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Short communication

Electrochemical tracking hydrogen peroxide secretion in live cells based on autocatalytic oxidation reaction of silver nanoparticles

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ABSTRACT

In this work, stable silver nanoparticles (AgNPs) are prepared by borohydride reduction. Autocatalytic oxidation reaction of AgNPs in the presence of hydrogen peroxide (H_2O_2) is investigated. Sharp silver stripping peak in linear sweep voltammogram is used to reflect H_2O_2 concentration and the detection limit of 0.5 μM is achieved. We have also explored the application of the simply prepared AgNP modified electrode for electrochemical tracking H_2O_2 secretion in live cells. This facile strategy shows excellent sensitivity, stability and has great potential use in physiological and pathological applications.

1. Introduction

Hydrogen peroxide (H_2O_2) is a kind of reactive oxygen species, which is produced in cells in a tightly controlled manner. It regulates numerous cellular functions and is involved in many physiological and pathological procedures such as immune, stem and cancer [1,2]. For example, as a response to pathogen invasion, H_2O_2 is produced by certain oxidase enzymes of oxygen metabolism [3]. In normal cell states, H_2O_2 is kept at a constant level. Abnormally high level of H_2O_2 is able to cause many biological damages [4]. Thus, effectively monitoring H_2O_2 in biological systems has aroused tremendous interest. Nowadays, remarkable progress has been made for the detection of H_2O_2. Most methods rely on the catalytic reactions by horseradish peroxidase or its nonenzymatic mimetics. Different fluorescent probes are developed which respond to H_2O_2 [5,6]. Some colorimetric, photoacoustic, chemiluminescent and electrochemical assays are also applied for H_2O_2 analysis [7–11]. Among all these methods, electrochemical techniques are always optimal choices owning to their inherent advantages including simplicity, high sensitivity, low cost, and so on [12,13]. However, due to the slow electrode kinetics of certain electrode materials and the requirements of high overpotentials, it is difficult to achieve sensitive and selective detection of H_2O_2.

Herein, we present a novel electrochemical method for H_2O_2 detection based on autocatalytic oxidation reaction of silver nanoparticles (AgNPs). AgNPs have been extensively applied as biosensing elements, antibacterial materials, catalysts, and many other products [14–17]. Citrate functionalized AgNPs are much stable in water at room temperature. Although AgNPs slowly release silver ions, only partial nanoparticles dissolve even after a long time [18]. However, in the presence of strong oxidizing species like H_2O_2, dissolution of AgNPs is greatly enhanced [19]. Electron transfer between AgNPs and H_2O_2 is an initiating step of the reaction. H_2O_2 then decomposes and generates hydroxyl radical and superoxide anion, which finally turn to O_2 and H_2O. In addition, in the presence of Cl^-, AgCl precipitation forms from the product of Ag^+. The possible reactions are as follows.

$$Ag_n(solid) + H_2O_2 + H^+ \rightarrow Ag_{n-1}(solid) + Ag^+ + HO\bullet + H_2O \quad (1)$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \quad (2)$$

$$HO_2\bullet \rightarrow O_2\bullet^- + H^+ \quad (3)$$

$$O_2\bullet^- + HO\bullet + H^+ \rightarrow O_2 + H_2O \quad (4)$$

The total reaction is

$$Ag_n(solid) + 3H_2O_2 + 2H^+ \rightarrow Ag_{n-2}(solid) + 2Ag^+ + O_2 + 4H_2O. \quad (5)$$

The autocatalytic oxidation reaction of AgNPs in the presence of H_2O_2 can then be applied for sensitive detection of H_2O_2. The AgNP

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modified electrode is used as the sensing interface, which exhibits a highly characteristic solid-state Ag/AgCl reaction and provides a sharp stripping peak in the electrolyte of KCl. The mechanism is as follows.

$$Ag_n(solid) \rightarrow Ag_{n-1}(solid) + Ag^+ + e^- \quad (6)$$

$$Ag^+ + Cl^- \rightarrow AgCl(solid) \quad (7)$$

$$AgCl(solid) + e^- \rightarrow Ag(solid) + Cl^- \quad (8)$$

The electrochemical response to H_2O_2 is also checked in cell culture medium, which shows excellent performance in the complex biological fluids. Therefore, this facile strategy may have great potential use for H_2O_2 quantification in physiological and pathological applications.

2. Experimental section

2.1. Materials and chemicals

H_2O_2 and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich (USA). Silver nitrate was obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). HeLa cells were provided by the Institute of Biochemistry and Cell Biology, Chinese Academy of Sciences. Fetal bovine serum was from Hangzhou Sijiqing Biological Engineering Material Co., Ltd. (Hangzhou, China). DMEM was from Gibco (Gaithersburg, USA). Other reagents were of analytical grade and were used as received. All solutions were prepared with double-distilled water with a specific resistance of 18 MΩ cm. Fresh H_2O_2 solutions were prepared daily.

2.2. Synthesis of AgNPs and H_2O_2-induced AgNP dissolution

AgNPs were synthesized by borohydride reduction of $AgNO_3$ [20]. Briefly, 10 mM $NaBH_4$ solution and a mixed solution of 0.25 mM

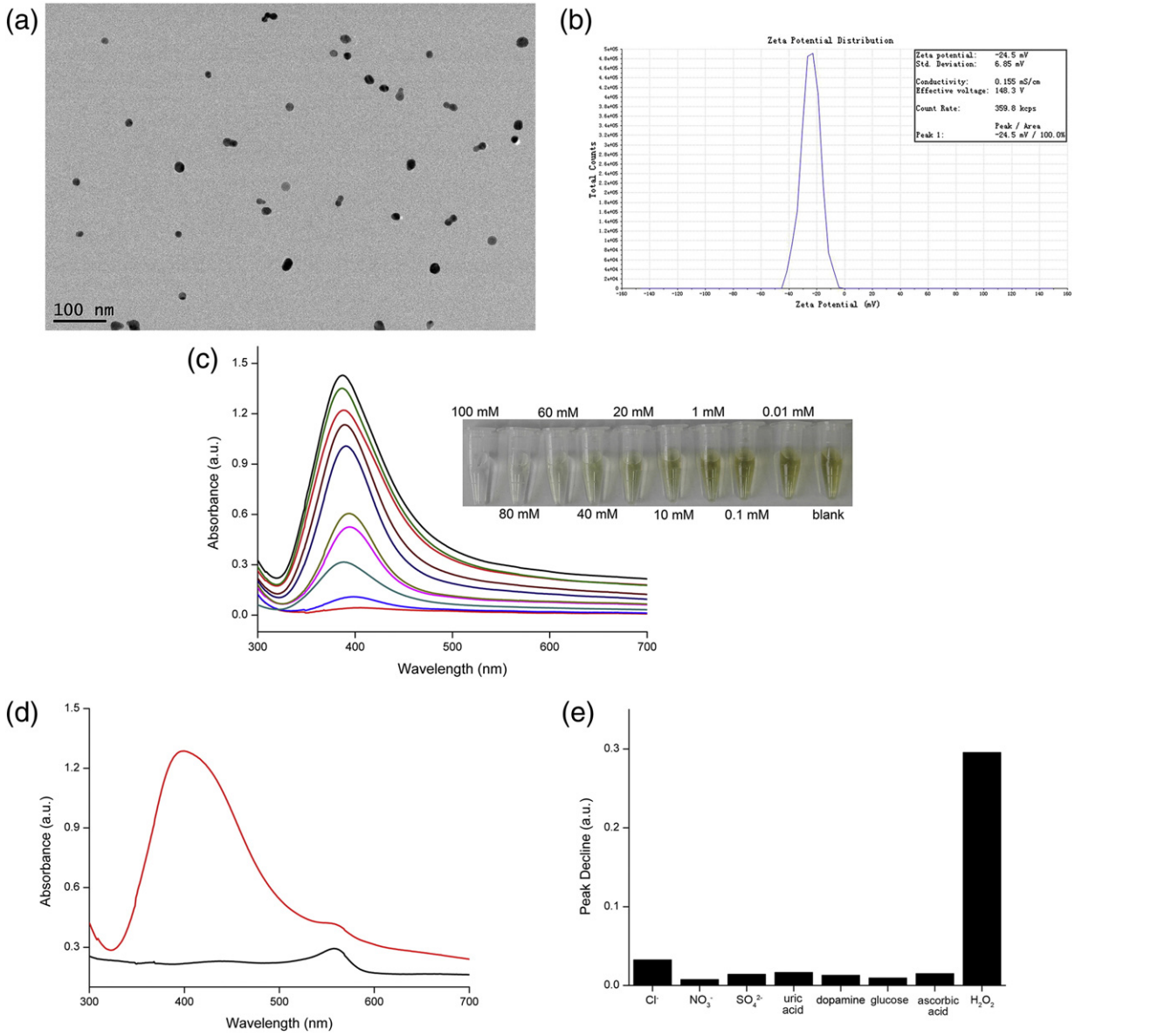

Fig. 1. (a) TEM image and (b) Zeta potential distribution of AgNPs. (c) UV–vis spectra of AgNPs mixed with 0, 0.01, 0.1, 1, 10, 20, 40, 60, 80, and 100 mM H_2O_2 (from top to bottom). Inset shows corresponding solution colors. (d) UV–vis spectra of DMEM/H_2O (1:9, bottom curve) and DMEM/AgNPs (1:9, top curve). (e) Absorbance peak declines of the AgNPs incubated with H_2O_2 and potential interferents with the concentration of 1 mM.