

Silver nanoparticles prepared in presence of ascorbic acid and gelatin, and their electrocatalytic application

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Abstract. In this paper, we reported a simple and low-cost procedure to synthesize silver nanoparticles (AgNPs) by using ascorbic acid as reducing agent and gelatin as stabilizer. The synthesized AgNPs were characterized by various means such as transmission electron microscope (TEM), powder X-ray diffraction (XRD) and energy-dispersive X-ray (EDX). TEM observations and XRD analysis demonstrated that the size of AgNPs is about 20 nm. Silver nanoparticles modified with carbon-paste electrode (AgNPs-CPE) displayed excellent electrochemical catalytic activities towards hydrogen peroxide (H_2O_2). The reduction overpotential of H_2O_2 was decreased significantly compared with those obtained at the bare CPE. The sensor responded linearly to hydrogen peroxide (H_2O_2) in the concentration of 10–350 μM , with detection limit of 5.6 μM at 3σ using amperometry. The studied sensor exhibited good reproducibility and long-term stability.

Keywords. Silver nanoparticles; gelatin; ascorbic acid; hydrogen peroxide.

1. Introduction

Nanocatalysis has recently been a rapidly growing field which involves the use of nanoparticles as catalysts for a variety of organic and inorganic reactions (Hernández-Santos *et al* 2002; Roucoux *et al* 2002; Widegren and Finke 2003). Ag nanoparticles show excellent catalytic and electrocatalytic activities (Jana *et al* 1999; Zhang *et al* 2005). For the past few years, various rapid chemical methods have been developed for the synthesis of silver nanoparticles (Shankar *et al* 2004; Panacek *et al* 2006). Reduction of AgNO_3 by reductants such as citrate (Turkevich *et al* 1951; Lee and Meisel 1982; Pillai and Kamat 2004), ascorbic acid (Sondi *et al* 2003; Velikov *et al* 2003) or borohydride (Creighton *et al* 1979; Ahmadi *et al* 1996) is among the most used methods for the preparation of silver nanoparticles in aqueous solution. The morphology and size of the nanoparticles can be controlled by using a suitable polymerization agent such as gelatin in chemical methods (Qin *et al* 2010). Gelatin, which is the denaturation product of collagen, consists of one single chain of amino acids. A gelatin hydrogel is a three-dimensional hydrophilic polymer network, which can provide a desirable water-rich buffering environment because of its attractive properties of film-forming ability, biocompatibility, non-toxicity, high mechanical strength and low cost (Falk *et al* 2002; Zhang *et al* 2004, 2006; Yao *et al* 2005; Qian and Yang 2006; Zhang and Gorski 2011).

Detection of hydrogen peroxide (H_2O_2) has become extremely important in recent years because of its wide and varied applications. These include uses in the textile, paper, cleaning product and food industries (Patterson *et al* 1984; Schliefer and Heidemann 1989). Up to now, many techniques including spectrometry, titrimetry, chemiluminescence and electrochemistry have been employed for determination of H_2O_2 (Willner and Katz 2000; Xiao *et al* 2003; Song *et al* 2006; Guo *et al* 2007; Bui *et al* 2010). Among them, electrochemical technique is a promising tool for the construction of simple and low-cost sensors due to their high sensitivity, good selectivity and ease of operation (Bui *et al* 2010). The presence of nanoparticles in electrochemical sensors can decrease the overpotentials of many analytes that occur at unmodified electrodes. Metal nanoparticles (NPs), such as PtNPs, AgNPs, AuNPs and PdNPs, have been proposed as electrocatalysts for sensing H_2O_2 , owing to their excellent conductivity, extraordinary electrocatalytic property and larger specific surface area. Among these materials, silver nanoparticles (AgNPs) show excellent electrocatalytic activity for H_2O_2 (Lian *et al* 2009; Song *et al* 2009; Zhao *et al* 2009). Recent studies (Welch *et al* 2005; Wu *et al* 2006) indicate that the size distribution of AgNPs plays an important role in their electrocatalytic activity for H_2O_2 .

In this paper, we report on the construction of AgNPs using ascorbic acid as the reducing agent stabilized by gelatin. It was found that the AgNPs can effectively catalyze the H_2O_2 reduction. The linear range is estimated to be from 10 to 350 μM and the detection limit is estimated to be 5.6 μM , at a signal-to-noise ratio of 3.

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2. Experimental

2.1 Chemicals and apparatus

Gelatin from bovine skin, ascorbic acid and silver nitrate were purchased from Aldrich. A stock solution of H_2O_2 , freshly diluted from 30% solution, was from Aldrich (Germany). Electrochemical measurements were performed with an Autolab Potentiostat/Galvanostat (Metrohm, Autolab, Amsterdam, The Netherlands). The three-electrode system consisting of an AgNPs–CPE as working electrode, $Ag|AgCl|KCl_{3M}$ as the reference electrode and a platinum wire as an auxiliary electrode (Metrohm, The Netherlands) was used in all voltammetric experiments. TEM images were taken using LEO-Libra 120 transmission electron microscope. Hitachi S-3500N scanning electron microscope (SEM) with energy-dispersive X-ray (EDX) spectroscopy was used for surface image measurements and chemical characterization of a specimen. The crystallization and purity of the synthesized samples were characterized by X-ray diffraction.

2.2 Preparation of Ag nanoparticles

The precursor solution to synthesize AgNPs was prepared by dissolving 1.8 g gelatin in the 80 mL deionized water. The solution was stirred at 60 °C and 10 mL silver nitrate solution (1 M) and 10 mL ascorbic acid (2 M) were added to the above solution with continuous stirring. Then the container was moved to a water bath at 80 °C. The stirring was continued for 30 min. The final product was calcined at 500 °C for 8 h to obtain silver nanoparticles. Also, this method for the synthesis of AgNPs was compared with the reported papers and are given in table 1 (Bar *et al* 2009; Zielinska *et al* 2009; Qin *et al* 2010; Bhatte *et al* 2012; Kim *et al* 2012; Raja *et al* 2012). As can be seen from table 1, the present method is comparable with the results reported in the literature.

2.3 Fabrication of AgNPs–CPE

A 1% (w/w) AgNPs-spiked carbon powder was made by dissolving the given quantity of AgNPs in diethyl ether

and hand mixed with 99 times of its weight of graphite powder in a mortar and pestle. The solvent was evaporated by stirring a mixture of 1% AgNPs-spiked carbon powder and paraffin was blended by hand mixing, and the resulting paste was placed in the bottom of a glass tube (with internal radius 1.5 mm). The electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without AgNPs was used as a blank to determine the background current.

3. Results and discussion

3.1 Characterization

The XRD pattern of the synthesized AgNPs is illustrated in figure 1. Peaks related to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffractions of the face-central-cubic Ag structure (JCPDS no. 87-0597) can be seen, indicating that the Ag particles are made of pure crystalline Ag.

The TEM image (figure 2) of AgNPs is a useful approach to determine the size of Ag nanoparticles. The TEM image shows that the main particle size of the AgNPs, prepared with gelatin in presence of ascorbic acid, was about 20 nm.

The EDX (figure 3) results confirmed the presence of respective constituent element in AgNPs.

3.2 Electrochemical properties of AgNPs–CPE

Cyclic voltammetry (CV) is one of the most common techniques used in electrochemistry to determine electroactivity. Figure 4 shows the cyclic voltammetric response obtained at the CPE and AgNPs–CPE in 0.1 M PBS (pH 7). At CPE (curve a), no obvious redox peak was observed, but a couple of quasi-reversible and well-defined peaks with $E_{1/2}$ of 390 mV and ΔE of 220 mV were observed at 20 mV s⁻¹ for AgNPs–CPE (curve b) due to Ag nanoparticles.

The redox potential of the AgNPs–CPE is scan-rate dependent. Figure 5(A) shows the cyclic voltammograms of the AgNPs–CPE in 0.1 M PBS (pH 7) at various scan rates. It was observed that the values of E_{pa} and E_{pc} shift

Table 1. Comparable parameters for the synthesis of Ag nanoparticles by different methods.

Synthesis procedure	Reducing agent	Stabilizer	Particle size (nm)	References
Electron beam irradiation	Ag(I)–S12 polymer	Ag(I)–S12 polymer	3.1–100	Kim <i>et al</i> (2012)
Chemical	Hydrogen	Polyvinyl alcohol	40	Bhatte <i>et al</i> (2012)
Biosynthesis	<i>Prosopis juliflora</i> leaf	–	35–60	Raja <i>et al</i> (2012)
Green synthesis	<i>Jatropha curcas</i> seed	–	15–50	Bar <i>et al</i> (2009)
Wet chemical	Hydrazine	Polyvinyl alcohol	48	Zielinska <i>et al</i> (2009)
Wet chemical	Ascorbic acid	Polyvinyl alcohol	44	Zielinska <i>et al</i> (2009)
Wet chemical	Sodium borohydride	–	140	Zielinska <i>et al</i> (2009)
Green synthesis	Ascorbic acid	Citrate	31–73	Qin <i>et al</i> (2010)
Green synthesis	Ascorbic acid	Gelatin	20	This work

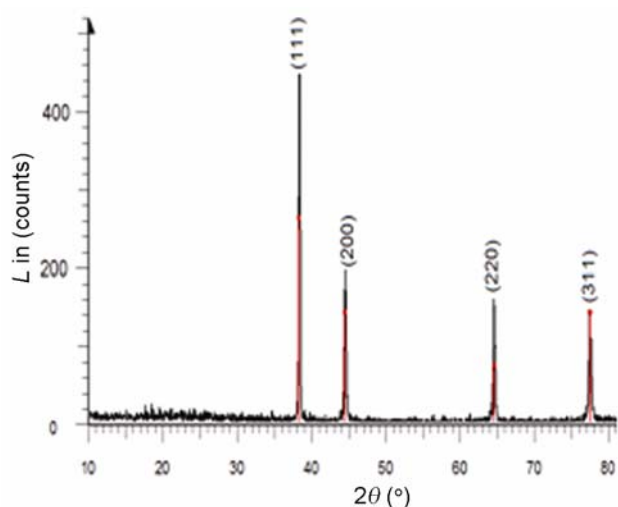


Figure 1. XRD pattern of the AgNPs.

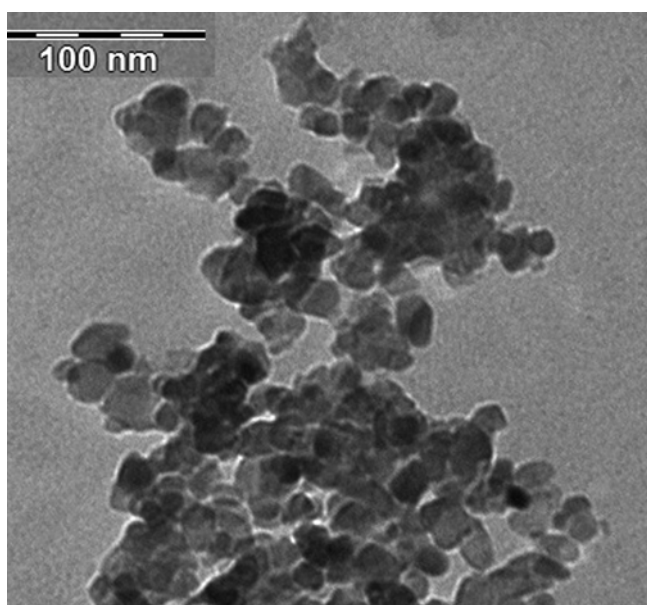


Figure 2. TEM image of AgNPs.

slightly to the positive and negative directions, respectively, and ΔE_p increases with increasing scan rate. The anodic and cathodic peak currents are linearly proportional to scan rates (figure 5(B)), suggesting a surface-controlled process.

A plot of E_p vs $\log \nu$ yields a straight line with slopes of $-2.3RT/anF$ and $2.3RT/(1-a)nF$ for the cathodic and anodic peaks, respectively, so that a can be estimated as 0.63 from the slope of the straight lines. The surface concentration of the electroactive Ag on AgNPs-CPE, Γ (in mol/cm^2), can be estimated using the equation (Laviron 1979)

$$\Gamma = Q/nFA, \quad (1)$$

where Q is the charge consumed in coulombs, obtained from integrating the anodic (or cathodic) peak area in

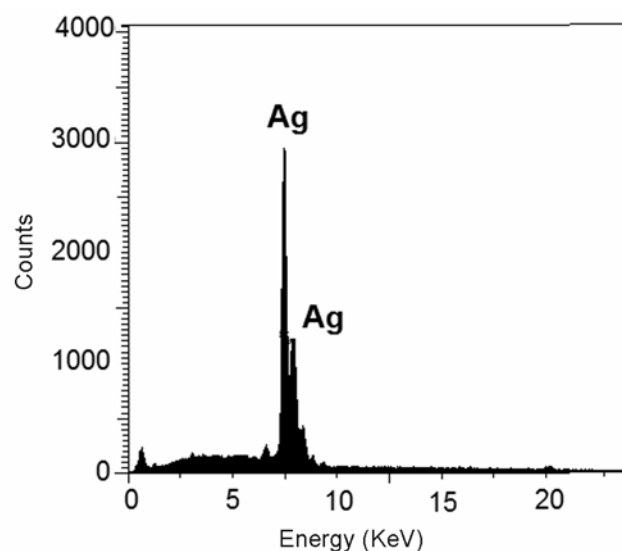


Figure 3. EDX spectrum of AgNPs.

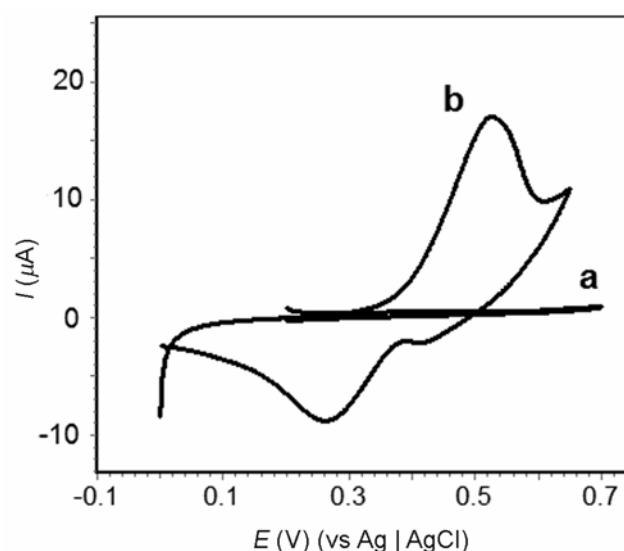


Figure 4. Cyclic voltammograms of the CPE (a) and AgNPs-CPE (b) in PBS with pH 7 at a scan rate of 20 mV s^{-1} .

cyclic voltammograms under the background correction. The average Γ value of $(2.73 \pm 0.81) \times 10^{-10} \text{ mol}/\text{cm}^2$ was obtained.

3.3 Electrocatalytic behaviour of AgNPs-CPE

In order to investigate the electrocatalytic properties of the AgNPs-CPE, its response to the reduction of H_2O_2 was studied in a pH 7 PBS using cyclic voltammetry. As shown in figure 6, at the AgNPs-CPE, the cathodic peak current at around -150 mV increases with increase of H_2O_2 concentration, demonstrating a typical electrocatalytic

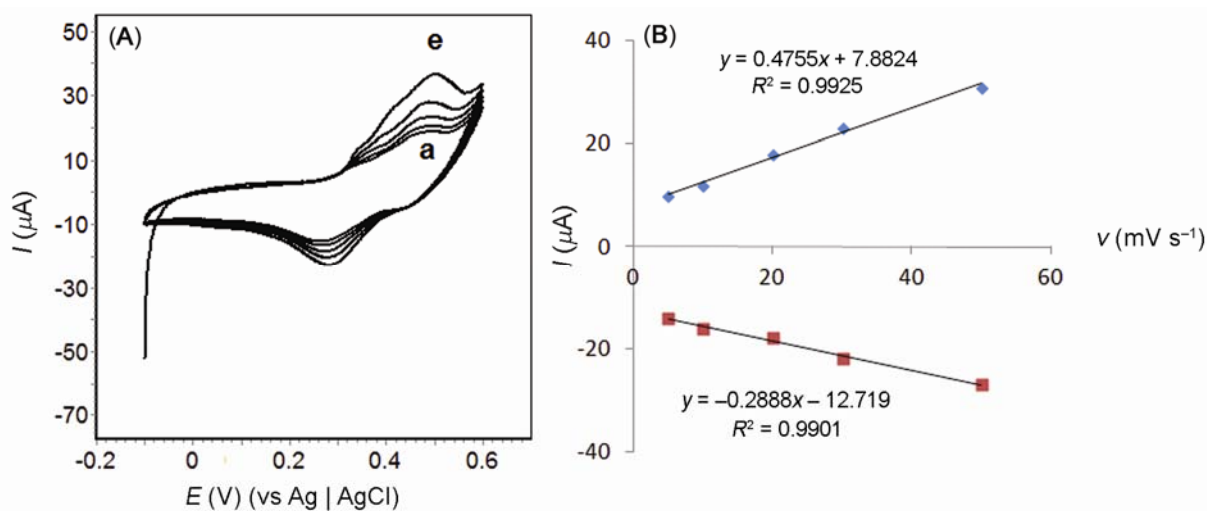


Figure 5. (A) Cyclic voltammograms of AgNPs-CPE in 0.1 M PBS solution (pH 7) at various scan rates: (a) 5, (b) 10, (c) 20, (d) 30 and (e) 50 mV s^{-1} . (B) Plot of peak currents vs scan rates.

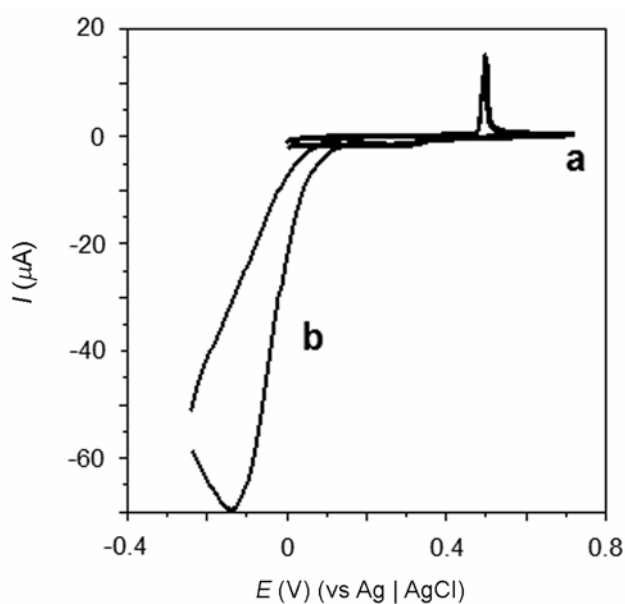


Figure 6. Cyclic voltammograms of AgNPs-CPE in the (a) absence and (b) presence of 1 mM of H_2O_2 in 0.1 M PBS solution (pH 7) and 0.1 M KCl as supporting electrolyte saturated with N_2 at a scan rate of 25 mV s^{-1} .

reduction process of H_2O_2 . The effect of pH value on the reduction of H_2O_2 at the surface of AgNPs-CPE was investigated using different 0.1 M phosphate buffer solutions (pH 3–9). The current response of H_2O_2 at AgNPs-CPE increases from pH 3 to 7 and then a decrease is observed at pH values higher than 7 (not shown). Therefore, pH 7 was chosen as optimum pH and further studies were performed at pH = 7.

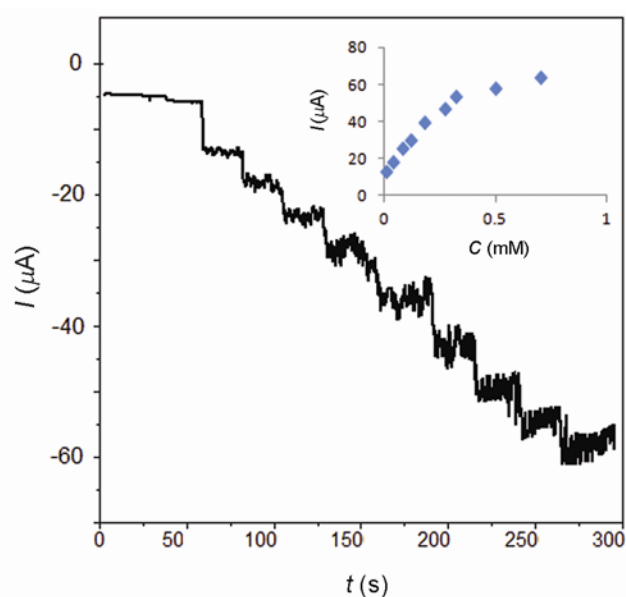


Figure 7. Current-time curve of AgNPs-CPE with successive addition of H_2O_2 to a stirred 0.1 M PBS (pH 7) and 0.1 M KCl as supporting electrolyte saturated with N_2 . The inset is the calibration curve.

The H_2O_2 reduction on AgNPs-CPE was explored for amperometric responses of different concentrations of H_2O_2 at AgNPs-CPE with an applied potential of -250 mV in 0.1 M PBS (pH 7) (figure 7). We use the current value to plot with the concentration of H_2O_2 (inset). There was a linear relation of the current with concentration of H_2O_2 between 10 and 350 μM . Detection limit is 5.6 μM of H_2O_2 with the signal-to-noise ratio of 3. Also, the sensor responded to H_2O_2 with sensitivity of 2533.8 $\mu\text{A mM cm}^{-2}$. The analytical parameters are

comparable with results reported for analytical determination of H₂O₂ at the surface of different modified electrodes (Song *et al* 2009a, b; Lin *et al* 2010; Chen *et al* 2011; Liu *et al* 2011; Lu *et al* 2011).

3.4 Reproducibility and stability of the AgNPs–CPE

The operational stability of AgNPs–CPE was tested by the CV method every 2 days in 2 weeks. The response to 1 mM H₂O₂ decreased less than 19% after 2 weeks, so it has good stability. The fabrication reproducibility of four electrodes independently made showed an R.S.D. of 8.9% for detecting 1 mM H₂O₂. The excellent reproducibility and stability of the sensor may be mainly attributed to the strong immobilization of the Ag nanoparticles in CPE.

4. Conclusion

We developed a novel green synthesis protocol of preparing silver nanoparticles (AgNPs) involving the reduction of silver nitrate in the presence of gelatin as stabilizer and ascorbic acid as reducing agent in aqueous medium. The prepared AgNPs were characterized by TEM, XRD and EDX and studied for their activity as a catalyst for the modification of CPE (AgNPs–CPE). This modified electrode exhibited high electrocatalytic activities towards the reduction of H₂O₂ by significantly decreasing their reduction overpotential and enhancing the peak current. This electrochemical sensor showed high sensitivity, good reproducibility and long-term stability.

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