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Photocurrent determination ascorbic acid using an n-silicon electrode modified by platinum and cobalt hexacyanoferrate films

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ABSTRACT

By depositing a film of cobalt hexacyanoferrate (CoHCF) on silicon electrode coated by a platinum layer, a novel photoelectrochemical sensor for the detection of ascorbic acid (AA) has been developed. The stable film of CoHCF was electrochemically deposited onto a phosphorus heavy doped silicon (n^+-Si) with 9 μm epitaxial layer (n–n^+-Si) wafers coated with about 40 nm platinum layer (Pt/n–n^+-Si). Scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD) and cyclic voltammetry (CV) were used to characterize the CoHCF film on the Pt/n–n^+-Si electrode. The CoHCF modified Pt/n–n^+-Si electrode has been used for determination of AA with a two-electrode cell in absence of reference electrode by photocurrent measurement at a zero bias. The composite modified electrode demonstrated good photocurrent responses by adding different concentrations of AA with a good stability. The linear range for the detection of AA was 1.0×10^{-6} to 1.0×10^{-3} M, with a detection limit (S/N = 3) of 1.0×10^{-6} M. This provides a facile way of detecting AA and succeeds in averting from inconvenient reference electrode.

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1. Introduction

Photoelectrochemistry, as a newly developed analytical method based on the photoelectrochemical properties of the materials, has a promising potential in biological analysis [1]. So design, fabrication and application of sensitive and selective photoelectrochemical sensors have been of considerable interests in resent years [2]. The photoelectrochemical sensors based on good photoelectrochemical materials have been used for the detection of biologically important compounds [3–5]. Compared with compound semiconductor photoresponse materials, such as CdS [6], FeS [7], and TiO_2 [8] silicon materials show better photoelectrochemical performance owing to its excellent capability for photoresponse, non-toxicity and ease of passivation and texturing [9]. Nevertheless, under determined conditions, silicon (Si) suffers photocorrosion which limits its applicability [10]. Notwithstanding, the Si photocorrosion could be avoided if a surface film of platinum or a compound like a metal hexacyanoferrate (MHCF) film could be formed on it [11]. It is expected, therefore, Si would exhibit more attractive advantages as photoresponse materials than the other photoresponse materials when it is modified using electron mediators [12]. On the other hand, taking into account the semiconductor character of Si and the wide range of redox potential that is present the family of MHCF [13], it is possible to imagine that an adequate coupling of silicon/MHCF would be the base for the design of efficient photovoltaic systems for photoelectrochemical sensors.

Among the MHCFs, cobalt hexacyanoferrate (CoHCF) would be especially attractive because of its excellent properties in electro catalysis, capacity to store counter cations, and ion exchange selectivity [14]. It exhibits excellent reversible redox centers very similar to those of Prussian blue while its electrochemical activity affected by electrolyte cation behaves differently from Prussian blue (PB) [15]. CoHCF has well defined and reproducible electrochemical responses because both the oxidized and reduced CoHCF structures seem to be fairly open and permit transport of alkali metal cations providing charge balance during redox reactions [16]. CoHCF does not undergo dissolution upon reduction or oxidation as the electrolyte ion diffuse in and out of the zeolitic structure of the compound to maintain charge neutrality [17]. Thus, this material is an ideal candidate for surface modification of Si photoelectrode.

Ascorbic acid (AA), vitamin C, is used clinically in the treatment and prevention of scurvy [18]. AA/ascorbate is a vital component in the diet of humans [19]. Ascorbate is known to take part in several biological reactions and is present in mammalian brain

Abbreviations: AA, ascorbic acid; CB, conduction band; CV, cyclic voltammetry; CoHCF/Pt/n–n^+-Si, cobalt hexacyanoferrate modified Pt/n–n^+-Si; CoHCF, cobalt hexacyanoferrate; FTIR, Fourier transform infrared; L, liter (dm^{-3}); M, mol dm^{-3}; MHCF, metal hexacyanoferrate; n–n^+-Si, phosphorus heavy doped silicon with epitaxial n-type layer; Pt/n–n^+-Si, platinum layer modified n–n^+-Si; Si, silicon; PB, Prussian blue; PBS, phosphate buffer solution; SEM, scanning electron microscopy; SCE, saturation calomel electrode; VB, valence band; XRD, X-ray diffraction.

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[20]. Ascorbate is possibly the primary antioxidant in human blood plasma [21]. In addition, AA is found in high concentration in some fruits, vegetables and pharmaceuticals [22]. Though the literature is replete with the different types of methods for the analysis of such diversified products, efforts continue in the search of better methods in regards to their simplicity, rapidity, sensitivity, selectivity and utility [23].

Previously, we reported the electrochemical behaviors of n–n^+-Si electrode modified by nickel–platinum dual metal layer [24] and the Schottky barrier effect on the photo-electrochemical cells based n–n^+-Si or p-n^+-Si [25]. Recently, we report a Prussian blue (PB) film prepared on the surface of Pt-coated n–n^+-Si wafer and used as a sensor for photocurrent determination of hydrogen peroxide [26]. In the present study, we propose a novel, convenient and effective photoelectrochemical sensor to detect AA using a Si electrode modified with a platinum film and CoHCF films. Photoelectrochemical properties of the modified electrode, selectivity, and stability of the sensor were also investigated in details.

2. Experimental

2.1. Materials, chemicals and main apparatus

A (1 1 1) oriented and phosphorus heavy doped Si wafers (resistivity: 0.003 Ω cm) with 10–13 μm epitaxial n-type layer (resistivity: 3–5 Ω cm) were purchased from Semiconductor Materials Factory, Shanghai Nonferrous Metals Institute and referred to as n–n^+-Si. High purity platinum (Pt) and aluminum (Al) wire (>99.99%) were purchased from Shanghai Chemical Reagent Station. Analytical grade cobaltous sulfate heptahydrate and 99.5% potassium hexacyanoferrate (analytical grade) were purchased from Xi'an Chemical Reagent Station and used as received. Ascorbic acid was obtained from the Shanghai Chemical Reagent Factory. Other chemicals were of analytical grade and were used without further purification. All solutions were prepared with doubly distilled water. Standard AA solutions were freshly prepared in a buffer solution before each experiment. A DM220 high vacuum evaporating system (Shanghai Optical Electron Company China) was used to coat Pt and Al film on the n–n^+-Si polished surface and back surface, respectively. Cyclic voltammetry (CV) and chronoamperometry experiments were performed using a LK 2005 electrochemical workstation (Lanlike Company, Tianjin, China). Scanning electron microscopy (SEM) images were obtained using a HITACHI H-800 scanning electron microscopy.

2.2. Electrode fabrication

The CoHCF films were electrochemically deposited on a Pt film coated n–n^+-Si (1 1 1) substrate. Before electrodeposition of CoHCF film, silicon wafers were cleaned in HF solution, rinsed with doubly distilled water and then dried with nitrogen gas. In order to increase ohmic contact area [26], the backs of the Si wafers were coated with about 500 nm aluminum film in high vacuum evaporating system. About 40 nm platinum layer was coated on the front surface of n–n^+-Si (1 1 1) wafers. The coated wafers were heated in argon atmosphere at 673 K for 40 min and the electrode was abbreviated as Pt/n–n^+-Si herein. In order to deposit NiHCF film, the Pt/n–n^+-Si electrode was mounted in the Teflon holder leaving 0.5 cm^2 as the electrode surface area exposed to the solution [11]. The CoHCF films were electrodeposited [27] by CV with a conventional three-electrode system composed of a platinum counter electrode, a saturation calomel reference electrode (SCE), and the Pt/n–n^+-Si working electrode. An irradiation was made from a 50 W bromine–tungsten lamp located 20 cm from the surface of the working electrode. The formation of CoHCFe film was

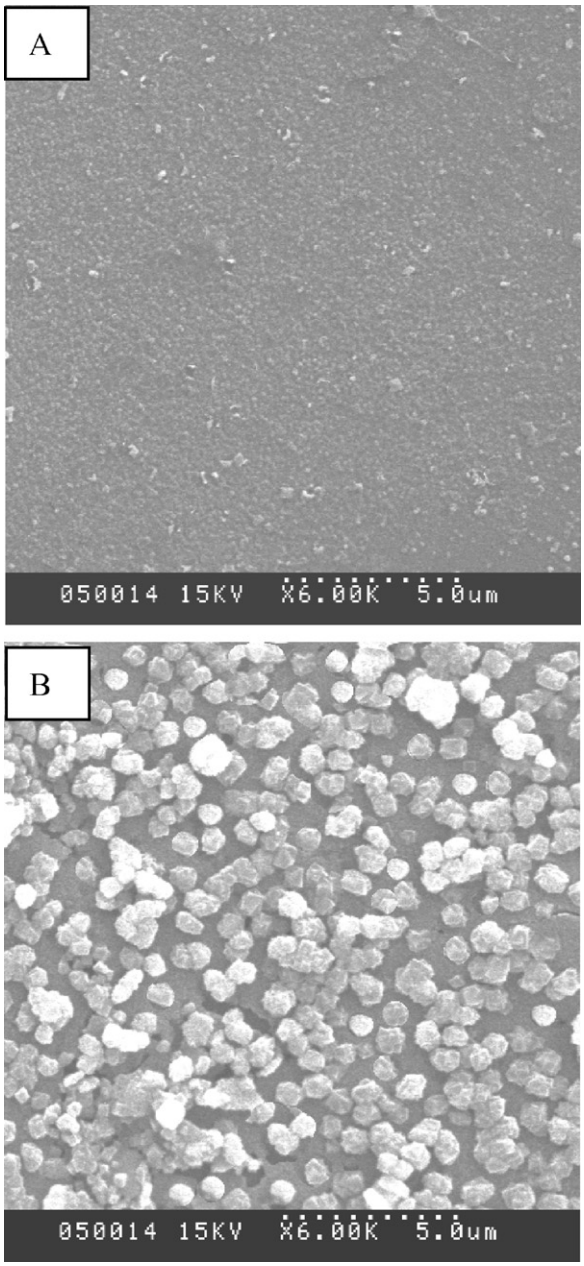

Fig. 1. SEM images of before ((A) Pt/n–n^+-Si) and after ((B) CoHCF/Pt/n–n^+-Si) the CoHCF modified electrode surfaces.

obtained by 20 successive potential cycles from 0.0 to 0.8 V (vs. SCE) at a scan rate of 30 mV s^{-1} in a 1×10^{-3} M $CoSO_4$, 1.0×10^{-3} M $K_3Fe(CN)_6$ solution with 0.5 M KNO_3, as the supporting electrolyte under irradiation [28]. After removing from the solution and rinsing thoroughly with distilled water, red–brown films were clearly seen on the electrode surface. Fig. 1 shows SEM images of the before (A) and after electrodeposition of CoHCF on the Pt/n–n^+-Si electrode surface. The cubic structures of the CoHCF particles about 500 nm in diameter are clearly visible.

The electrode with CoHCF films was dipped into a phosphate buffer solution (PBS: 0.2 M KH_2PO_4, 0.2 M K_2HPO_4 and 1.0 M KNO_3, pH 6.93) for photoelectrochemical activation of the CoHCF film. The photoelectrochemical activation was performed by cycling between 0.0 and 0.8 V (vs. SCE) at a scan rate of 30 mV s^{-1} till steady redox curves under irradiation [29]. After being photoelectrochemically activated, the electrode was ready for use and abbreviated as CoHCF/Pt/n–n^+-Si herein.

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