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Chiral recognition of penicillamine enantiomers using hemoglobin and gold nanoparticles functionalized graphite-like carbon nitride nanosheets via electrochemiluminescence

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ABSTRACT

A new stable and stereo-selective electrochemiluminescence (ECL) interface has been designed for specific recognition of penicillamine (Pen) enantiomers by using hemoglobin (Hb) and gold nanoparticles functionalized graphite-like carbon nitride nanosheets composite (Au-g-C_3N_4 NHs) modified glassy carbon electrodes (Hb/Au-g-C_3N_4/GCE). The advantages of Hb as chiral selector and Au-g-C_3N_4 NHs as luminophore were perfectly displayed in this novel interface. The obviously different ECL intensity was exhibited after L-Pen and D-Pen adsorbed on Hb/Au-g-C_3N_4/GCE, and a larger response was observed on D-Pen/Hb/Au-g-C_3N_4/GCE. Under the optimum conditions, the developed ECL chiral sensor showed excellent analytical property for detection of Pen enantiomers in a linear range of 1.0×10^{-4} M to 5.0×10^{-3} M, and the detection limits of L-Pen and D-Pen were 3.1×10^{-5} M and 3.3×10^{-5} M (S/N = 3) respectively. This work with high selectivity, stability and reproducibility may open a new door based on ECL to discriminate Pen enantiomers.

1. Introduction

Chirality is a fundamental property for most biological molecules [1]. As we know, enantiomers possess similar physical properties, but different configurations may express different pharmacological activity and toxicity on living organisms [2]. Penicillamine (Pen) as a non-physiological sulfur-containing drug shows close relation with organisms. D-Pen can be used for the treatment of Wilson's disease, hepatitis, rheumatoid arthritis and prevent retinopathy of prematurity in preterm infants [3–6]. On contrary, L-Pen may contribute to some pernicious reactions like neuritis and osteomyelitis due to its toxic features [7]. Thus, the chiral identification of Pen enantiomers is becoming an increasingly significant topic of research.

Different analysis methods including capillary electrophoresis (CE), thin-layer chromatography (TLC) and high performance liquid chromatography (HPLC) have been proposed to discriminate Pen enantiomers [8–12]. However, these methods still have several drawbacks such as complex operation process, high cost effectiveness and time consuming. Electrochemiluminescence (ECL) is a better alternative approach to overcome these deficiencies because of its outstanding features of low background signal, controllability, good temporal and high sensitivity [13–15]. In addition, there are few reports applying ECL method for recognition of chiral compounds [16,17].

Recently, graphite-like carbon nitride (g-C_3N_4) has attracted intensive research interests and widely applied in the fields of catalysis, degradation and sensor [18–22]. Nevertheless, the poor water-solubility of bulk g-C_3N_4 limits its applications in aqueous solution. Fortunately, g-C_3N_4 nanosheets with high water-dispersibility, good biocompatibility, and higher photocatalytic property have been synthesized by the ultrasonication-assisted liquid exfoliation of bulk g-C_3N_4 [23,24]. Some metal nanomaterials containing Pt, Au, Pd, and Ru have been reported to decorate g-C_3N_4 nanosheets to make hybrids suitable for applications [25–28]. In particular, gold nanoparticles (AuNPs) functionalized g-C_3N_4 nanosheets (Au-g-C_3N_4 NHs) can amplify the ECL signal [26,29], and the other hand couple with nucleic acids or proteins through Au—S or Au—N bonds [30,31]. Accordingly, Au-g-C_3N_4 NHs may be used as a favorable material to fabricate a biosensor.

To the best of our knowledge, proteins possess the ingenerate ability to discriminate chiral molecules. For instance, tyrosine and mandelic acid enantiomers can be specifically recognized by bovine serum albumin and γ-globulin respectively [32,33]. As the

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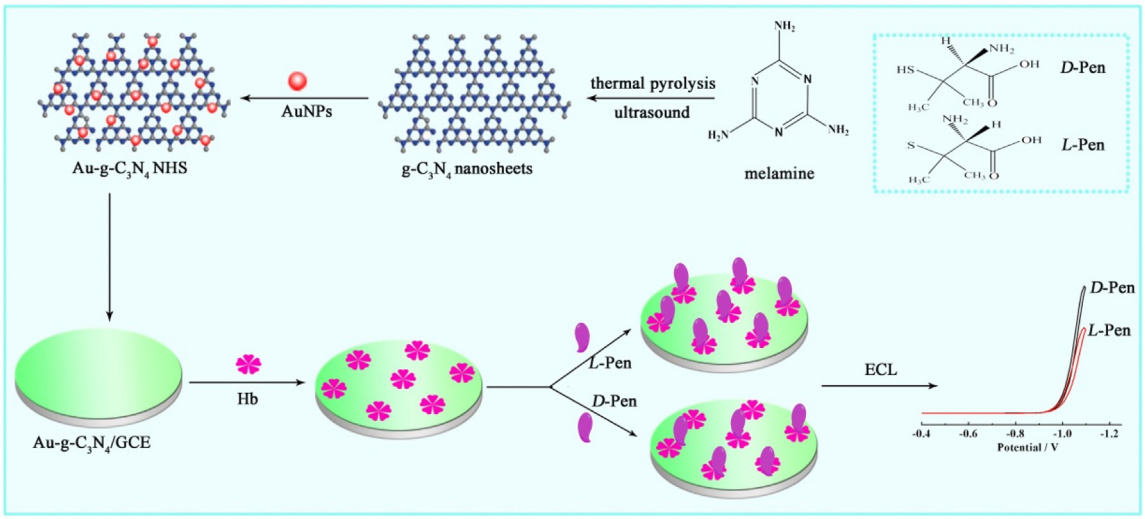

Scheme 1. The preparation process of the chiral sensor and reaction scheme for generating different ECL signals towards L- and D-Pen.

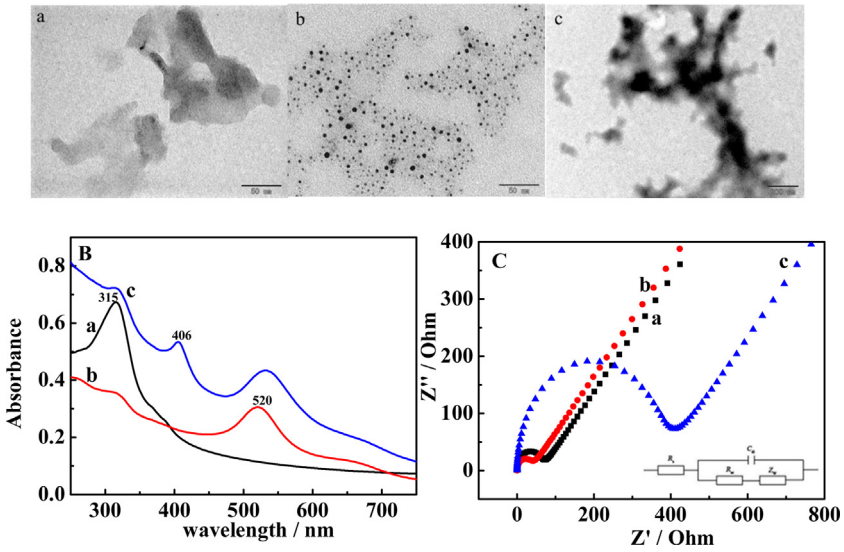

Fig. 1. TEM characterization and (B) UV–vis absorption spectra of (a) g-C_3N_4 nanosheets, (b) Au-g-C_3N_4 NHs, (c) Hb/Au-g-C_3N_4 hybrids; (C) EIS of (a) bare GCE, (b) Au-g-C_3N_4/GCE, (c) Hb/Au-g-C_3N_4/GCE in 5.0×10^{-3} M $[Fe(CN)_6]^{4-/3-}$ solution (pH 7.4).

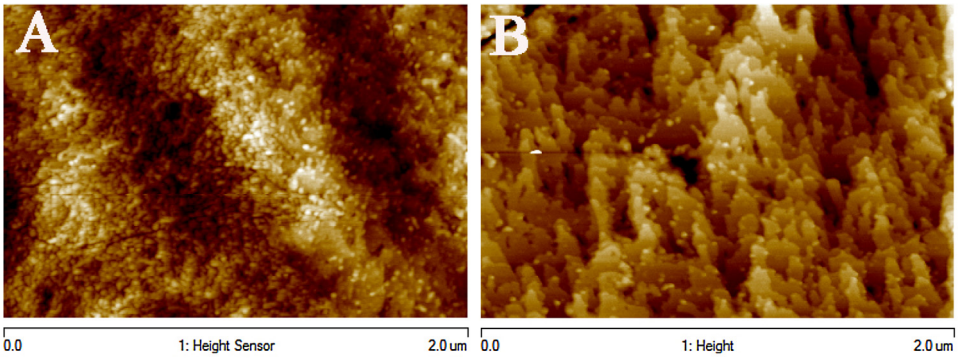

Fig. 2. AFM images of different surface: (A) L-Pen/Hb/Au-g-C_3N_4, (B) D-Pen/Hb/Au-g-C_3N_4.

momentous redox protein in red blood cells for electron transfer reactions, hemoglobin (Hb) has been selected as a chiral selector to fabricate chiral interface [34,35]. Inspired by above observations, a novel ECL chiral sensor has been constructed by employing Hb and Au-g-C_3N_4 NHs modified electrodes to specifically distinguish Pen enantiomers.