



## Direct electron transfer of hemoglobin in a CdS nanorods and Nafion composite film on carbon ionic liquid electrode

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### ARTICLE INFO

#### Article history:

Received 15 March 2008  
Received in revised form 8 June 2008  
Accepted 13 June 2008  
Available online 21 June 2008

#### Keywords:

1-Butyl-3-methylimidazolium hexafluorophosphate  
Hemoglobin  
Direct electrochemistry  
Carbon paste electrode  
Ionic liquid

### ABSTRACT

In this paper the direct electron transfer of hemoglobin (Hb) was carefully investigated by using a room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>) modified carbon paste electrode (CILE) as the basal working electrode. Hb was immobilized on the surface of CILE with the nanocomposite film composed of Nafion and CdS nanorods by a step-by-step method. UV-vis and FT-IR spectra showed that Hb in the composite film remained its native structure. The direct electrochemical behaviors of Hb in the composite film were further studied in a pH 7.0 phosphate buffer solution (PBS). A pair of well-defined and quasi-reversible cyclic voltammetric peaks of Hb was obtained with the formal potential ( $E^0'$ ) at  $-0.295$  V (vs. SCE), which was the characteristic of heme Fe(III)/Fe(II) redox couples. The direct electrochemistry of Hb was achieved on the modified electrode and the apparent heterogeneous electron transfer rate constant ( $k_s$ ) was calculated to be  $0.291$  s<sup>-1</sup>. The formal potentials of Hb Fe(III)/Fe(II) couple shifted negatively with the increase of buffer pH and a slope value of  $-45.1$  mV/pH was got, which indicated that one electron transfer accompanied with one proton transportation. The fabricated Hb sensor showed good electrocatalytic manner to the reduction of trichloroacetic acid (TCA).

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### 1. Introduction

Electrochemistry is a useful way to probe the protein conformation, protein electron transfer and protein–ligand interact. Direct electrochemistry of proteins or enzymes on the electrode surface can also be used to establish the foundation for devising the new kinds of bioreactors, biosensors or biomedical devices without mediators. The results can also provide a working model for the mechanistic investigation on the electron transfer of enzymes in the real biological systems. So the direct electron transfer (DET) between redox proteins and the electrodes has aroused considerable interests in recent years [1–3]. Since the electroactive center of proteins was embedded deeply in the protein molecular structure, the DET rate was often slowly due to the unfavorable orientation or the partly denaturation of protein on the electrode surface. Many modifiers or promoters had been used to enhance the DET rate between the electrode surface and the prosthetic groups in the proteins. Different kinds of films were devised for the study on the electrochemical behaviors of redox proteins and further applied to biosensors and biocatalysis, which could facilitate faster DET

between the proteins and the electrode. The films such as insoluble surfactants [4,5], hydrogel [6,7], polymer [8,9], nanoparticles [10–13] and polyions grown layer-by-layer [14–16], had been successfully applied in the protein film electrochemistry.

In recent years the application of one-dimensional semiconductors had aroused great interest due to their significant physical and chemical characteristics. Cadmium sulfide (CdS) is one kind of important direct-band II–VI semiconductor with a band gap of 2.4 eV and had been used in the field of optical devices, luminescence materials or laser light-emitting diodes [17,18]. Different methods had been proposed for CdS nanorods preparation such as thermal evaporation [19], template method [20], aqueous solution [21] and solvothermal [22] process. Due to the remarkable size-dependent optical properties and interface effect, CdS nanorods show the potential application in the bioelectrochemistry. Li et al. applied a CdS nanoparticle for the investigation of the direct electrochemistry of glucose oxidase (GOD) [23]. Similar quantum dots such as CdSe–ZnS [24] or CdTe [25] were also used for the study of the protein electrochemistry.

Room temperature ionic liquids (RTILs) are ionic compounds consisted of organic cations and various of anions, which are in liquids state at ambient or even far below ambient temperature. RTILs have many specific physico-chemical properties such as high chemical and thermal stability, relatively high ionic conductivity,

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negligible vapor pressure and wide electrochemical windows [26,27]. It has been widely used in the field of electrochemistry, organic synthesis, material science, liquid–liquid extraction processes and biocatalysis [28,29]. Compton and coworkers [30] and Endres [31] had reviewed the recent progress of RTILs in electrochemistry. Maleki et al. [32] applied *N*-octylpyridinium hexafluorophosphate (OPFP) as a binder for the construction of a high-performance carbon composite electrode. Zhao et al. [33] used a RTILs/carbon composite materials for the investigation of direct electrochemistry of microperoxidase (MP-11). Li et al. proposed a chitosan and 1-butyl-3-methyl-imidazolium tetrafluoroborate (BMIMBF<sub>4</sub>) composite material for hemoglobin (Hb) or horseradish peroxidase (HRP) immobilization [34,35]. Sun et al. also investigated the direct electrochemistry of Hb immobilized on the surface of carbon ionic liquid electrode (CILE) [36,37]. As a green solvent and reaction media, the presence of ionic liquid as a modifier in the chemical modified electrode showed improved characteristics due to the higher ionic conductivity, wider electrochemical windows and inherent catalytic ability.

In this paper, the direct electron transfer of Hb on the surface of carbon ionic liquid electrode was successfully achieved with the Nafion and CdS nanorods composite films. Nafion is a perfluorosulfonate linear polymer with good proton-conductivity and has been often used as an immobilization matrix to entrap enzymes and proteins due to their unique ionic-exchanging, film-forming and biocompatible properties [38,39]. While CdS nanorods are semiconductors with unique electronic and biocompatible properties. Combined the advantages of RTILs and CdS nanorods, the fabricated Hb modified electrode showed excellent electrochemical behaviors and the direct electron transfer between Hb and the modified electrode was easily achieved. The electrochemical parameters were carefully calculated and the fabricated Hb sensor showed good electrocatalytic ability to the reduction of trichloroacetic acid (TCA).

## 2. Experimental

### 2.1. Reagents

Bovine hemoglobin (Hb, MW, 64,500, Tianjin Chuanye Biochemical Limited Company, China), the ionic liquid of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>, Hangzhou Kemer Chemical Limited Company, China), Nafion (0.5% ethanol solution, Sigma), graphite powder (Shanghai Colloid Chemical Company, average particle size 30 μm) were used as received. CdS nanorods were prepared according to Ref. [20] with the length and the width in the range of 1–2 μm and 30–40 nm, respectively. 0.1 mol/L phosphate buffer solution (PBS) was used as the supporting electrolyte. Other reagents were of analytical grade and doubly distilled water was used in all the experiments.

### 2.2. Apparatus

All the electrochemical experiments were carried out on a CHI 750B electrochemical workstation (Shanghai CH Instrument, China) using a traditional three-electrode system. A saturated calomel electrode (SCE) and a platinum wire electrode were served as reference and counter electrode. The Hb modified working electrode was prepared by the following procedure. All the solutions were purged with highly purified nitrogen for 30 min before the experiments and a nitrogen environment was kept over the solution during the electrochemical measurements. Cary 50 probe UV–vis spectrophotometer (Varian Company, Australia) and Tensor 27 FT-IR spectrophotometer (Bruker Company, Germany) were used for recording absorption and infrared spectra. Scanning electron

microscopy (SEM) was done with a JSM-6700F scanning electron microscope (Japan Electron Company, Japan).

### 2.3. Preparation of modified electrode

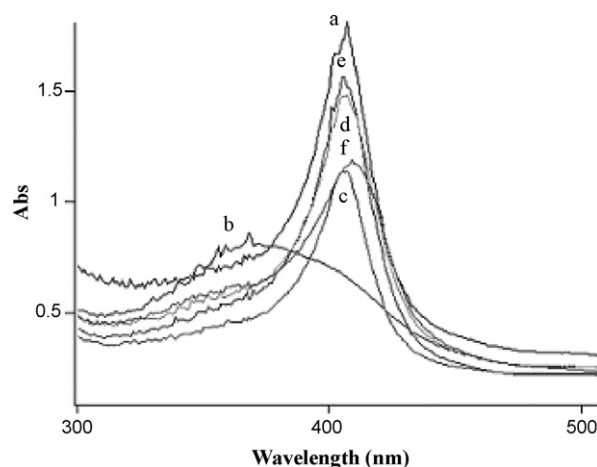
The BMIMPF<sub>6</sub> modified carbon paste electrode (CILE) was prepared by mixing BMIMPF<sub>6</sub> with graphite powder at a ratio of 25/75 (w/w) in an agate mortar. The homogeneous paste was packed into a cavity of glass tube ( $\Phi = 3.8$  mm) and the electrical contact was got with a copper wire connected to the paste in the tube. The electrode surface was smoothed on a weighing paper just before use.

The Hb modified CILE was fabricated according to the following procedure. A 10.0 μL of 15.0 mg/mL Hb water solution was cast on the surface of CILE and left to dry at room temperature. Then 10.0 μL of 11.0 mg/mL CdS nanorods suspension solution was applied on the electrode surface and then the electrode was placed to dry. At last 10.0 μL of 0.5% Nafion ethanol solution was cast on the electrode surface and then the electrode was placed to dry for more than 6 h. The modified electrode was noted as Nafion/nano-CdS/Hb/CILE. Other modified electrodes such as Nafion/nano-CdS/CILE and Nafion/Hb/CILE were also prepared by the similar procedure. All the modified electrodes were stored at 4 °C in a refrigerator when not in use.

## 3. Result and discussion

### 3.1. UV–vis absorption spectra

UV–vis absorption spectrum of the Soret band for heme proteins may provide information on the tertiary structure, especially on the conformational change of the heme protein. The UV–vis absorption spectra of Hb in different pH solution were shown in Fig. 1. The position of the Soret band was depended on pH of the external solution when Nafion/nano-CdS/Hb films were immersed into different pH solution. At pH range between 5.0 and 10.0, the Soret band appeared at 407 nm (curves c–f), which was very close to that of natural Hb at 406 nm (curve a). The results suggested that Hb in Nafion/nano-CdS film essentially retained the secondary structure similar to the native state in the medium pH range. So the composite film provided a suitable microenvironment to keep the native structure of Hb in a wide range of pH. When buffer pH was changed toward a more acidic direction, the peak shape of Soret band became smaller and broader or even disappeared. For example at pH 3.0, the peak



**Fig. 1.** UV–vis absorption spectra of Hb in the different solutions: (a) water, (b–f) Hb mixed with CdS nanorods and Nafion with the pH of PBS as 3.0, 5.0, 7.0, 9.0 and 10.0, respectively.

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