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Ultrasensitively photoelectronchemical determination of cysteine and coenzyme A with CdSe quantum dots-covered ZnO nanorods photoelectrode

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ABSTRACT

A new photoelectrochemical system was fabricated by incorporating the cysteine or coenzyme A as electron donor into photoelectrochemical reaction of the nanostructured CdSe/ZnO photoelectrode to develop a photoelectrochemical method for the ultrasensitive determination of the cysteine and coenzyme A. The CdSe/ZnO photoelectrode was prepared by covering the CdSe quantum dots on the surface of ZnO nanorods arrays. The property of photoelectrode was investigated as photosensitive interface and electron acceptor, and its photoelectrochemical reaction was study with substrate. Under the 20 mW/cm^2 410 nm visible light illuminations, the sensitive photocurrent response to the cysteine or coenzyme A was obtained at bias voltage 0 V. After the optimized experimental conditions, the photocurrent was proportional to the concentration of cysteine or the logarithm of coenzyme A concentration in the range of 1.00×10^{-2}–20.0 μmol/L and 2.00×10^{-2}–50.0 μmol/L, respectively. The detection sensitivity was 71.7 nA/μmol/L for cysteine. The detection limit was estimated to be 6.00×10^{-3} μmol/L ($S/N = 3$) and 1.00×10^{-2} μmol/L ($S/N = 3$) for cysteine and coenzyme A, respectively. The other amino acids or common coenzymes were not interfering with the determination of cysteine and coenzyme A. Compared with other methods for the determination of cysteine and coenzyme A, the proposed method exhibits a wide measurement range, high sensitivity, and low cost.

1. Introduction

L-Cysteine (CysH), a natural amino acid, has been widely used in medicine, food additives and cosmetics. CysH has the general effect in the detoxification, and can alleviate and repair the radiation damage to body. Among the amino acids that compose the protein, CysH is the only amino acid with reducing activity and has a high reactivity. It is not only mutual transformation with cysteine, but also through the pro-nuclear reactions, redox-catalyzed reactions, metal binding and allosteric regulatory sites to play a very important part in the structure and function of proteins [1–3]. Coenzyme A (CoASH), a natural coenzyme of existence in all animal and plant organisms, is a more important biomolecule for acetylation in vivo, which is synthesized by CysH, pantothenic acid, and adenosine triphosphate in the cell. CoASH is usually used to treat leucocytopenia primary, thrombocytopenic purpura and functional low fever. It can also obviously improve the symptoms of anorexia and spiritlessness. Most importantly, it can promote the metabolism of sugar, fat, protein, and the energy supply in the body [4–7]. Owing to the importance of CysH and CoASH in the life processes, it is very meaningful to develop a precise, sensitive and simple method for detecting CysH and CoASH. Several methods have been reported for determining CysH and CoASH, including spectrophotometry [8,9], spectrofluorimetry [10–12], capillary electrophoresis [13,14], LC-MS/MS [15], and electrochemical method [16–18]. The spectrophotometry and spectrofluorimetry are popularly used technique, but they might require some special reagents and be subject to background interference. The capillary electrophoresis and LC-MS/MS are high sensitive and selective methods. However, in addition to high cost, they might also need specialized technology or materials. Although the electrochemical method is a low cost, simple and fast technology, but its sensitivity and selectivity are generally lower, unless a special reagent or electrode modification method is used. The photoelectronchemical

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(PEC) method on account of nano-interfaced photoelectrode has achieved great progress [19], and it has been widely applied in the areas of protein [20], immunity [21], and DNA [22] analysis. Relative to electrochemical methods, some undesired background signal can be eliminated, because of the separation of its excitation and detection in PEC detection. And the sensitivity of the method is significantly improved, due to the generation of photocurrent is similar to the photocatalytic process. The PEC analysis use light to excite photoelectric active materials, and excited species reacts with electron donor/acceptor to generate photocurrent. Consequently, the sensitivity of PEC method can be influenced by various factors such as electrode and photoelectric materials, type of electron donor or acceptor, etc. [23]. The quantum dots (QDs) have been employed as photoactive materials, owing to their excellent photoelectric properties, including size controllable, high quantum yield, and good stability against degradation, high molar absorption coefficients, photoluminescence, and electrochemiluminescence. Based on these excellent properties of QDs, it has been used in solar cells, drug carriers, cell imaging, and biochemical sensors [24]. The CdSe QDs, a metastable semiconductor material between macroscopic and microscopic structures, has the advantages of broad absorption spectrum, good stability and large specific surface area, and has been used to prepare PEC sensors [25]. On the other hand, both CysH and CoASH are compounds containing mercapto (−SH), which can be used as electron donor to produce the electron transfer reaction, and can restrain the recombination of light-excited electron-hole pairs of photosensitive semiconductor nanomaterials, resulting in photoelectric effect. In this paper, the nanostructured CdSe/ZnO photoelectrode was prepared and used as a photosensitive interface. Based on the photosensitivity and property as electron acceptor, CdSe/ZnO photoelectrode formed a PEC system with CysH or CoASH, developing a novel PEC method for the analysis of CysH and CoASH.

2. Experimental

2.1. Reagents and solutions

CysH (>95%) and CoASH (>95%) were purchased from J&K Scientific Ltd. (Beijing, China). The reference substances of CysH (ASB-00031031-100) and CoASH (ASB-140666-050) was obtained from PTBT Co., Ltd. (Beijing, China) and used as the certified reference materials (CRMs). Poly (diallyldimethyl-ammonium chloride) (PDDA, 20%, w/w) was obtained from Sigma–Aldrich, and was diluted into 1% aqueous solution when in use. All other chemicals were superior to the analytical reagent grade, and were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), unless stated otherwise and standard. All glassware used during the experiments for storage of reagents and standards were pre-cleaned with 20% hydrochloric acid and thoroughly washed with ultrapure water (UPW, >17 MΩ cm). Bicarbonate buffer solution (CBS) with the concentration of 0.1 mol/L was a blend of moderate $NaHCO_3$ and Na_2CO_3, and its pH value can be adjusted by changing the ratio of the two salts. The stock solutions (0.100 mmol/L) of CysH and CoASH were made in UPW, and stored at 4° in the brown bottles. The standard solutions were obtained by serially diluting the stock solution with CBS.

2.2. Apparatus

Cyclic voltammetry and amperometric determination were carried out in a traditional three electrode system. The CdSe/ZnO coated on the ITO conductive glass (thickness 1.0 mm, 5.0 × 0.8 cm, 15 Ω/cm^2, CSG Display Technology Co., Ltd, Shenzhen, China) was used as working electrode. A platinum wire and a Ag/AgCl electrode were used as the counter and the reference electrode, respectively. All electrochemical experiments were performed on a CHI660B electrochemical analyzer (Chenhua instrument Co., Ltd., Shanghai, China). PEAC200A PEC reaction apparatus with a light-electrolytic cell (PEC cell, Tianjin Aida Hengsheng Science and Technology Development Co., Ltd., Tianjin, China) was used to perform photoelectric reaction. LP-3B optical power meter (Physcience Opto-electronics Co., Beijing, China) was used to monitor light intensity. Other instruments used are F-4600 fluorescence spectrophotometer (HITACHI Co., Japan), JSM-2100 F field emission scanning electron microscope (SEM, JEOL Co., Japan), H-800 transmission electron microscopy (TEM, Hitachi Co., Japan).

2.3. Preparation of CdSe quantum dot

Se powder of 0.05 g and 0.037 g $NaBH_4$ was added to a small Schlenk bottle, and oxygen was bubbled through nitrogen for 30 min. After adding 4.0 mL UPW, the reaction solution was heated to 80 °C. With a constant temperature of 80 °C and continuous deoxygenating for 30 min, Se powder was completely dissolved, and a colorless and transparent NaHSe solution (0.1 mol/L) was obtained. According to Cd:MPA:Se was a molar ratio of 1:2.4:0.5, 200 μL MPA (mercaptoacetic acid) as stabilizer was added to the nitrogen-saturated 1.25 mmol/L $CdCl_2$ solution, and 0.1 mol/L NaHSe was added after adjusting the pH of solution to 11. Then, the reaction solution was stirring for 10 min, heated to reflux for 3 h. After precipitation with ethanol, separation by centrifuge, washing and re-dissolved with ethanol, the yellow water-soluble CdSe QDs was obtained (Fig. 1A, the inset in the top right). The particle size of CdSe QD was inferred as 2.5 nm based on its UV–vis spectrum as according to the Chinese National Standard GB/T 24370-2009.

2.4. Preparation of CdSe/ZnO photoelectrode

The washed ITO conductive glass was cut to form ITO electrodes. ZnO NRs was prepared on the surface of ITO electrode by using electrodeposition (Fig. 1B). Subsequently, the obtained product was washed several times with UPW to remove the residual salt and then dried naturally in air, forming a ZnO/ITO electrode [26]. The 1% PDDA and the prepared CdSe QDs solution were respectively put into two centrifuge tubes, and then ZnO/ITO electrode was immersed into the two tubes three times in turn. The electrode was rinsed with UPW before the electrode was transferred from one solution to another. After the electrode was dried in the dryer, the surface of electrode appears slightly orange, indicating that CdSe QDs have been successfully modified on the surface of ZnO NRs to form a CdSe/ZnO photoelectrode.

2.5. Photocurrent measurements

After CdSe/ZnO photoelectrode and the other two electrodes were placed in PEC cell, they were connected to electrochemical analyzer. The excitation light (410 nm) supplied with LED of PEC reaction apparatus was monitored by the optical power meter. Its illuminating power to optical window was kept on 20 mW cm^{-2} through adjusting the energy output of PEC reaction apparatus. The photocurrent was detected with electrochemical analyzer at bias voltage of 0 V. After the sample was injected into PEC cell, the current was synchronously recorded. When the response current tends to be stable, the optical shutter was opened for 10 s every 20 s, forming a photocurrent-time curve. All experiments were repeated five times at least, and the results were presented with mean values and their relative standard deviations. The experiment was performed at room temperature.