole procedure involved two steps: first, glucose and O_2 were catalyzed by Au@Ag NPs to produce glucose acid and H_2O_2. Secondly, H_2O_2 and TMB were catalyzed by Au@Ag NPs to produce oxTMB and H_2O. What is interesting is that Au@Ag NPs play a role of GOx-like activity in the first step, and play a role in peroxidase-like activity in the second step. This reaction system can prove both the GOx-like activity of Au@Ag NPs and its tandem enzyme activity. In summary, Au@Ag NPs have tandem enzyme activities, namely peroxidase-like activity and GOx-like activity. Compared with the previous reported glucose analysis method, what's the different is that, with the absence of H_2O_2, nanoparticle-glucose-TMB reaction system in this research can still promote the detection process.

Taken together, Au@Ag NPs had dual enzyme-like activities (GOx-like and peroxidase-like activities), so Au@Ag NPs were one of the tandem enzymes as well. By contrast, Han [19] had successfully synthetized a unique nanozyme, which had the similar pH range of dual enzyme activities. So, Au@Ag NPs could be called as "tandem nanozyme," which could simultaneously catalyze the cascade reactions, and dual enzyme-like activities could be called "tandem enzyme-like activity".

Fig. 2 indicated that the UV–Vis spectrum of oxTMB had the largest absorption peak at 650 nm. However, whatever Nanoparticle-H_2O_2-TMB or Nanoparticle-Glucose-TMB system, there was no significant absorption peak at lower concentrations. The detection limit of the two systems are 0.01 mol L^{-1} H_2O_2 and 5×10^{-3} mol L^{-1} glucose. Raman spectroscopy has the advantages of higher sensitivity and higher limitation. So, we changed to get SERS signals.

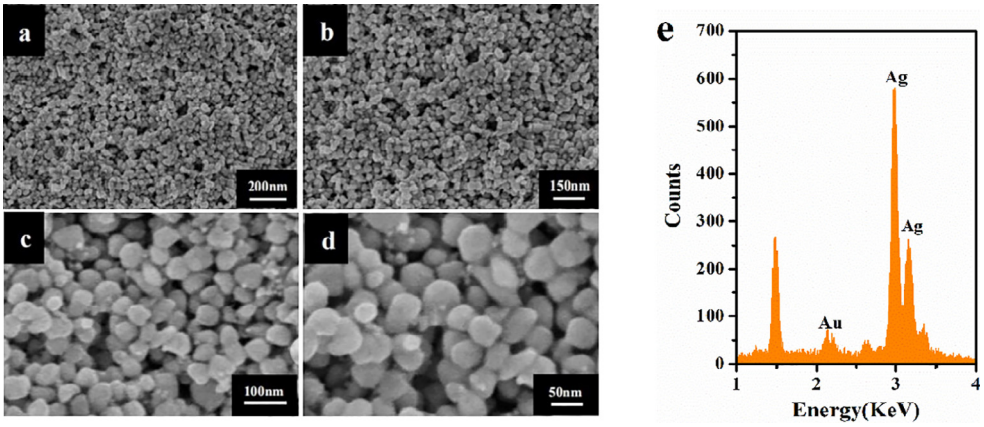

Fig. 1. SEM image spectrum of Au@Ag NPs nanoparticles with different magnification, (a) 25 k, (b) 50 k, (c) 100 k, (d) 200 k, (e) EDS energy spectrum.

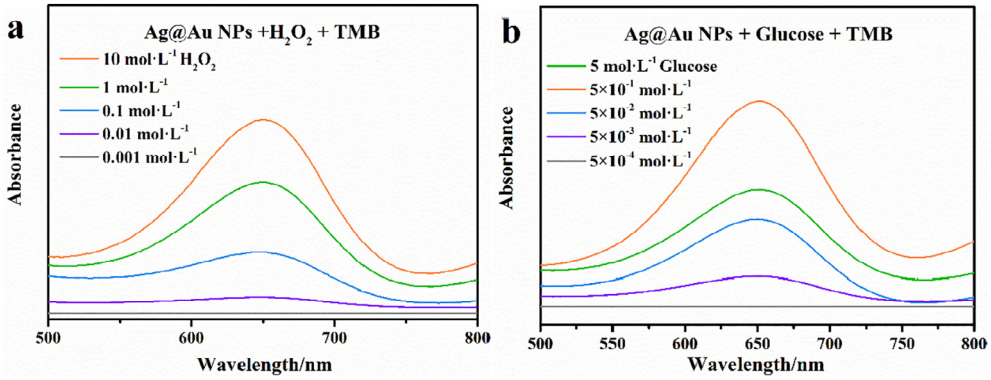

Fig. 2. UV–vis absorption spectra of (a) the Nanoparticle-H_2O_2-TMB system, (b) the Nanoparticle-Glucose-TMB system.

3.3. Optimization of enzyme-like activities

Like other artificial enzymes, pH and temperature have an effect on the enzyme-like activities. Thereupon, to further characterize the peroxidase-like and tandem enzyme-like activities of Au@Ag NPs, we respectively studied the effect of variation of experimental conditions on dual enzyme-like activities by SERS. Firstly, pH optimization (1.0–8.0) of buffer solution was conducted. Fig. 3a showed the SERS peaks of oxTMB oxidized by H_2O_2 in the presence of Au@Ag NPs at 1188, 1330 and 1605 cm^{-1}. Among them, the 1188 cm^{-1} Raman shift of SERS signal belonged to the C—N stretching vibration, the 1330 cm^{-1} Raman shift of SERS signal pertained to C—H stretching vibration, and the 1605 cm^{-1} Raman shift of SERS signal belonged to C=C stretching vibration. The result showed that SERS signal at 1188, 1330, and 1605 cm^{-1} were all sensitive. Therefore, these three Raman peaks were all used for the measurement of Nanoparticle-H_2O_2-TMB system. Each pH intensity was defined as the sum intensities of three peaks. Compared Fig. 3a with Fig. 3c, we concluded that H_2O_2 may get rise to the 1460 cm^{-1} Raman shift of SERS signal. Based on the system, the catalytic reaction of TMB with H_2O_2 was much faster in acid solution than in neutral or basic solutions (Fig. 3b). As the pH increased, the SERS intensity of the system increased in the pH range of 1–4, and then decreased in the pH range of 4–8. It was significant that, for the peroxidase-like activities, Au@Ag NPs based on the Nanoparticle-H_2O_2-TMB system showed the highest peroxidase-like activity on the condition of pH 4. Au@Ag NPs exhibited peroxidase-like activities at weakly acidic pH and remained more than 90% maximum activities in pH 2.0–5.0. These results in Fig. 3 demonstrated that Au@Ag NPs could be a good substitute for natural peroxides, such as HRP (Horse Radish Peroxidase).

On the other hand, for the tandem enzyme-like activity. Au@Ag NPs based on the Nanoparticle-Glucose-TMB system showed the highest tandem enzyme-like activities on the condition of pH 4, also kept more than 80% maximum activities in the pH range from 4 to 5. According to the above results, the peroxidase-like and GOx-like activities of Au@Ag NPs have overlapped optimal pH range. The previous reported that peroxidase-like activity worked at pH 4, while GOx-like activity worked at pH 7.4 [14]. The tandem enzyme-like activities demonstrated that individual optimal pH of peroxidase-like and GOx-like activities were different from the optimal pH of the tandem enzyme-like activity.

Secondly, varied temperature (20 °C-80 °C) dependent-activities of Au@Ag NPs was studied. The peroxidase-like and tandem enzyme-like activities were the highest at 60 °C. It increased in the temperature range from 20 °C to 60 °C, whereas decreased when the temperature over 60 °C. Hence, we can arrive a conclusion that optimized experimental conditions were under the following conditions of pH 4.0 and 60 °C Fig. 4.

3.4. Detection of glucose

Diabetes mellitus is a major public health problem [20], which can directly affect the daily life and the health of people. So far, many methods have been explored for the detection of glucose, such as fluorometry [21], spectrophotometry [22], chromatography [23], and electroanalysis [24]. As a common and commercial method, spectrophotometry has been widely used for clinical detection, where GOx and peroxidase are generally used as the catalysts of the colorimetric reaction.

Compared with spectrophotometry, Raman spectroscopy combines the advantages of shorter detection time, higher sensitivity, higher limitation, and higher surface selectivity. The signal peaks obtained by Raman are sharp, characteristic and can be easily screened out redundant peaks. Also, sample preparation is simple, without centrifugation and filtration. In our study, we could get significant SERS signals of each sample at lower concentrations in 30 s.

On the basis of tandem enzyme-like activity of the Au@Ag NPs, we developed a facile and label-free strategy for highly sensitive Surface-enhanced Raman Scattering detection of glucose, utilizing the blue color variation due to TMB oxidation. For the qualitative assay of glucose, the Nanoparticle-Glucose-TMB system was performed with different concentrations 5×10^{-10} to 5×10^{-3} mol L^{-1} of glucose. Fig. 5a showed the SERS intensity of oxTMB in the presence of Au@Ag NPs at 1188, 1330, and 1605 cm^{-1}, and the regular changes of blue color in the reaction solutions could be expediently observed by naked eye. The limit of detection (LOD) was 5×10^{-10} - mol L^{-1}, which was more sensitive than one-pot enzymatic assay (39 μmol·L^{-1}) [25]. As shown in Fig. 5b, SERS intensities at 1605 cm^{-1} had the best linear relationship with glucose concentrations from 5×10^{-7} mol L^{-1} to 5×10^{-3} mol L^{-1}. Then, the calibration curve was plotted (Fig. 5c). The regress equation was γ = 10395χ + 76402“ ”(R^2 = 0.996) with the liner rang of 5×10^{-7} - mol L^{-1} to 5×10^{-3} mol L^{-1}. In addition, the response time (30 s) was much shorter than that (more than 7 h) of the reported Au NPs-based enzyme-free assay method [12]. To further testify the feasibility, proposed Nanoparticle-H_2O_2-TMB system and the standard curve were used for the detection of glucose (about 5×10^{-3} - mol L^{-1}). The solution of glucose was diluted into the linear range of proposed method and the concentration of glucose was calculated to be 4.21 $\times$ 10^{-3} mol L^{-1} according to the standard curve, which was comparable with the result (5.02 $\times$ 10^{-3} mol L^{-1}) of glucose meter. The results showed that Au@Ag NPs had a huge potential to be a glucose sensor.

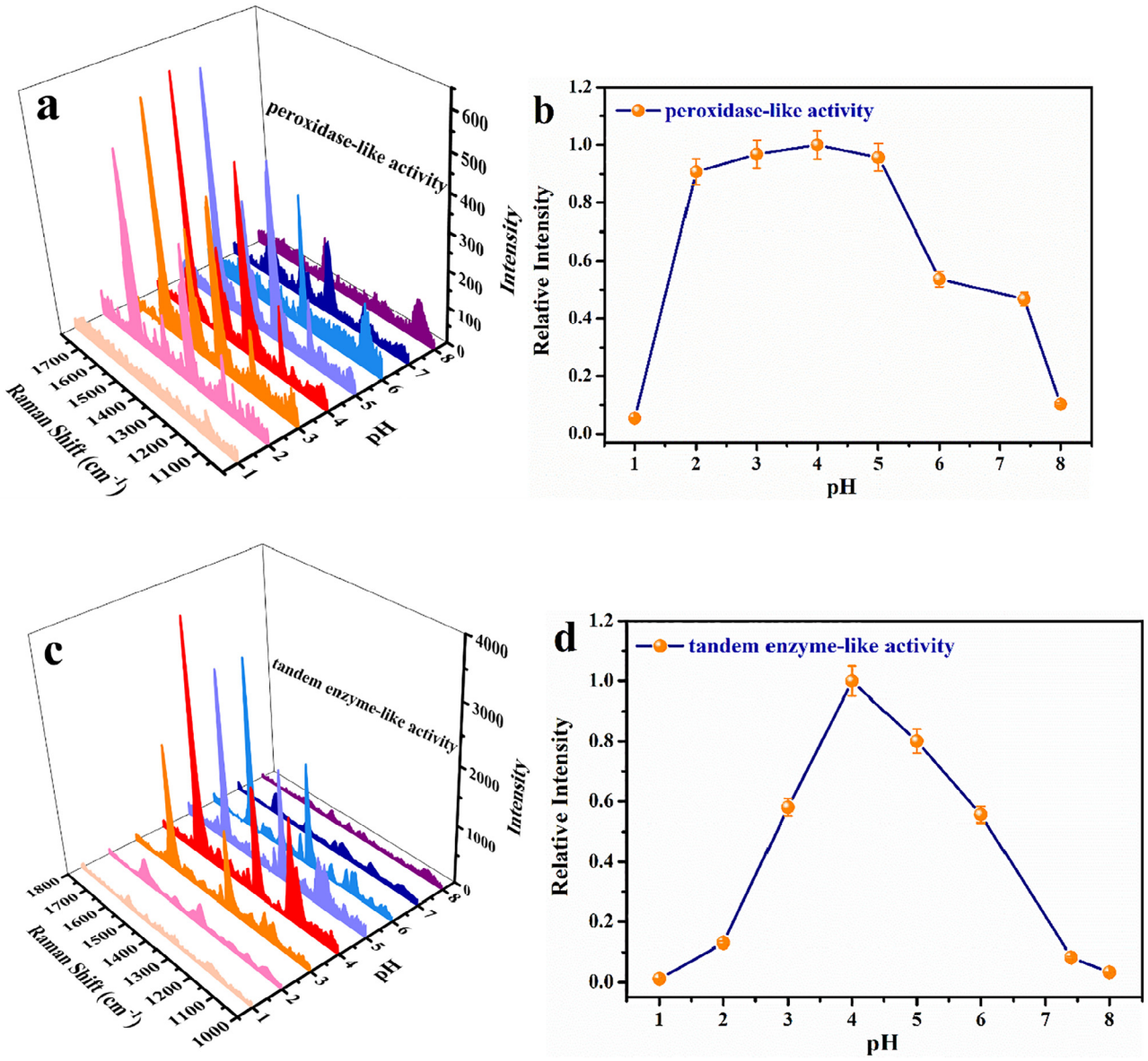

Fig. 3. pH optimization of enzyme-like activities, oxTMB was the SERS probe molecule, and its Raman characteristic peaks were at 1188, 1330 and 1605 cm^{-1}.(a) SERS spectra of peroxidase-like activities at different pH in the Nanoparticle-H_2O_2-TMB system, (b) The relative intensity of peroxidase-like activities of Au@Ag NPs at different pH, the highest point was defined as 100% of relative activities, (c) SERS spectra of tandem enzyme-like activities at different pH in Nanoparticle-Glucose-TMB system, (d) The relative intensity of the tandem enzyme-like activities of Au@Ag NPs at different pH, the highest point was defined as 100% of relative activities.

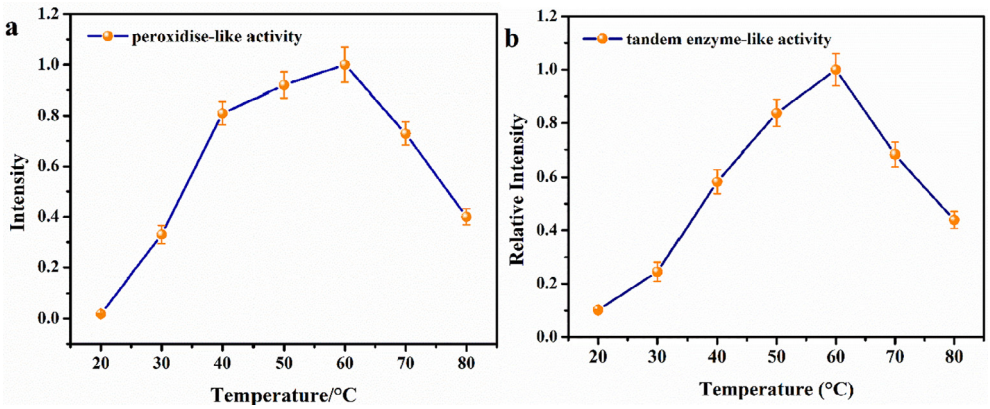

Fig. 4. (a) The relative intensity of peroxidase-like activities of Au@Ag NPs at different temperatures, the highest point was defined as 100% of relative activities, (b) The relative intensity of the tandem enzyme-like activities of Au@Ag NPs at different temperatures, the highest point was defined as 100% of relative activities.

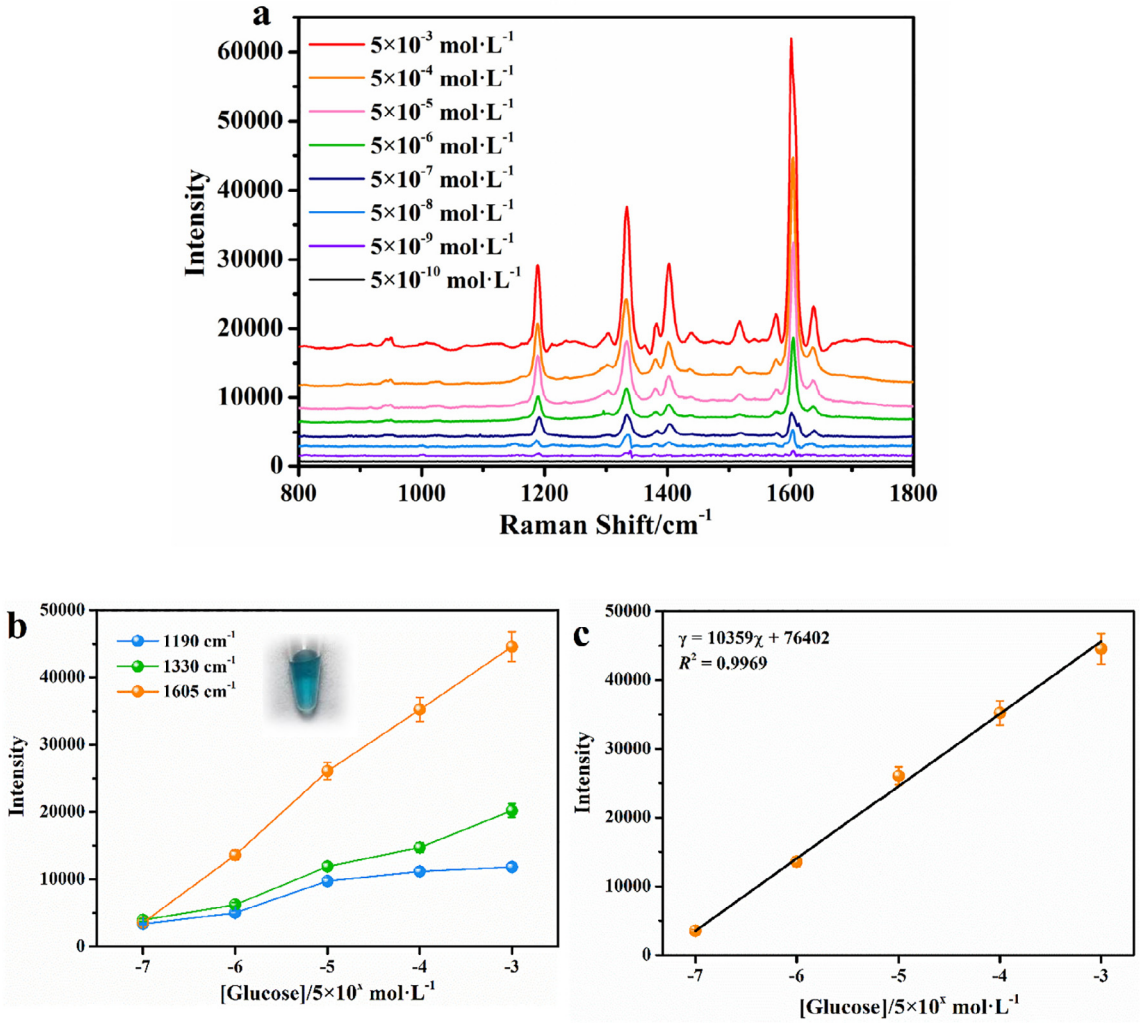

Fig. 5. (a) SERS spectra of different concentrations (5×10^{-10}–5×10^{-3} mol L^{-1}) of glucose based on Nanoparticle-Glucose-TMB system, (b) SERS intensities at 1190 cm^{-1}, 1330 cm^{-1}, 1605 cm^{-1} (5×10^{-7}–5×10^{-3} mol L^{-1}), (c) Calibration curve for glucose detection at 1605 cm^{-1}.

4. Conclusions

In summary, we have synthesized core-shell nanostructured Au@Ag nanoparticles utilizing seed growth method. Fortunately, Au@Ag NPs not only showed peroxidase-like activities, but also had GOx-like activities at the same pH. So, as-synthesized Au@Ag NPs could be called as "tandem nanozyme". Further, to maximize the advantages of tandem nanozyme activities, the optimized experimental conditions were pH 4.0, 60 °C. Based upon that, we developed a label-free, one-pot and nonenzymatic colorimetric method for glucose detection, where GOx and peroxidase were not generally used as the catalysts of the colorimetric reaction. Au@Ag NPs can be employed as an excellent substitute of the natural enzyme, such as HRP and GOx. Au@Ag NPs not only broadens the species of tandem nanozymes, but also facilitates the functionalization of nanozymes with some molecules, such as antibody, enzyme, and fluorescence probe, which are promising for immunoassay, biosensor, and medical treatment.

CRediT authorship contribution statement

Xuemin Xia: Conceptualization, Methodology, Software, Investigation, Writing - original draft. **Yijin Weng:** Validation, Formal analysis, Visualization, Software. **Lei Zhang:** Resources, Writing - review & editing, Supervision, Data curation. **Ruyi Tang:** Resources, Writing - review & editing, Supervision, Data curation. **Xia Zhang:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.saa.2021.119889.

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