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A high-performance electrochemical sensor for biologically meaningful L-cysteine based on a new nanostructured L-cysteine electrocatalyst

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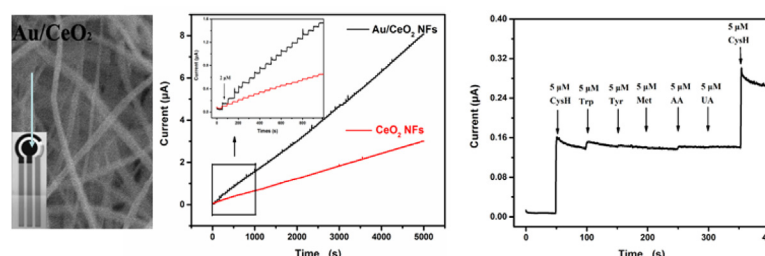
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HIGHLIGHTS

- Au/CeO₂ CNFs were employed as a novel electrochemical catalyst for L-cysteine.
- Au/CeO₂ CNFs exhibited high sensing performance for the detection of L-cysteine.
- The developed sensor possessed excellent selectivity against common interferents.

GRAPHICAL ABSTRACT



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ABSTRACT

As a new class of L-cysteine electrocatalyst explored in this study, Au/CeO₂ composite nanofibers (CNFs) were employed to modify the screen printed carbon electrode (SPCE) to fabricate a novel L-cysteine (CySH) electrochemical sensor with high performance. Its electrochemical behavior and the roles of Au and CeO₂ in the composite toward electro-oxidation of CySH were elucidated and demonstrated using cyclic voltammetry and amperometry techniques for the first time through the comparison with pure CeO₂ NFs. More specifically, the Au/CeO₂ CNFs modified SPCE possessed greatly enhanced electrocatalytic activity toward CySH oxidation. An ultra high sensitivity of 321 μA mM⁻¹cm⁻² was obtained, which is almost 2.7 times higher than that of pure CeO₂ NFs, revealing that the presence of Au imposed an important influence on the electrocatalytic activity toward CySH. The detailed reasons on such high performance were also discussed. In addition, the as-prepared sensor showed a low detection limit of 10 nM (signal to noise ratio of 3), a wide linear range up to 200 μM for the determination of CySH, an outstanding reproducibility and good long-term stability, as well as an excellent selectivity against common interferents such as tryptophan, tyrosine, methionine, ascorbic acid and uric acid. All these features indicate that the Au/CeO₂ composite nanofiber is a promising candidate as a new class of L-cysteine electrocatalyst in the development of highly sensitive and selective CySH electrochemical sensor.

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1. Introduction

L-cysteine (CySH) is an important amino acid present in natural proteins and also plays key roles in biological systems. For example, it could be used as a potential radiation protector and cancer indicator [1,2]. Therefore, the deficiency of CySH in a physiological sample provides insight into the diagnosis of the disease [3,4]. Consequently the determination of CySH is of paramount importance in physiological and clinical diagnosis [5,6]. In the past decades, many techniques have been developed to detect CySH, including flow injection, high performance liquid chromatography, spectrophotometry, colorimetry, gas chromatography, chemiluminescence, and mass spectrometry [7–12]. However, their application is greatly limited due to the high cost, tedious procedures, and the requirement of skilled personnel. On the other hand, L-cysteine can be oxidized to form L-cystine (CySSyC), thus the couple of L-cysteine/L-cystine (CySH/CySSyC) have been widely applied as a model system to study the role of the disulfide bond and thiol group in proteins in a variety of biological media [13]. Accordingly it provides the possibility to electrochemically detect CySH if an appropriate electrocatalyst for CySH oxidation can be identified [14–17]. Compared to aforementioned methods, the electrochemical sensor offers many potential advantages, such as cost effectiveness, high sensitivity, easy operation, miniaturization, and user friendliness [18–22].

To discover suitable electron transfer mediators for fast and low potential determination of CySH is critical and challenging in the pursuit of CySH electrochemical determination, since the direct oxidation of thiols at solid electrodes is typically slow and generally requires high over-potential [23]. A variety of substances including polymers [21,24], metal nanomaterials [18,20], carbon materials [25,26], and enzymes [27] have been explored for the electrochemical detection of CySH. Although those modifiers enhance the performance for the determination of CySH, there are still disadvantages, such as poor detection limit and sensitivity, narrow detection range, and/or high over-potential [28]. Therefore, to identify new sensing materials for electrochemical detection of biologically meaningful CySH has been a continuous effort, which has been recently shifted to widely used metal oxides (e.g. iron oxide, zinc oxide and manganese oxide, etc.) [26,29–32], because of their easy accessibility, low cost, and good chemical and thermal stability.

CeO₂ is one of the rare earth metal oxide materials which possesses many impressive properties, such as good oxygen ion conductivity, superior chemical and thermal stability, high specific capacitance and non-toxicity. More interestingly, the unique redox property of CeO₂ enables dual oxidation states (Ce(IV)/Ce(III)) to co-exist in cerium oxide, thus acting as an ideal oxidant for biomolecules to trigger the reaction of $\text{Ce}^{4+} + \text{BioRed} \rightarrow \text{Ce}^{3+} + \text{BioOx}$ [33,34]. Accordingly, CeO₂ based materials have been explored to electrochemically detect various molecules, such as acetaminophen, acetaldehyde, nitrobenzene, hydrogen peroxide, xanthine, hypoxanthine, uric acid, and dopamine [35–41]. Recently, CeO₂ has been seminally explored in the development of a fluorescent sensor for CySH detection. In this fluorescence sensing scenario, CeO₂ oxidizes CySH to form fluorescent Ce(III)-CySSyC complex through following reaction: $2\text{Ce(IV)} + 2\text{CysH} \rightarrow 2\text{Ce(III)} + \text{CySSyC} + 2\text{H}^+$ [34]. We hypothesize that in conjunction with electrochemistry, this reaction could be exploited for electrochemical determination of CySH with high performance. Moreover, due to the intrinsic strong interaction between Au with SH- group and electro-oxidation of CySH on Au, doping Au into CeO₂ could result in an excellent electrocatalyst for CySH due to the synergistic effects of Au and CeO₂ through the enrichment of CySH on the surface of catalyst and the enhanced electron transfer from doped Au. To the

best of our knowledge, there is no report based on the application of Au/CeO₂ for the determination of L-cysteine.

Therefore, our interest in this paper is to explore an electrochemical sensor toward CySH determination based on electrospun Au/CeO₂ composite nanofibers (Au/CeO₂ CNFs) modified screen printed carbon electrode (SPCE), in which Au/CeO₂ CNFs were employed as a new class of CySH electrocatalyst. The results from electrochemical measurements demonstrated that the resulting Au/CeO₂ CNFs possess highly enhanced electrocatalytic activity toward CySH oxidation, compared with pure CeO₂ nanofibers. The as-prepared CySH electrochemical sensor showed an ultra-sensitivity of $321 \mu\text{A mM}^{-1} \text{cm}^{-2}$ (2.7 times higher than that of pure CeO₂ nanofibers), which can be attributed to three factors: (1) the presence of Au effectively enhanced the conductivity of CeO₂ NFs; (2) the enrichment of CySH on the surface of Au/CeO₂ due to strong interaction between Au and CySH; and (3) the synergistic catalytic effect of Au and CeO₂ on CySH oxidation. Moreover, a low detection limit of 10 nM (S/N = 3), a wide linear range up to 200 μM and an excellent selectivity have been obtained, which are among the best values reported in literature. All these features indicate that the Au/CeO₂ composite nanofiber is a promising candidate as a new class of L-cysteine electrocatalyst in the development of highly sensitive and selective CySH electrochemical sensor.

2. Experimental

2.1. Materials and methods

Cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O), ascorbic acid (AA), and uric acid (UA) were purchased from Acros Organics. L-cysteine, tryptophan (Trp), tyrosine (Tyr), methionine (Met), poly(vinyl pyrrolidone) (PVP, MW = 1,300,000), human serum (from male AB clotted whole blood) and Nafion[®] perfluorinated resin solution (20 wt% in lower aliphatic alcohols and water, contains 34% water) were obtained from Sigma–Aldrich. All aqueous solutions were prepared with deionized water (18.2 M Ω -cm) generated by a Barnstead water system.

2.2. Preparation of Au/CeO₂ CNFs

Au/CeO₂ composite nanofibers were prepared from Ce(NO₃)₃/HAuCl₄/PVP nanofibers which were made via electrospinning process. Firstly, 1 g PVP powder was added into 6 mL ethanol with vigorous stirring to prepare a homogeneous PVP solution. 0.3 g of Ce(NO₃)₃·6H₂O and 0.1 g of HAuCl₄·4H₂O were dissolved in 4 mL of deionized water with continuous agitation for 1 h at room temperature. Next, the PVP and the Ce(NO₃)₃·6H₂O/HAuCl₄·4H₂O precursor solution were mixed together and stirred for 5 h to obtain the viscous precursory solution for electrospinning. Secondly, Ce(NO₃)₃·6H₂O/HAuCl₄·4H₂O/PVP precursory nanofibers were prepared by electrospinning the viscous precursory sol-gel solution between a syringe and an aluminum foil attached on a collector. The distance between the tip of spinneret and the aluminum foil was 15 cm. A high-voltage supply connected with the needle generated a negative voltage of 15 kV. The flow rate was controlled by a syringe pump at a constant value of 1 mL/h. This electrospinning process was carried out under ambient conditions. Finally, the electrospun precursory nanofibers were calcined in air at 500 °C at a heating rate of 2 °C/min and remained at the required temperature for 3 h to obtain Au/CeO₂ nanofibers. The preparation procedure of pure CeO₂ NFs and Au NFs were the same as that of Au/CeO₂ CNFs but only used PVP and Ce(NO₃)₃ or PVP and HAuCl₄·4H₂O, respectively.

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