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Construction of an electrochemical chiral interface by the self-assembly of chiral calix[4]arene and cetyltrimethylammonium bromide for recognition of tryptophan isomers

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ABSTRACT

Molecular self-assembly offers an effective route for the rational design of chiral sensing devices. Here, cetyltrimethylammonium bromide (CTAB) was linked with the chiral calix[4]arene (CCA) via ion–dipole interactions and then an electrochemical chiral interface was constructed from the resulting self-assembled CCA-CTAB. Highly efficient recognition of tryptophan (Trp) isomers ($I_{L\text{-}Trp}/I_{D\text{-}Trp}$ = 18.96) was achieved with the CCA-CTAB self-assembled interface. Possible mechanisms were proposed, based on density functional theory (DFT) and wettability measurements. Finally, the resulting electrochemical chiral interface was used to analyze the precise levels of L- and D-Trp in a racemic mixture of Trp isomers.

1. Introduction

Chirality is of significant importance in living systems because isomers, in particular chiral drugs, often exhibit quite different biological activity [1]. Amino acids are important chiral components of biological systems, and L-amino acids seem to be more prevalent in foods and beverages [2,3]. Recognition of chiral amino acids is a challenging task in pharmaceuticals, biochemistry and life sciences. Recently, electrochemical recognition of chiral amino acids has attracted increasing attention due to its advantages of low cost, simplicity and high sensitivity [4–8].

Calixarenes are a type of macrocyclic compound which can be obtained by the oligomerization of phenol and formaldehyde [9]. Chiral calixarenes may be prepared by attaching chiral groups to the lower (or upper) rim of calixarenes [10] and have been used in various fields. For example, chiral calix[4]arene phosphonic acid was prepared by Karpus et al. [11] and used in organocatalysis, showing good catalytic activity. Pang et al. [12] proposed a photo-responsive macroscopic switch using a silicon surface functionalized with a chiral azo-calix[4]arene derivative, which exhibited reversible and selective recognition ability through the variation of wettability. However, to the best of our knowledge no electrochemical sensors based on chiral calixarenes (or their derivatives) have been developed for the detection of chiral amino acids.

Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant which is often used as a template for the synthesis of 3D mesoporous materials [13]. CTAB can also induce the self-assembly of diphenylalanine (FF), and the morphology of the resulting self-assembled FF is different from that of FF [14]. An electrochemical chiral interface has been constructed via CTAB-induced FF self-assembly in our group [14]. In this work, CTAB was assembled with chiral calix[4]arene (CCA), and an electrochemical chiral interface was constructed based on the resulting self-assembled CCA-CTAB, which was then used to detect tryptophan (Trp) isomers. In addition, density functional theory (DFT) and wettability measurements were employed to suggest possible recognition mechanisms.

2. Experimental

2.1. Synthesis of chiral calix[4]arene (CCA)

Chiral (*S*)-N-(2-chloroacetyl)phenylalanine methyl ester was synthesized by the method reported previously [15]. This was then attached to the lower rim of 4-tert-butyl-calix[4]arene using the following procedure. (*S*)-N-(2-Chloroacetyl)phenylalanine methyl ester (130 mg), 4-tert-butyl-calix[4]arene (340 mg) and NaOH (20 mg) were added to anhydrous methanol (50 mL), and the mixture was stirred at room temperature for 18 h. Next, the solvent was

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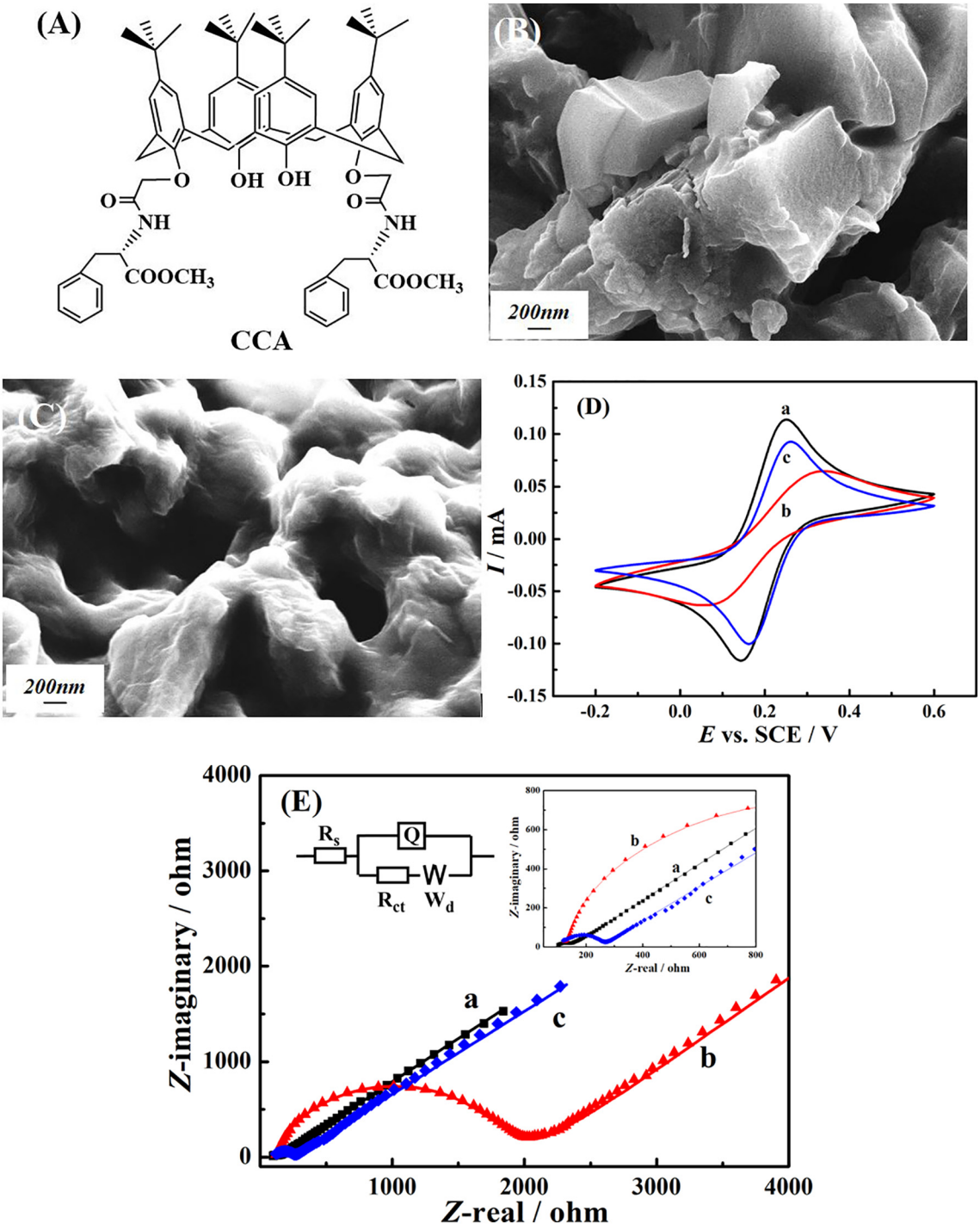

Fig. 1. (A) Structure of CCA. (B) SEM images of CCA and (C) CCA-CTAB. (D) Cyclic voltammograms and (E) Nyquist plots of bare GCE (a), CCA/GCE (b) and CCA-CTAB/GCE (c) in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{4-/3-}$. Insets: equivalent circuit (left); enlargement of the Nyquist plots in high frequency region (right).

evaporated under vacuum, and the residue was subsequently dissolved in ethyl acetate. After being washed with water, the organic phase was dried using anhydrous Na_2SO_4. Finally, the solvent (ethyl acetate) was removed by evaporation under vacuum to afford CCA (90 mg, 69%). The purity of CCA was characterized by ^1H NMR: (400 MHz, $CDCl_3$) δ: 1.21 (s, 36H), 3.11–3.21 (m, 4H), 3.50 (d, 4H), 3.74 (s, 6H), 4.03 (d, 4H), 4.27 (d, 4H), 4.85–4.90 (m, 2H), 7.05–7.33 (m, 18H), 10.34 (s, 2H). The structure of the resulting CCA is shown in Fig. 1A.

2.2. Construction of an electrochemical chiral interface

3.4 mg of CCA and 1.0 mg of CTAB were dispersed in 3 mL of water to allow the self-assembly of CCA and CTAB. After 6 h, the dispersion of self-assembled CCA-CTAB (10 μL) was cast onto the surface of a glassy carbon electrode (GCE) and dried in ambient air. Next, 10 μL of Nafion (0.05 wt%) was dropped onto the surface of the CCA-CTAB/GCE as a coating to immobilize the self-assembled structure, producing an electrochemical chiral interface.