Sensors and Actuators B 221 (2015) 28–36

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Fabrication and electrochemical determination of L-cysteine of a composite film based on V-substituted polyoxometalates and Au@2Ag core–shell nanoparticles

Li Zhang, Li Ning, Zhuanfang Zhang, Shaobin Li, Hong Yan, Haijun Pang, Huiyuan Ma*

Key Laboratory of Green Chemical Engineering and Technology of College of Heilongjiang Province, College of Chemical and Environmental Engineering, Harbin University of Science and Technology, Harbin 150040, China

ARTICLE INFO

Article history:
Received 22 April 2015
Received in revised form 3 June 2015
Accepted 6 June 2015
Available online 25 June 2015

Keywords:
L-cysteine
Polyoxometalates
Electrochemistry
Layer-by-layer self-assembly

ABSTRACT

In this work, a novel composite film containing $H_7P_2Mo_{17}V_1O_{62}$ ($P_2Mo_{17}V$) and Au-Ag bimetallic core–shell nanoparticles (Au@Ag NPs) has been fabricated on quartz slides, silicon wafers and ITO electrodes by the layer-by-layer self-assembly technique. The composite film was characterized by UV–vis spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV) measurements. Due to the synergistic effect between Au and Ag, the composite film modified electrode showed excellent electrocatalytic activity toward the oxidation of L-cysteine with a broad linear range of 2.5×10^{-8}–7.625×10^{-6} M, a low detection limit of 2.76×10^{-8} M (S/N = 3), a high sensitivity of 1.7946 μA/μM and fast response time (<2 s). In addition, the electrode exhibited excellent reproducibility and long-term stability as well as negligible interference from L-tryptophan, L(+)-glutamic acid, citric acid, lactic acid and glucose. Furthermore, the applicability of this sensor was successfully employed to detect L-cysteine in milk samples.

1. Introduction

L-cysteine (CySH) is one of the most important amino acids that plays a crucial role in biological systems, lower CySH concentrations can cause many diseases, such as slowed growth in children, depigmentation of hair, edema, lethargy, liver damage, loss of muscle and fat, skin lesions, and weakness [1,2]. CySH is also employed in the food and medicine industries [3,4]. As a consequence, developing a simple, rapid and low-cost method for CySH detection is necessary in physiological and clinical diagnosis.

Various analytical methods have been utilized for determination of CySH that include chromatographic separation [5,6], spectrometric methods [7,8], electrophoretic [9,10] and electrochemical methods [11–16]. Among these methods, electrochemical techniques have received considerable attentions due to their inherent advantages of high sensitivity, relatively low cost, simple instrumentation and selectivity by proper choice of the electrochemical potential. Nevertheless, the electrochemical detection of CySH still remains some defects. The electrooxidation of CySH on the conventional solid electrodes (Pt, Au, graphite, and carbon) is usually followed by sluggish electron transfer kinetics. Additionally, it needs a large overpotential for the electrooxidation process at a desirable rate to attain reasonably good sensitivity [1,17]. Moreover, the necessity of high overpotential significantly reduces the detection selectivity. On the other hand, electrooxidation of CySH on these electrodes at highly positive potentials causes surface oxide formation as well as the fouling effect. In order to circumvent these inherent difficulties, the surface of bare electrodes is being modified with suitable electrocatalysts to improve interfacial electron transfer [1,18]. As a consequence, polyoxometalates and noble metal nanoparticles are introduced.

Polyoxometalates (POMs), a well-known class of inorganic nanoclusters with a metal-oxygen framework, exhibit a wide range of application fields, including energy storage, photochemistry, electrochromism, material science, medicine, magnetism, biotechnology and catalysis [19–26]. In recent years, more attention has been focused on the catalytic redox activity of polyoxometalates [27–30]. Heteropolyanions as a kind of polyoxometalates and especially their metal-substituted derivatives have some very useful and interesting properties. Such features include the high stability of most of their redox states, the possibility to tune their redox potentials by changing the heteroions and/or the addenda ions without affecting their structure, the variability of the transition metal cations which can be incorporated into the

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* Corresponding author. Tel.: +86 0451 86392716.
E-mail address: mahy017@163.com (H. Ma).

http://dx.doi.org/10.1016/j.snb.2015.06.070
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heteropolymetalate structure, and the possibility of multiple electron transfer. These properties make heteropolyanions attractive as redox catalysts (mediators) for indirect electrochemical processes [31]. Vanadium, molybdenum, and tungsten are the main constitutive metals in polyoxometalates, and the oxidizing ability in the order V > Mo > W [32]. Therefore, in the current work, we select Dawson-type vanadium-substituted POMs as the research subject due to their excellent properties besides the above advantages. For example, vanadium-substituted POMs are stable in a large pH domain including the physiological pH domain [4]; furthermore, solutions of their oxidized (V^{V}) and reduced (V^{IV}) forms are stable in the open air [4].

In recent decades, noble metal nanoparticles have been widely explored as catalytic materials for a variety of reactions due to their particular shape, small size, highly active surface to volume ratio, and high surface activity [33–36]. Apart from these excellent characteristics, several other factors have motivated the use of noble metal in biological applications, such as conductivity, stability, and biocompatibility [37–40]. Thus, they have been widely used in the electrocatalysis of biomolecules.

Among various nanoparticles, bimetallic core–shell structures are of particular interest because their unique physicochemical properties, which are distinct from those of the corresponding monometallic components, the properties of core–shell nanoparticles can vary dramatically not only with size but also with chemical composition. It is well-known that adding a second metallic component enhances the activity, selectivity, and stability by the synergetic effect of bimetallic electrocatalysts [41–43]. In particular, it is worth mentioning that among of all bimetallic core–shell structures reported hitherto, the Au@Ag core–shell NPs (NPs with Au cores and Ag shells) have been studied extensively in various fields ranging from antibacterial materials [44], catalysts [45], sensors [46] to surface-enhanced Raman scattering [47].

Based on reasons mentioned above, in this work, a novel L-cysteine sensor consisting of Dawson-type vanadium-substituted POMs $H_7P_2Mo_{17}V_1O_{62}$ ($P_2Mo_{17}V$) and Au@Ag core–shell NPs has been constructed by the layer-by-layer (LbL) self-assembly method, which shows good performances for detecting L-cysteine with high sensitivity, excellent selectivity, fast response, wide detection range and good stability. In addition, the analysis results indicate that it can act as a promising electrochemical platform for L-cysteine detection.

2. Experimental details

2.1. Materials

$H_7P_2Mo_{17}V_1O_{62}$ was synthesized according to the literature [48]. Poly(ethylenimine) (PEI MW 750,000), poly(sodium-p-styrenesulfonate) (PSS MW 70,000), Chloroauric acid tetrahydrate ($HAuCl_4{\cdot}4H_2O$) and silver nitrate ($AgNO_3$) were purchased from Aldrich and used without further purification. Sodium borohydride, ascorbic acid, ethanol, anhydrous sodium acetate and ethylic acid were purchased from Yongchang Chemical Company. All chemical reagents were of analytical grade or better. The water used in all experiments was deionized to a resistivity of 18 MΩ.

2.2. Instrumentation

UV–vis absorption spectra were recorded on a quartz slide using a U-3900 UV-vis spectrophotometer from Hitachi (Japan) and used to detect the growth of the composite film. The element compositions of the composite film were identified by X-ray photoelectron spectra (XPS), which were performed on an ESCALAB-MKII spectrometer with Mg Ka X-ray radiation as the X-ray source for excitation. The surface morphology of the composite film was observed by atomic force microscopy (AFM), which was taken by Digital Nanoscope IIIa instrument (DI, Santa Barbara, CA) operating in the tapping mode with silicon nitride tips. Scanning electron microscopy (SEM) images were obtained with S-4300. All the electrochemical experiments were performed on a CHI760D electrochemical workstation with the ITO electrode coated by the self-assembled film as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode and platinum coil as the counter electrode.

2.3. Preparation of the composite film

2.3.1. Substrates treatment

The composite films were prepared and characterized on quartz slides, ITO-coated glass and silicon wafers, respectively. The substrates were cleaned according to the literature [49,50]. The surface of quartz slides was made hydrophilic by treatment with Piranha solution (H_2SO_4:H_2O_2 = 7:3 v/v) for 20 min at 80 °C, and rinsed with deionized water. Further purification was carried out by immersing the slides in an $H_2O/H_2O_2/NH_3OH$ (5:1:1) (v/v/v) bath for 20 min at 70 °C, thoroughly rinsed with deionized water, and dried under a nitrogen stream. The ITO glass slides were continuously immersed in a series of ultrasonically agitated solvents (30% KOH alcohol solution, ethanol, H_2O) at 40 °C for 20 min. The silicon wafers were cleaned respectively in a 40 °C propanol, ethanol absolute and deionized water bath for 20 min. Then they were rinsed with deionized water and dried under a nitrogen stream.

2.3.2. Preparation of $[PEI/PSS]_2$ precursor film

PEI is a hydrophilic polymer with the dual properties which can function as an anionic exchanger or a chelator to metal cations, PSS is a hydrophilic polymer with abundant negative charge in the neutral aqueous solution [51,53]. They can change the nature and charge of the outermost layer in multilayer films. So in this work, we utilize the electrostatic interacts between positively charged PEI and negatively charged PSS to construct a precursor polyelectrolyte layer. The precursor polyelectrolyte layer is usually deposited to minimize interference by the substrate and to render a more uniformly charged surface. It is believed that this precursor layer can facilitate the subsequent nanoparticle deposition [52,53]. Following a previously reported procedure [54], a $(PEI/PSS)_2$ film was assembled by sequential dipping of the substrate into PEI (1.0 mg/mL) and PSS (1.0 mg/mL) aqueous solutions for 5 min each until the desired number of bilayers, 2, was obtained. The $(PEI/PSS)_2$ film with an additional PEI capping layer is denoted $(PEI/PSS)_2PEI$. Every dipping was followed by sufficient water rinse. NaCl of 1.5 M concentration was maintained in all polyelectrolyte solutions.

2.3.3. Synthesis of Au@2Ag core–shell nanoparticles

In this paper, Au@2Ag core–shell nanoparticles are formed directly on the electrode surface [55]. The specific process is summarized as follows, a $(PEI/PSS)_2$ PEI film was dipped into a $HAuCl_4$ solution (10 mL, 1 mM) for 5 min, removed and rinsed with water, and then treated with a freshly prepared aqueous solution of $NaBH_4$ (10 mL, 0.1 M, for the first reduction only) for 5 min. This exchange/reduction reaction cycle was to produce a $(PEI/PSS)_2PEI$ film loaded with Au NPs. And $(PEI/PSS)_2PEI$ film loaded with Ag NPs were prepared using the same procedure. The $(PEI/PSS)_2PEI$ film loaded with Au NPs was dipped into the $AgNO_3$ solution for 5 min, removed and rinsed with water, and then treated with a freshly prepared aqueous solution of ascorbic acid (10 mL, 0.1 M, for all subsequent reduction) for 5 min. This exchange/reduction reaction cycle was repeated for two times. At last, Au@2Ag core–shell nanoparticles were obtained, which was confirmed in the results and discussion section.