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A facile avenue to prepare chiral graphene sheets as electrode modification for electrochemical enantio recognition

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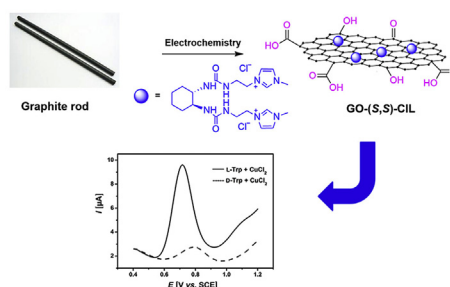
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HIGHLIGHTS

- A new chiral ionic liquid is synthesized and used as the electrolyte.
- Functionalized graphene sheets are prepared directly from graphite rods.
- An electrochemical sensor is developed by the novel material.
- The approach is successfully applied in chiral recognition.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical enantio recognition has attracted much interest due to its advantages of low cost and simple equipment. In this work, a new chiral ionic liquid is prepared and applied as an electrolyte for the one-step synthesis of functional graphene sheets (GO-(S,S)-CIL). More importantly, an electrode is modified by the material for the construction of an electrochemical sensor (GO-(S,S)-CIL-GCE). Enantiomers including L/D-tryptophan, (R)-/(S)-mandelic acid, (R)-/(S)-malic acid, and L/D-tyrosine are successfully distinguished by GO-(S,S)-CIL-GCE in the response of peak currents to different forms. In addition, the peak potential of the L form is located negatively compared to the D form for tryptophan, and the value of the peak-to-peak potential separation approaches 72 mV. The recognition mechanism is assessed by the density functional theory calculation in detail. In brief, the present method offers great promise for the preparation of functional graphene sheets and their further application in chiral recognition.

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1. Introduction

Chiral recognition is of pivotal importance in the life science and medical industries. Different techniques with certain chiral environment are widely used in chiral recognition, such as HPLC [1–3],

NMR [4,5], mass spectrometry (MS) [6,7], and circular dichroism (CD) [8,9]. Compared with these methods, electrochemical enantio recognition is of great interest due to its advantages of low cost and simple equipment [10]. To date, a series of electrochemical sensors have been developed, mainly by an achiral electrode modified with chiral molecules like proteins [11–13], DNA [14], β-cyclodextrin [15,16], and artificial polymers [17–19]. In addition, materials with relatively good electrical conductivity are regarded

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as the appropriate platform [20,21]. For example, Zor et al. reported that the hybrid of reduced graphene oxide with γ -cyclodextrin is an efficient electrochemical chiral sensor for the recognition of tryptophan [20]. To obtain the target material bearing electroactive units, the whole synthetic process usually requires two or more steps, including the fundamental oxidation of graphite and the covalent graft of chiral molecules. Thus, the one-pot synthesis of the working electrode is desirable and promising.

Recently, some strategies have been established for the synthesis of functional graphene with direct binding, such as electrochemical exfoliation [22,23], free radical reactions [24,25], reduction reactions [26], Diels-Alder reactions [27], and click reactions [28]. Among them, electrochemical exfoliation is an effective approach to produce the target graphene under mild conditions [29]. Choosing an appropriate electrolyte plays a key role and is capable of driving ions into the stacked graphite sheets effectively, thus leading to improved reaction yields [30]. Nevertheless, there are still limitations to obtain the functional single-layer graphene sheets with relatively high yields due to the strong π - π intersheet effect in the starting materials. Ionic liquids (ILs) consist of entire ions and present unique properties containing excellent conductivity and negligible vapor pressure. They have been regarded as the designer solvents for a broader usage via the proper choice of the cation and anion [31–34]. Recent research studies have suggested that ILs can be directly applied as the electrolyte for the preparation of few-layer graphene sheets from graphite rods [35]. Interestingly, the electron belonging to the C_2 carbon of the cationic ring in the ILs can form stable covalent bonds, with the electron of the π -bond belonging to the graphene through a free radical reaction. This reaction provides a good opportunity to prepare novel functional material and enlarge their potential application. However, further application by using the material is rarely reported. Therefore, it is highly desirable to explore the potential of the graphene decorated with functional ILs.

Herein, as shown in Fig. 1, we report a simple and rapid method that aims to prepare functional graphene sheets (GO-(*S,S*)-CIL) from graphite rods in one step. During preparation, a novel chiral ionic liquid ((*S,S*)-CIL) derived from (1*S*,2*S*)-1,2-diaminocyclohexane is synthesized and used as the working electrolyte. Furthermore, the electrode is modified by using the produced GO-(*S,S*)-CIL to construct an electrochemical sensor (GO-(*S,S*)-CIL-GCE).

Remarkably, we show that GO-(*S,S*)-CIL-GCE exhibits favorable enantiomeric recognition potency for the tested enantiomers by comparing the electrochemical signals, including the peak current and peak potential. Furthermore, the mechanism is assessed by density functional theory (DFT) calculations in detail.

2. Experimental section

2.1. Chemicals

In this study, all chemicals were of at least analytical reagent grade, and reverse osmosis Milli-Q water (18 M Ω , Millipore, Bedford, MA, USA) was used throughout. L-Tryptophan (L-Trp), D-tryptophan (D-Trp), (*R*)-mandelic acid, (*S*)-mandelic acid, (*R*)-malic acid, (*S*)-malic acid, L-tyrosine (L-Tyr), D-tyrosine (D-Tyr), NaH₂PO₄·2H₂O, Na₂HPO₄·12H₂O and cupric chloride dehydrate (CuCl₂·2H₂O) were purchased from Aladdin Industrial Inc. (Shanghai, China). High-purity graphite rods were obtained from Sinopharm Chemical Reagent Co. Ltd. 3-Chloropropylisocyanate, (1*S*,2*S*)-1,2-diaminocyclohexane and *N*-methyl-imidazole were purchased from Aladdin Industrial Inc, which were used for the synthesis of the designed chiral ionic liquid. (Shanghai, China).

2.2. Apparatus

An ANS JS3030 DC power supply (Wuxi ANS Energy Co. Ltd. China) was used to provide the static potential. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 400 spectrometer (Bruker, Germany) at 400 MHz in [D₆]DMSO. The HRMS was obtained using a Bruker 7-T FT-ICR MS (Bruker, Germany) equipped with an electrospray source. An S-4800 scanning electron microscope (SEM) (Hitachi, Japan) was used to examine the surface microstructures of the material. The transmission electron microscopy (TEM) images were achieved on an FEI Tecnai G²20S-TWIN instrument (FEI Company, Netherlands) operating at an acceleration voltage of 200 kV. The tested samples were prepared by placing a drop on a carbon-coated copper grid that was then dried at room temperature. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer (Thermo Fisher Scientific, USA). Electrochemical experiments were carried out with a CHI 660D electrochemical workstation (CH Instruments, Inc.,

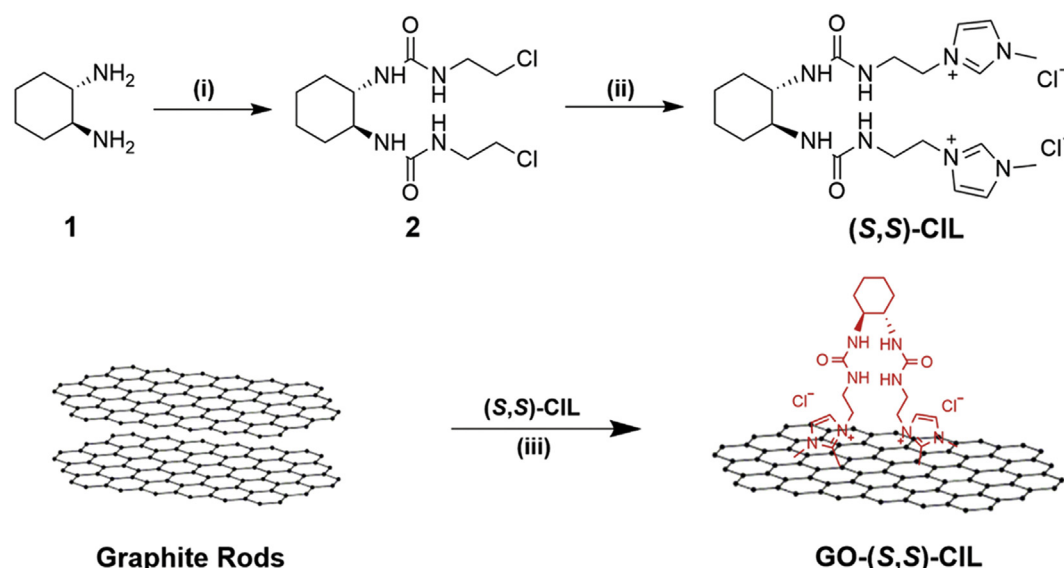


Fig. 1. Synthetic reagents and conditions: (i) thionyl chloride, CH₂Cl₂, 0 °C, 4 h (ii) *N*-methyl-imidazole, CH₃CN, 85 °C, 36 h (iii) 15 V, H₂O, 25 °C, 8 h.

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