



Electrochemical enantio recognition of tryptophan enantiomers based on graphene quantum dots–chitosan composite film



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ABSTRACT

A graphene quantum dots (GQDs)–chitosan (CS) composite film was prepared via successive electrodeposition of GQDs and CS on the surface of a glassy carbon electrode (GCE). The strong interactions between GQDs and CS resulted in the formation of a regular and uniform film, which can be applied in the electrochemical chiral recognition of tryptophan (Trp) enantiomers. CS in the composite film provides a chiral microenvironment, meanwhile, GQDs can amplify the electrochemical signals and improve the recognition efficiency. Due to the synergetic effect of GQDs and CS, chiral recognition of Trp enantiomers is achieved successfully. Compared with previous reports utilizing GQDs in photoluminescent research, this work opens a new avenue for broadening the applications of GQDs in the electrochemically chiral sensors.

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1. Introduction

Graphene quantum dots (GQDs) are a class of “zero-dimensional” carbon material which have recently attracted increasing attention due to their outstanding properties, such as excellent photostability and water solubility, biocompatibility and low toxicity [1,2]. Recent research on GQDs is mainly focused on photoluminescence because of the fluorescent characteristic of GQDs [3–5]. Though GQDs have been applied in electrochemical sensing [6–8], the applications of GQDs in electrochemical enantio recognition have not been explored until very recently, which might be due to the absence of chiral center in GQDs. Recently, Trojanowicz [9] reviewed that successful chiral recognition can be achieved via combining multi-walled carbon nanotubes (CNTs) and optically active substances, opening a new avenue in electrochemical enantio recognition with modified GQDs.

As a kind of biocompatible polysaccharide, chitosan (CS) exhibits excellent chiral selectivity attributed to the existence of a large quantity of chiral sites [10], and it has been widely adopted as chiral stationary phase for chromatographic techniques [11–14]. As far as we know, little or no attention has been paid to the use of CS for electrochemical recognition of chiral compounds due to the dielectric and insulating features of CS. However, a recently proposed strategy by our group using β -cyclodextrin, another kind of natural

polysaccharide, combined with poly(L-glutamic acid) for the electrochemical enantio recognition of tryptophan (Trp) enantiomers [15] suggests the feasibility of chiral recognition of Trp enantiomers with CS from the electrochemical point of view.

Herein, we first report on a chiral interface based on GQDs–CS composite film modified glassy carbon electrode (GCE), GQDs–CS/GCE, for recognizing Trp enantiomers. The electrodeposited GQDs–CS composite film combines the advantages of GQDs and CS, i.e., it not only possesses chiral center for recognition, but also has excellent electrical conductivity for amplifying electrochemical signals. Therefore, the composite film is applied for electrochemical enantio recognition of Trp enantiomers, and the enantio recognition ability of the GQDs–CS/GCE is evaluated by differential pulse voltammetry (DPV), revealing a higher affinity to L-Trp.

2. Experimental

2.1. Reagents and apparatus

All reagents used were analytical grade and used as received. Electrochemical experiments were performed with a CHI 660E electrochemical workstation in a three-electrode cell comprising of a GCE or modified GCE as working, a platinum foil as auxiliary and a saturated calomel electrode (SCE) as reference electrode, respectively. The UV–vis and fluorescence spectra were recorded on a UV-2450 spectrometer and a F-280A fluorescence spectrophotometer, respectively. The FT-IR

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spectra were measured by a FTIR-8400S spectrometer. SEM and TEM images were recorded on a Supra55 field-emission scanning electron microscope and a JEM-2000 transmission electron microscope.

2.2. Construction of chiral interface

GQDs were prepared according to a bottom-up method previously reported by directly pyrolyzing citric acid (CA) [16]. Cyclic voltammetry (CV) was carried out for the electrodeposition of GQDs on GCE (3 mm diameter) from GQD aqueous solution (2 g L^{-1}) in the potential range from 0 to 1.0 V at a scan rate of 100 mV s^{-1} . After 50 repeating cycles, the three-electrode system was transferred into 0.1 M HCl containing 2 g L^{-1} CS, and a negative potential of -0.5 V was applied on the working electrode (GQDs/GCE) for 200 s for the deposition of CS film and the construction of GQDs-CS/GCE.

2.3. Electrochemical recognition of Trp enantiomers

The obtained GQDs-CS/GCE was immersed into a 20 mL 0.1 M phosphate buffer saline (PBS) containing 0.5 mM L- or D-Trp (pH 7.0) for 60 s at 15°C , and then the electrochemical responses of L- and D-Trp combined with the GQDs-CS/GCE were monitored by DPV in the potential range from 0.4 to 1.0 V with a step potential of 4 mV and an amplitude of 50 mV. The electrochemical enantio-recognition of Trp enantiomers is based on the differences of the oxidation peak currents of L- and D-Trp

combined with the GQDs-CS/GCE. The stepwise procedure for construction of the chiral interface and recognizing Trp enantiomers is illustrated in Fig. 1A.

3. Results and discussion

3.1. Characterization of GQDs

The typical UV-vis absorption spectra and fluorescence spectra of GQDs are shown in Fig. 1B. The GQDs exhibit a broad UV-vis absorption below 400 nm without any obvious peak, implying that the sp^2 clusters contained in GQDs are not uniform in size [16], and a weak shoulder at 344 nm is attributed to the $n-\pi^*$ transition of the $\text{C}=\text{O}$ band and the $\pi-\pi^*$ transition of the conjugated $\text{C}=\text{C}$ band [17]. The maximum excitation and emission wavelengths appear at 381 and 458 nm, respectively. FT-IR spectra of GQDs and CA were recorded to obtain further structural insights of the prepared GQDs (Fig. 1C). A broad peak at 3341 cm^{-1} is attributed to the stretching vibration of $-\text{OH}$ from GQDs, and the two peaks at 1766 and 1716 cm^{-1} are assigned to the antisymmetric stretching vibration and symmetric stretching vibration of $\text{C}=\text{O}$ [18]. A small peak at 1631 cm^{-1} is related to the stretching vibration of $\text{C}=\text{C}$ [17]. Additionally, the $\text{C}-\text{OH}$ stretching vibration (1112 cm^{-1}) in CA is changed to the $\text{C}-\text{O}-\text{C}$ stretching vibration (1182 cm^{-1}) in the GQDs, suggesting that CA is completely carbonized to GQDs after pyrolyzation treatment. TEM image (Fig. 1D) reveals that the GQDs

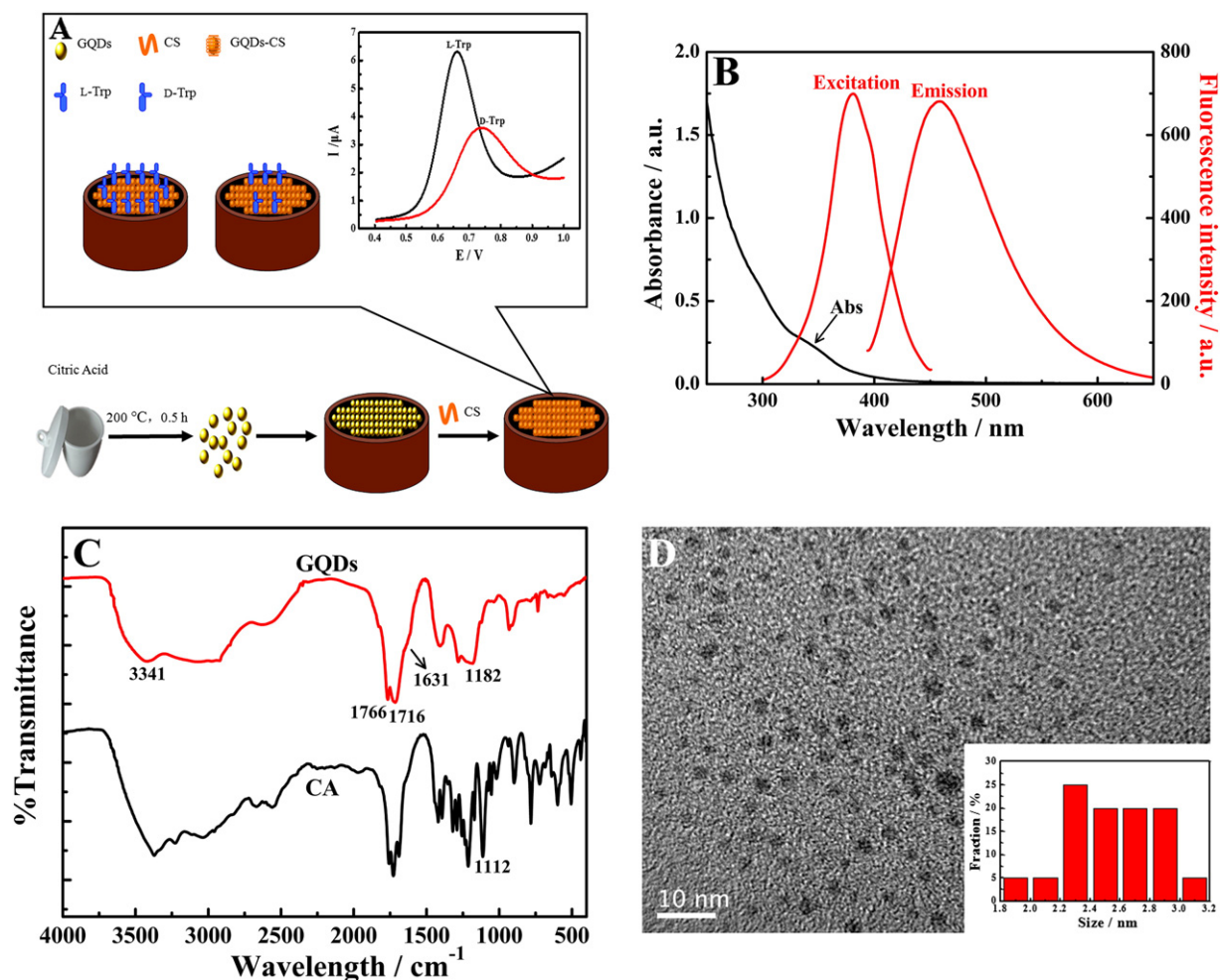


Fig. 1. (A) Schematic illustration for construction of chiral interface and recognition of Trp enantiomers. (B) UV-vis absorption spectra and fluorescence spectra of GQDs. (C) FT-IR spectra of GQDs and CA. (D) TEM image of GQDs, and the inset is the particle size histogram.

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