



Synthesis of stabilizer-free gold nanoparticles by pulse sonoelectrochemical method

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ABSTRACT

In this paper, stabilizer-free gold nanoparticles (Au NPs) were synthesized by a facile pulse sonoelectrochemical method in the absence of stabilizer. The size and shape of the Au NPs can be controlled by adjusting current density, reaction time and the pH value of the precursor solution. The morphology and structure of the Au NPs were characterized by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), UV–visible spectra (UV–vis), energy-dispersive X-ray (EDX) and X-ray diffraction (XRD). The pH value has a great effect on the size and dispersion of the obtained Au NPs. The Au NPs could further used as substrate for fabrication of HRP biosensor which exhibited excellent biocatalytic activity with high sensitivity and rapid response. This method provides a facile route for the synthesis of stabilizer-free Au NPs. Since the preparation process do not need the addition of any surfactants/capping agent, the resulting Au NPs are suitable for the applications in fields of biology and catalysis.

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1. Introduction

As one kind of the most extensively studied nanomaterials, gold nanoparticles (Au NPs) have received increasing attention because of their distinctive physical and chemical properties and their widely applications in optics [1,2], electronics [3,4], catalysis [5,6], biology [7–9], sensors and biosensors [10,11], and other domains [12,13].

In 1857, Faraday reported the preparation of Au NPs by the reduction of an aqueous solution of chloraurate (AuCl_4^-) using phosphorus [14], representing the first documented preparation of Au NPs. Since then, various methods for the synthesis of Au NPs have been developed, such as chemical reduction method [15], sonochemical method [16], electrochemical method [17–19], X-ray irradiation [20], laser ablation [21], annealing from high-temperature solutions [22], metal evaporation [23], Ar^+ ion sputtering [24], etc. Among them, electrochemical method has been proven to have some distinct advantages in the synthesis of size-selective or shape-controlled Au NPs [17–19], such as ease of operation, high yield, absence of side products, and easily controlled size and shape of Au NPs by adjusting the applied potential or the current. The notable features of this method make it can be widely applied in the synthesis of various metallic nanomaterials.

Pulse sonoelectrochemical method, which combines sonochemistry and electrochemistry, has been proven to be a simple, fast and

effective route for the shape-controlled synthesis of various nanomaterials [25–31]. The method is accomplished by applying an electric current pulse to nucleate and perform the electrodeposition, followed by a burst of ultrasonic wave to remove the products from the sonic probe cathode. It possesses the advantages of pulse electrodeposition and ultrasonic, and the shape and size of the obtained nanomaterials could be controlled by simply adjusting various parameters such as current density, time of deposition and sonication, temperature, and shape-controlling agents. Furthermore, with the termination of electric current, the obtained NPs could not grow up due to the absence of reduce reagent in the reaction solution. Liu et al. have synthesized Au NPs by a modified sonoelectrochemical method [32]. In their work the bulk gold substrate was served as the sacrificial anode to obtain gold-containing complex solution. Then the bulk gold substrate was replaced by a Pt electrode, and a cathodic overpotential was applied under sonication to synthesize Au NPs. It should be pointed out that this method is not very ideal. First, the gold precursor is the gold-containing complex which was obtained from the oxidation of the bulk gold substrate. Second, the working electrode must be replaced, which led to the relative complicated operation and the low production. In addition, Au NPs have been synthesized using sonoelectrochemical method in the presence of some stabilizers, which were needed to avoid the aggregation of Au NPs [31,33]. However, the stabilizers can reduce AuCl_4^- ion at ultrasonic condition, probably due to the thermal decomposition that occurs at the interfacial region between cavitation bubbles and bulk solution and provides reducing radicals [16]. It indicates that in those sonoelectrochemical procedures, the stabilizers may also act as

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reductant for the reduction of AuCl_4^- ion. Therefore, developing the sonoelectrochemical method to synthesize Au NPs in absence stabilizers is still a great challenge and has been rarely concerned.

Here, we report the synthesis of stabilizer-free Au NPs by a simple, clean and fast pulse sonoelectrochemical method without using reductant and stabilizer. The prepared Au NPs exhibit good colloidal stability explained by the electrostatic stabilization effect of OH⁻ groups, and provides a well biocompatible surface for enzyme loading. Horseradish peroxidase (HRP) was immobilized on the Au NPs and fabricated a good biosensor response to H_2O_2 . This method may open a general approach for the synthesis of noble metal nanomaterials.

2. Experimental section

2.1. Materials

Hydrogen tetrachloroaurate tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), potassium nitrate (KNO_3) and sodium hydroxide (NaOH) were purchased from Chinese Shanghai Regent Co. Hydrochloric acid (HCl , 36–38%) was obtained from Nanjing Chemical Reagent Co., Ltd. All solutions were prepared with de-ionized water (18.2 M Ω cm, Millipore, Milli-Q, MA, USA).

2.2. Sonoelectrochemical setup

The pulse sonoelectrochemical device employed in our experiments has been described elsewhere [25–31]. In brief, a titanium horn (ultrasonic liquid processor VC-750, 20 kHz, Sonics & Materials) acts both as the cathode and the ultrasound emitter. The electroactive part of the sonoelectrode is the planar circular surface with an area of 1.23 cm² at the bottom of the horn. The immersed cylindrical part is covered by an isolating plastic jacket. A CHI6301B electrochemical workstation (CH Instruments Co., USA) is operated in the pulse current regime without using a reference electrode. A platinum sheet (1.0 cm $\times$ 1.0 cm) is used as a counter electrode. The sonoelectrode produces a sonic pulse that is triggered immediately following a current pulse. The pulse width of the current was 0.5 s. The resting time of the current pulse was 0.5 s, and the duration of the ultrasonic pulse was 0.5 s.

2.3. Sonoelectrochemical synthesis of Au NPs

First, 2 mL of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (24.3 mM) solution and 1 mL of KNO_3 (1.0 M) solution were added into 60 mL water while stirring. Then, the pH value of the solution was adjusted to 10 with NaOH solution (0.1 M). The Au NPs were produced with a current intensity of 20 mA ($\sim 16.3 \text{ mA} \cdot \text{cm}^{-2}$), an ultrasound intensity of approximately 20 W, and a reaction time of 1.5 h. After the reaction, the resulting wine red solution was purified by centrifugation, and the precipitate was washed with de-ionized water for several times and then dried in air.

Because of the absence of reduce agent in the Au NPs solution, the obtained Au NPs were sufficiently stable in water, even after storage at room temperature for several weeks. Various reactions were carried out with different current densities and pH values.

2.4. Characterization

The TEM images were recorded on a FEI Tecnai-12 transmission electron microscope with an accelerating voltage of 120 kV. HRTEM images were taken using a JEOL 2010 electron microscope at an accelerating voltage of 200 kV. Samples for TEM and HRTEM were prepared by placing two drops of the dispersed Au NPs solution on a carbon film coated copper grid (400 mesh), and then dry-

ing under air. Wide-angle powder X-ray diffraction (XRD) patterns were obtained with a Philips X'pert Pro X-ray diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$). The UV–vis spectra of Au NPs were recorded by a Shimadzu UV-3600 spectrophotometer. The surface charge of Au NPs dispersions was measured by a PALS Zeta Potential Analyzer (Brookhaven Instruments Co., USA).

2.5. Fabrication of the biosensor

The working electrode was made of glassy carbon electrode (GCE, diameter: 3.0 mm) that was polished successively with 1.0, 0.3, and 0.05 μm alumina powder and rinsed thoroughly with de-ionized water between each polishing step. Next, the polished electrode was sonicated in acetone and de-ionized water and then allowed to dry at room temperature. The Au/GCE was fabricated by casting 5 μL of Au NPs suspension (1 mg/mL) onto the surface of the pretreated GCE with a microsyringe. The solvent was allowed to evaporate at room temperature before use. HRP was assembled on Au by incubating the Au/GCE electrode in the HRP solution (5 mg/mL in PBS, pH 7.0) at 4 °C for 5 h. The electrode (denoted as HRP-Au/GCE) was then thoroughly rinsed with water, left to dry and stored at 4 °C when not in use. Amperometric and cyclic voltammetric experiments were performed using a three-electrode system on an Autolab PGSTAT-30 potentiostat/galvanostat (Eco Chemie BV, The Netherlands).

3. Results and discussion

3.1. Characterization of the Au NPs

Fig. 1 shows the TEM images of the obtained Au NPs. As shown in Fig. 1a, the uniform spherical Au NPs with a diameter of about 20 nm were obtained in aqueous solution without any surfactants and capping agents. In the HRTEM image (Fig. 1b), it can be clearly seen that the marked interplanar d spacing is 0.23 nm, which corresponds to that of the (111) lattice planes for face-centered cubic (fcc) gold.

The XRD pattern of Au NPs (Fig. 2a) reveals that the products possess cubic structure with a high crystallinity. The four major peaks can be indexed to the (111), (200), (220), and (311) planes of the fcc lattice of Au (JCPDS Card No. 04–0784), respectively. The peak broadening is consistent with the nanoscaled structural features of Au NPs. The mean size of the nanocrystals can be calculated from the peak width at half-maximum by using the Scherrer formula [34]. The particle size obtained from the width of the (111) reflection is about 18.5 nm, which matches well with the result from the TEM image ($\sim 20 \text{ nm}$).

The chemical composition of the obtained Au NPs was determined by EDX analysis. In the EDX spectrum (Fig. 2b), except for the copper and carbon signals from the TEM grid, only peaks of Au are observed, indicating that the obtained NPs are exclusively composed of Au.

3.2. Influence of pH value

The pH value was found to have an important effect on the size and dispersion of the obtained Au NPs. Fig. 3 shows the TEM images of Au NPs prepared in aqueous solution with the different pH values. When the pH was 4, the agglomerated Au NPs with a diameter in range of 20–100 nm were obtained (Fig. 3a). As the pH was increased to 7, the obtained Au NPs were also aggregated (Fig. 3b), and the size was in the range of 10–50 nm. In solution of pH 10, uniform Au NPs with a diameter of $\sim 20 \text{ nm}$ were produced (Fig. 3c). With the pH value was continuously increased to 12, the Au NPs with a polyhedral shape were obtained (Fig. 3d).

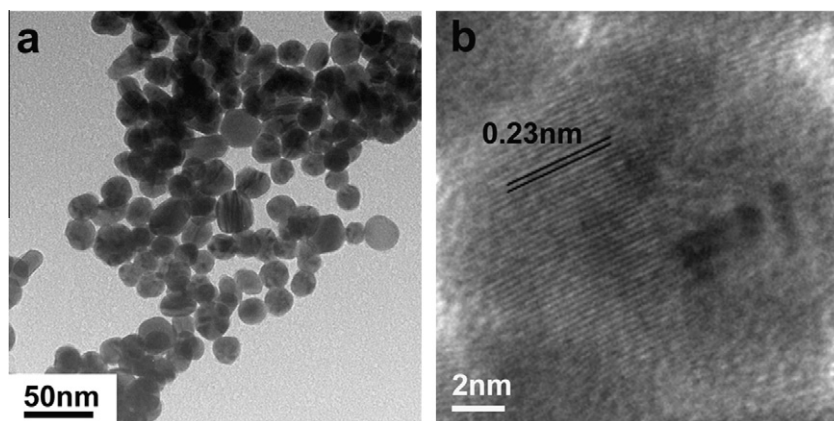


Fig. 1. (a) TEM and (b) HRTEM image of the Au NPs synthesized by sonoelectrochemical method without surfactant (pH 10, $I = 10$ mA, $t_{\text{current}}/t_{\text{sono}} = 0.5$ s/0.5 s).

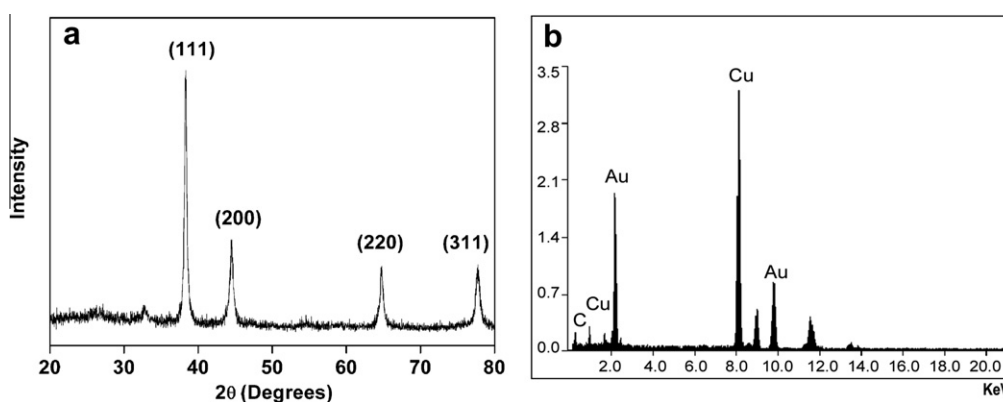
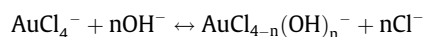


Fig. 2. (a) XRD pattern and (b) EDX spectrum of the Au NPs synthesized by sonoelectrochemical method.

The effect of pH value on the size and dispersion of the Au NPs was also investigated by the UV–vis absorption spectroscopy. Fig. 4 shows the UV–vis absorption spectra of Au NPs solutions at different pH values (4, 7, 10, and 12). The characteristic absorption peak due to the surface plasmon resonance (SPR) of Au NPs [35] was found at 523.0 nm for pH 10 (curve a). The narrow and symmetric absorption peak reveals that the product has a rather uniform size distribution. As for pH 12 (curve d), two absorption peaks at 542.5 nm and 715.5 nm was observed. The two different wavelengths of SPR absorption peak are due to the existence of two different Au NPs shapes, which is in agreement with the TEM image (Fig. 3d). For pH 4 and 7, only broad peak was observed at 556.5 nm and 550.2 nm, respectively. The aggregation and size increase of Au NPs lead to the red shift and broadening of the SPR absorption peak (curve b, c).

In addition, it should be noted that as the pH value was decreased to 2 with the addition of HCl solution, no products could be obtained, suggesting that the Au^{3+} ion can not be electrically reduced at this pH value. There are two reasons for this. First, there are more Cl^- anions which coordinate with Au^{3+} , and thus inhibit the electroreduction of Au^{3+} . Second, the H^+ ions are more easily to be electrically reduced at a lower pH value, and the production of Au NPs is seriously inhibited. When the pH value of precursor solution is increased by adding NaOH, the Cl^- complex anion can be partly replaced by OH^- . These processes can be represented by the following equation [19,20,36]



The different pH values of Au solution resulted in the different forms of Au complex, therefore, leading to the different redox potential and the reduction rate of gold. Fig. 5 shows the cyclic vol-

tammograms of the precursor solutions with different pH values. It can be clearly seen that as the pH value is increased, the reduction peaks of different Au complex shift obviously to a more negative potential. It reveals that the electrodeposition of Au is highly sensitive to the pH value.

The pH value of the precursor solution has a great effect not only on the size and shape of the Au NPs, but also has on the dispersion of the Au NPs. As we can see, well dispersed Au NPs can be synthesized in the basic condition (pH 10 and 12, Fig. 3c and Fig. 3d). The surface potential of the Au NPs under the condition of pH 10 was -54.65 mV as measured using a Zeta Potential Analyzer. This indicates that the OH^- groups adsorbed on the Au NPs surfaces cause the electrostatic repulsion between NPs and thus prevent the aggregation of Au NPs.

3.3. Influence of current intensity

The influence of current intensity on the size and shape of Au NPs was also studied. Fig. 6 shows the UV–vis spectra of Au NPs at different current intensities (5 mA, 10 mA, 20 mA, 40 mA). It can be seen that the UV–vis spectra of the different Au NPs at different current intensities are very similarly, indicating that the shape and size of these Au NPs are same. Therefore, the current intensity has little effect on the shape and size of Au NPs in the range of 5–40 mA.

3.4. Influence of pulse time of current/sonication

The pulse time of the current has a great effect on the shape and size of the product. Fig. 7 shows the TEM images of the Au NPs at

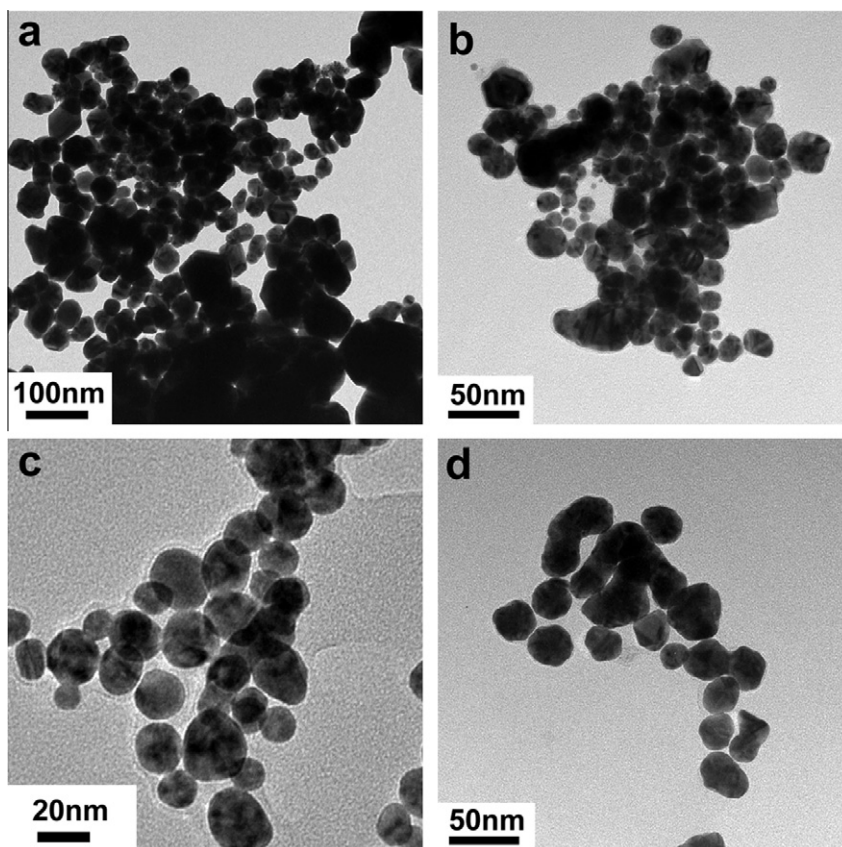


Fig. 3. TEM images of the Au NPs synthesized by sonoelectrochemical method at different pH values. (a) pH 4, (b) pH 7, (c) pH 10, (d) pH 12.

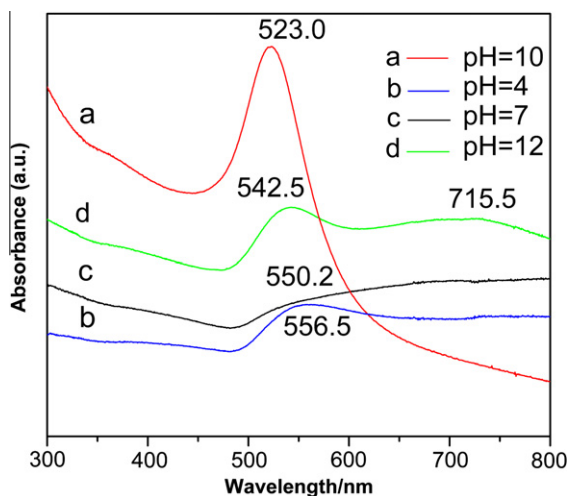


Fig. 4. The UV-vis spectra of the Au NPs synthesized by sonoelectrochemical method at different pH values. (a) pH 10, (b) pH 4, (c) pH 7, (d) pH 12.

different pulse times ($t_{\text{current}}/t_{\text{sono}}$: 0.3 s/0.3 s, 0.4 s/0.4 s, 0.5 s/0.5 s and 1.0 s/1.0 s) under the condition of $I = 10$ mA, and pH 10.

From Fig. 7a, it can be seen that, at the pulse time of $t_{\text{current}}/t_{\text{sono}}$: 0.3 s/0.3 s, the product are Au NPs with a diameter of ~ 10 nm and a few of bigger Au NPs (~ 30 nm). The reason is that as the pulse time is shorter, the Au NPs formed on the sonoelectrode is smaller. While few of the small Au NPs are attached on the electrode tightly, and grow up until they are removed by the sonication. When the pulse time is increased to $t_{\text{current}}/t_{\text{sono}}$: 0.4 s/0.4 s, the particle size is increased to ~ 20 nm (Fig. 7b). It

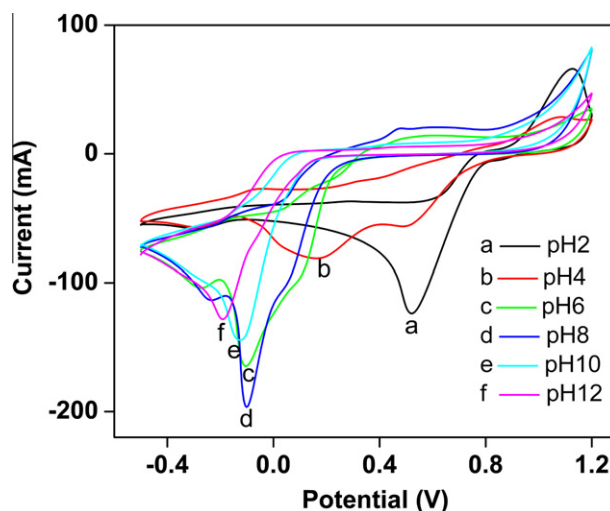


Fig. 5. Cyclic voltammograms of the precursor solutions with different pH values.

means that the size of Au NPs is increased with the increasing of the pulse time of current. From Fig. 7c, it can be seen that at the pulse time of $t_{\text{current}}/t_{\text{sono}}$: 0.5 s/0.5 s, uniform Au NPs with a diameter of ~ 20 nm are obtained. With the pulse time is increased further to $t_{\text{current}}/t_{\text{sono}}$: 1.0 s/1.0 s, the particles grow up (20–50 nm) and aggregated together (Fig. 8d).

3.5. Influence of reaction time

In order to investigate the reaction process of the Au NPs synthesized by sonoelectrochemical method, the products at different

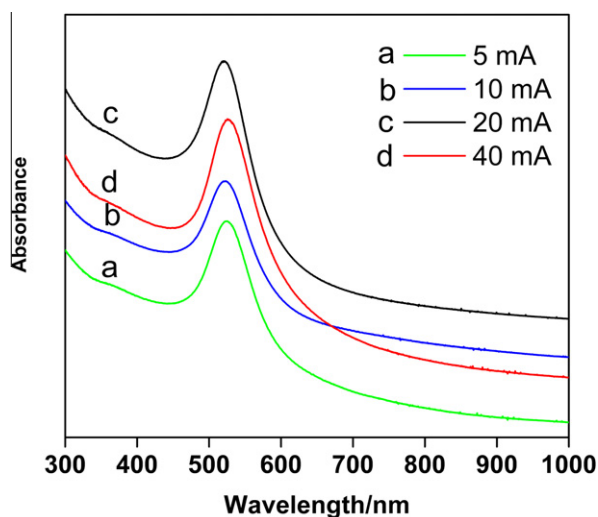


Fig. 6. UV-vis spectra of the Au NPs synthesized by sonoelectrochemical method at different current intensities. (a) 5, (b) 10, (c) 20, (d) 40 mA.

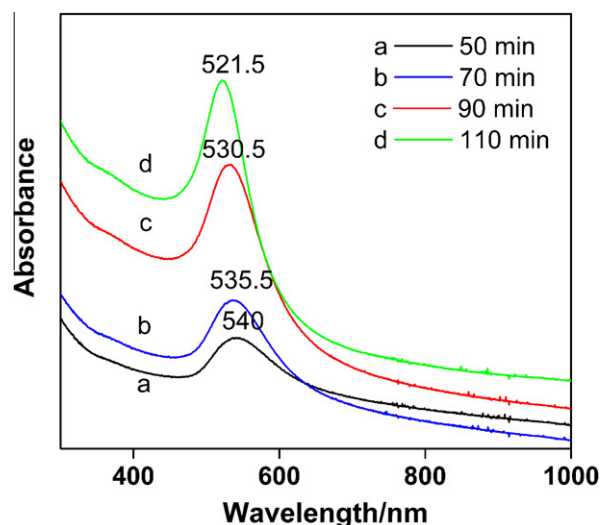


Fig. 8. UV-vis spectra of the Au NPs synthesized by sonoelectrochemical method at different reaction time. (a) 50 min, (b) 70 min, (c) 90 min, (d) 110 min.

reaction times were studied. Fig. 8 shows the UV-vis spectra of Au NPs at different reaction times under the condition of $I = 10$ mA, $t_{\text{current}}/t_{\text{sono}}: 0.5$ s/ 0.5 s and pH 10. The narrowing and blue shift of SPR absorption peak with the reaction time increased indicate a more uniform size distribution and the size decrease of Au NPs as the reaction time is increased. As in the early stage of reaction, the concentration of the precursor is higher, and thus the Au NPs with a large size were obtained. With the reaction continues, the concentration of the precursor is lowered down, and the smaller

Au NPs were obtained. The higher and higher percentage of the smaller sized Au NPs result in the blue shift of the SPR absorption peak.

The TEM images of the Au NPs at different reaction times are shown in Fig. 10. When the reaction time was 50 min, the Au NPs with a diameter of ~ 30 nm were obtained (Fig. 9a). At a reaction time of 70 min, the average diameter of the Au NPs was decreased to 25 nm (Fig. 9b). When the reaction time was prolonged to 90 min, the uniform spherical Au NPs with a diameter

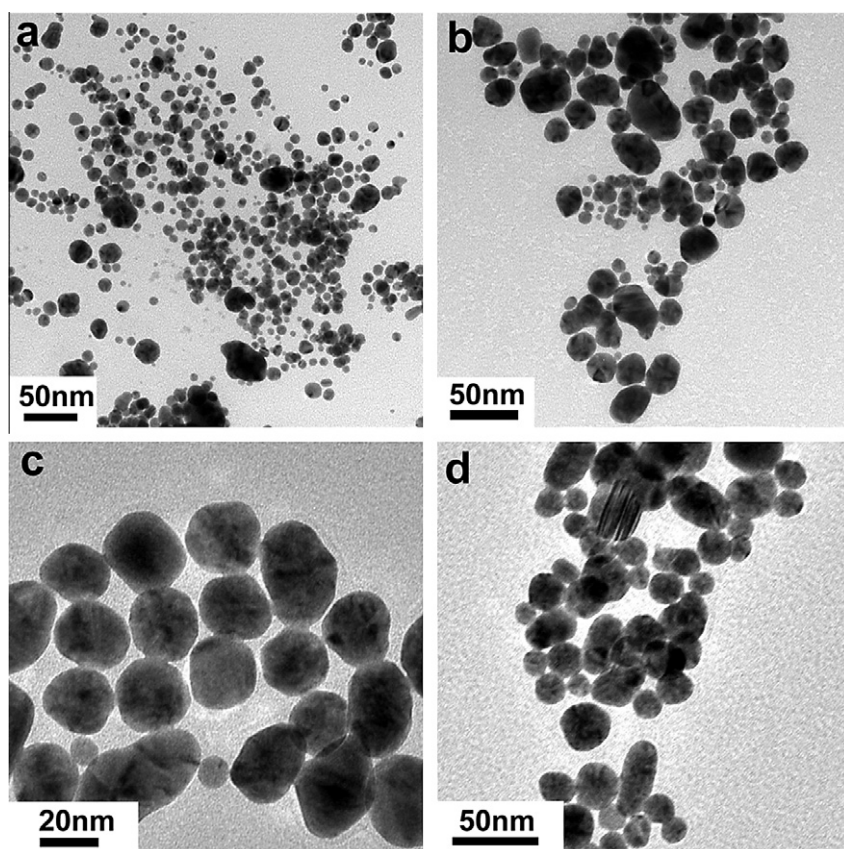


Fig. 7. TEM images of the Au NPs synthesized by sonoelectrochemical method at different pulse times ($t_{\text{current}}/t_{\text{sono}}$). (a) 0.3 s/ 0.3 s, (b) 0.4 s/ 0.4 s, (c) 0.5 s/ 0.5 s, (d) 1.0 s/ 1.0 s.

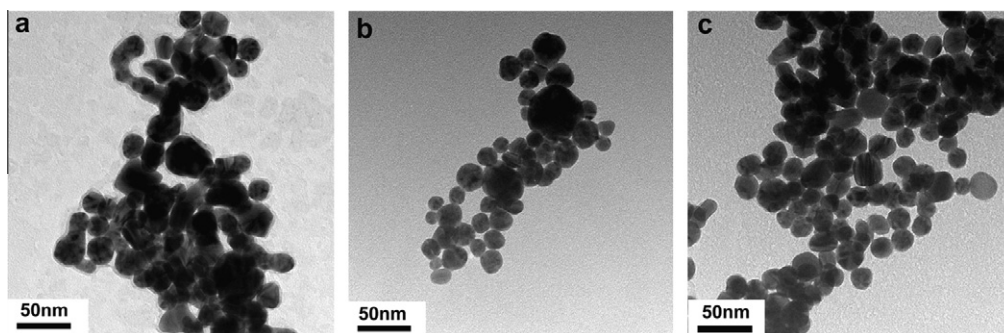


Fig. 9. TEM images of the Au NPs synthesized by sonoelectrochemical method at different reaction times. (a) 50 min, (b) 70 min, (c) 90 min.

of ~ 20 nm were obtained (Fig. 9c). These TEM image are consistent with the results of the UV–vis spectra.

3.6. Direct electrochemistry of the HRP-AuNPs

It is well known that the electrical contacting of redox enzymes with electrodes is the fundamental prerequisite for the development of electrochemical biosensors. Therefore, to decrease the electron transfer resistance between electrode surface and bioactive molecules is of the first importance. The stabilizer-free Au NPs make it a wonderful material for fabricating electrochemical biosensor. First, the stabilizer-free Au NPs supply a well biocompatible interface for enzyme immobilization and biosensor fabrication. In our experiment, HRP was used as a simple model enzyme to study the feasibility of using this material in bioelectroanalysis. With the PI at 8.8, HRP was positively charged at pH 7.0, and thus could easily assemble on this Au NPs because of electrostatic interactions and interactions between Au NPs and the amine groups of the enzyme [37]. Second, the connatural properties of Au NPs provide an excellent electron transfer between immobilized HRP and the electrode [38–40]. Here, HRP-Au NPs bioconjugates were fabricated in which HRP is directly assembled onto the stabilizer-free Au surface and applied to construct an amperometric hydrogen peroxide (H_2O_2) biosensor.

As is shown in Fig. 10, in pH 7.0 PBS, neither bare GCE (curve a) nor Au/GCE (curve b) showed any redox peaks. However, HRP-Au/GCE (curve c) displayed a pair of well defined redox peaks at $E_{pc} = -0.40$ V, $E_{pa} = -0.32$ V (vs. SCE), which were in accordance

with the characteristic of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox couples of heme proteins. The shapes of the reduction and oxidation peaks were nearly symmetric. Therefore, the stabilizer-free Au NPs provided a well biocompatible environment for HRP to orient the heme edge toward its electron donor or acceptor and facilitate its electron-transfer process [38–40].

To further investigate the bioactivity of immobilized HRP, we used this biosensor for the determination of H_2O_2 . Fig. 11 shows the CVs of the HRP-Au NPs modified electrode in pH 7.0 PBS with different H_2O_2 concentration. It can be seen that with increasing of H_2O_2 concentration, the reduction peak current of the modified electrode increased obviously, indicating that the HRP-Au NPs can act as a good catalyst for the reduction of H_2O_2 . Fig. 12 shows a typical amperometric response of HRP-Au/GCE on successive injections of H_2O_2 at -0.35 V. The time required to reach the steady-state response is within 2.5 s, shows good electron transfer efficiency. From the inset calibration curve of H_2O_2 concentration, we can conclude that the modified HRP-Au/GCE responses to H_2O_2 with a good linear dependence in a H_2O_2 concentration range from 0.025 to 1.975 mM. The detection limit is down to $0.5 \mu\text{M}$ estimated at a signal to noise ratio of 3. It is worth noting that when the biosensor was stored in a dry state at 4°C and measured every week, the current response for 0.1 mM H_2O_2 decreased by only about 7% of the original value after 28 days. The long lifetime of the biosensor may be attributed to the strengthened biocompatibility and stability of the stabilizer-free Au NPs.

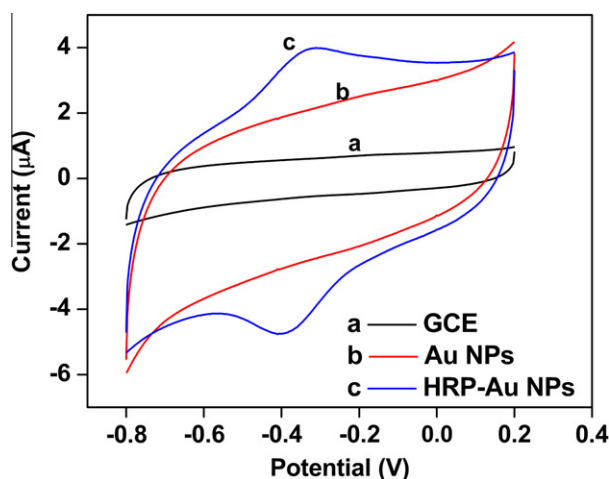


Fig. 10. Cyclic voltammograms obtained on (a) GCE, (b) Au/GCE, and (c) HRP-Au/GCE in 0.1 M PBS (pH 7.0) at 100 mV/s.

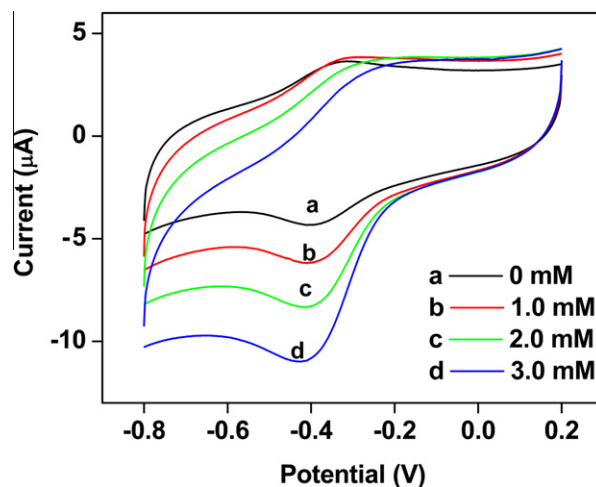


Fig. 11. Cyclic voltammograms of HRP-Au/GCE in different H_2O_2 concentrations (a) 0 mM, (b) 1.0 mM, (c) 2.0 mM and (d) 3.0 mM, respectively. Data were recorded in 0.1 M PBS (pH 7.0) at 100 mV/s.

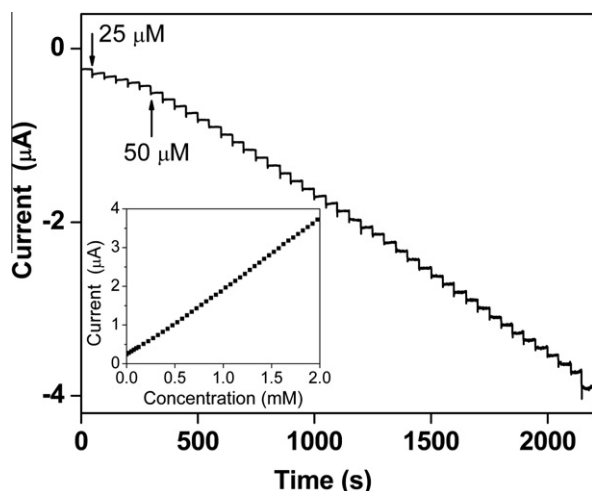


Fig. 12. Typical steady-state response of the HRP-Au/GCE on successive injection of different concentrations of H_2O_2 into 0.1 M PBS (pH 7.0) while stirring, with an applied potential of -0.35 V. The inset shows the calibration curve of H_2O_2 concentration at the HRP-Au/GCE.

4. Conclusion

In summary, a convenient, one-step sonoelectrochemical method was developed for the synthesis of Au NPs without adding a reductant or a stabilizer. The size and shape of the Au NPs can be easily controlled by adjusting the experiment parameter. Furthermore the Au NPs were used as built blocks for fabrication of HRP biosensor, which exhibited excellent biocatalytic activity with high sensitivity and rapid response. This simple approach can be a useful method for making Au NPs which can be used in the fields of catalysis, biology, and other related fields.

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