



Sub-picomole level photoelectrochemical sensing of L-cysteine based on plasmonic silver nanoparticles modified hierarchically structured zinc oxide



Hongbo Li ^{a,*}, Daye Chen ^b, Hongmei Wang ^a, Jing Li ^a, Wei Wang ^{a,*}

^a School of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng 224051, PR China

^b Maternal and Child Health Hospital of Yancheng, Yancheng 224002, PR China

ARTICLE INFO

Article history:

Received 28 March 2015

Received in revised form 13 May 2015

Accepted 16 May 2015

Available online 19 May 2015

Keywords:

Nano silver

Plasmonic

Photoelectrochemical

Biosensing

Zinc oxide

ABSTRACT

A novel photoelectrochemical (PEC) sensor for L-cysteine was fabricated using in situ plasmonic silver nanoparticles modified hierarchically structured zinc oxide. The fabricated PEC sensor was based on Ag–S coordination chemistry and the collective oscillatory motion of electrons resulting from the coherent excitation of the “free” electrons in the conduction band of silver nanoparticles. The energetic electrons from the surface plasmon of the silver nanoparticles may be injected into the conduction band of the hierarchically structured zinc oxide and then fast transferred to the ITO electrode. However, the enhanced photocurrent produced by the plasmonic silver nanoparticles can be efficiently inhibited due to the bonding of Ag–S upon the simulated sunlight irradiation and at the bias voltage of 0.2 V. Under the optimized condition, the fabricated PEC sensor was linear with the concentration of L-cysteine in the range from 0.67 to 34.77 pmol L⁻¹ with the detection limit of 0.21 pmol L⁻¹. The presence of definite concentration of conventional species did not interfere in the detection of L-cysteine and the results agreed well with those obtained by HPLC. This novel plasmonic PEC sensor has good performances in high sensitivity, good selectivity, easy operation, economy, short detection time, and portability. The strategy of localized surface plasmon resonance by in situ generation of silver nanoparticles provides an alternative way to construct a PEC sensor of L-cysteine.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In the last few decades, the properties of plasmonic metal nanoparticles such as Au, Ag, and Cu have been the subject of intense research due to the interesting properties of their localized surface plasmon resonance (LSPR) [1]. The LSPR is the collective oscillatory motion of electrons resulting from the coherent excitation of the “free” electrons in the conduction band of the metal [2]. Plasmonic metal nanoparticles exhibit unique absorption, scattering, and surface localized electric-field intensities [3]. Based on the properties listed, most research has been focused on the applications of optical wave guiding [4,5], biological imaging [6,7], Surface Enhanced

Raman Scattering (SERS) [8,9], selective photothermal therapy [10,11], and optical biosensing [12,13]. Recently, plasmonic response has been successfully used in the construction of photoelectrochemical (PEC) sensing [14–17] because the stronger electromagnetic wave and hot electrons can be produced by the surface plasmon resonance of nano gold coupled with light irradiation, which is advantageous to the improvement of sensitivity of PEC sensing. Also, the PEC sensors based on the exciton–plasmon interactions between quantum dots and noble metal nanoparticles have been developed for biosensing applications [18–20]. To the best of our knowledge, however, there is only one report about the plasmonic silver nanoparticle in PEC sensing [18]. Actually, Silver exhibits intrinsically stronger plasmonic performance than gold because of its lower losses in the UV and visible spectrum [21]. Therefore, there is much work to be explored because PEC sensing of plasmonic silver is still in its infancy.

L-Cysteine is one of the low-molecular-mass thiols, which has been proved an important role in cellular metabolism and antioxidation

* Corresponding authors.

E-mail addresses: hbli@ycit.edu.cn (H. Li), wangw@ycit.edu.cn (W. Wang).

protection [22]. The level of L-cysteine is correlated with many diseases such as arteriosclerosis [23], leukemia [24], and cancer [25]. Therefore, careful monitoring of L-cysteine concentration in physiological samples such as plasma, urine, and saliva can be regarded as a valuable biomarker in clinical applications. Many analytical methods, including high performance liquid chromatography (HPLC) [22], fluorescent assays [26], chemiluminescence [27], colorimetric sensing [28], and electrochemical sensing [29–32] have been proposed for the analysis of L-cysteine. Although the methods listed are promising for the potential applications, each of them suffers from at least one undesirable limitation such as limited selectivity, low sensitivity, operational complexity, and lack of economy or speed. Therefore, there is still a challenge to develop an alternative approach for a facile, portable, selective, and sensitive detection of L-cysteine.

In this work, the environmental-friendly and hierarchically structured ZnO, as a photoelectric beacon, was successfully prepared by simply sonochemistry method. It can provide a large surface area to ensure sufficient sites for photochemical reactions, and their micro-sized dimensions can reflect the incident photons to prolong their traveling distance to enhance light capture [33]. Therefore, the photocarriers of hierarchically structured ZnO can be efficiently separated and the enhancement of photoelectric conversion efficiency was achieved [34]. Silver nanoparticles were generated on the surface of hierarchically structured ZnO by the reduction of electrons, which were produced by the separated photocarriers of hierarchically structured ZnO under the incident UV-light. Based on the surface plasmon resonance of silver nanostructure coupled with light in order to produce a stronger electromagnetic wave and generate hot electrons, which are then injected into the conduction band of ZnO to form a photoelectric current [35]. Upon a simulated sunlight irradiation and a bias voltage of 0.2 V, and then the enhanced photocurrent was obtained compare to that of single ZnO. Due to the specific Ag-S bond [36], the photocurrent was decreased with the increased concentration of L-cysteine. The more L-cysteine, the less photocurrent. According to the decreased photocurrent caused by the increased concentration of L-cysteine, a novel plasmonic silver enhanced PEC sensing was constructed. The fabricated PEC sensing has many good performances in sensitivity, simplicity, selectivity, economy, portability, and speed. Finally, the fabricated PEC sensor had been successfully applied to the detection of L-cysteine in urine and the results agreed well with those obtained by HPLC. In addition, the possible mechanism was also investigated in detail (Scheme 1).

2. Experimental

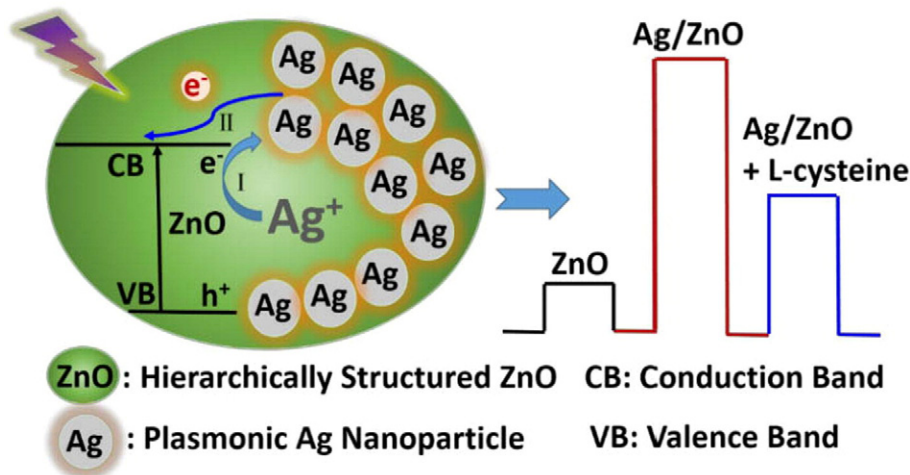
2.1. Materials and reagents

All chemicals were obtained from commercial sources and used without further purification. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$) and NaOH ($\geq 98\%$) were purchased from sinopharm chemical reagent Co., Ltd. AgNO_3 ($\geq 99.8\%$) and L-cysteine ($\geq 99\%$) were from Aladdin Chemistry Co. Ltd. The urine samples for real sample determination were from the volunteers of Maternal and Child Health Hospital of Yancheng. All other chemicals were of analytical grade. In this work, 0.1 mol L^{-1} phosphate-buffered saline (PBS) was always employed as the supporting electrolyte for PEC determination if there were no other statements. Aqueous solutions were prepared with ultrapure water (Milli-Q, Millipore), and the pH value of PBS was 7.0.

2.2. Apparatus

Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 scanning electron microscope (Hitachi, Tokyo, Japan). X-ray diffraction (XRD) patterns of ZnO and Ag/ZnO were measured in the range of $2\theta = 10\text{--}80^\circ$ by step scanning on the Bruker D8 Advance (super speed) diffractometer (Bruker-AEX, German) with Cu K α radiation ($k = 0.15406 \text{ nm}$) operated at 40 kV and 100 mA. UV-visible spectra were recorded at room temperature with a Cary 5000 ultraviolet and visible spectrophotometer (Varian, USA). PEC measurements were performed with a home-built PEC system. Photocurrent was measured by the current-time curve experimental technique on a CHI660D electrochemical workstation (CH Instruments, Shanghai, China) with a 250 W tungsten halogen lamp light as the irradiation source (simulated sunlight irradiation, 250–2500 nm). The distance between the light source and the electrode was fixed at 10 cm. All experiments were carried out at room temperature using a conventional three electrode system with the modified ITO substrates ($\Phi 5 \text{ mm}$, resistivity $10 \Omega/\text{square}$, Zhuhai Kaivo Electronic Components Co. Ltd., China) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as the reference electrode.

The controlled quantitative analyses were performed with an Agilent 1200 HPLC, using a $250 \text{ mm} \times 2.1 \text{ mm i.d.}$, $5 \mu\text{m}$, 100 Å Alltima C18 column operated at 25°C and protected by a $7.5 \text{ mm} \times 2.1 \text{ mm i.d.}$ guard cartridge of the same material,



Scheme 1. Schematic illustration of the PEC detection of L-cysteine by silver nanoparticles modified hierarchically structured ZnO-based photoelectrode.

Download English Version:

<https://daneshyari.com/en/article/218127>

Download Persian Version:

<https://daneshyari.com/article/218127>

[Daneshyari.com](https://daneshyari.com)