Preparation and application of sunset yellow imprinted ionic liquid polymer – ionic liquid functionalized graphene composite film coated glassy carbon electrodes

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ABSTRACT

A novel water-compatible molecularly imprinted ionic liquid polymer – ionic liquid functionalized graphene composite film coated glassy carbon electrode (MIP – rGO-IL/GCE) is presented. It is fabricated by coating a GCE with amine-terminated ionic liquid functionalized graphene (rGO-IL) and then with water-compatible MIP suspension. The water-compatible MIP is prepared by free radical polymerization in methanol-water system using sunset yellow (SY) as template and ionic liquid 1-(α-methyl acrylate)-3-allylimidazolium bromide (1-MA-3AI-Br) as functional monomer, which can interact with SY through π-π, hydrogen-bonding and electrostatic interaction. The resulting MIP – rGO-IL/GCE shows good performance when it is used for the differential pulse voltammetric determination of SY. Under the optimized conditions (i.e. pH 7.5, 0.1 M phosphate buffer, preconcentration under open-circuit for 570 s), the peak current is linear to SY concentration in the ranges of $0.010\,\mu M – 1.4\,\mu M$ and $1.4\,\mu M – 16\,\mu M$ with sensitivities of $5.0\,\mu A/\mu M\,mm^2$ and $1.4\,\mu A/\mu M\,mm^2$ respectively; the detection limit is 4 nM (S/N = 3). The electrode has been successfully applied to the determination of SY in some soft drinks, and the recoveries for the standards added are 95% – 107%.

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1. Introduction

Sunset yellow (SY) is a highly used synthetic dye which is usually added in foods such as beverages, candies and bakery products [1,2]. It can not only improve the appearance and texture of foods, but also make the foods to maintain the natural colour during process and storage [3,4]. However, SY has harmful effects on human beings if excessively consumed [5,6]. Therefore, the use of SY in food products is strictly controlled. In some countries, the permitted maximum content of SY is $100\,\mu g\,mL^{-1}$ (individually or in combination) in nonalcoholic beverages with added juices or flavours [7]. Considering the food safety, the detection of SY is important.

Various methods have been developed for the detection of SY, including high-performance liquid chromatography (HPLC) [6], capillary electrophoresis [8], spectrophotometry [9] and electrochemical method [10]. Among these methods, the electrochemical method has recently become more attractive and a number of electrochemical detection methods have been reported for SY. For example, Song et al. [11] used a multiwalled carbon nanotube (MWCNT) modified glassy carbon electrode (GCE) to detect SY;

the linear detection range was $2.6\,\mu M – 0.59\,mM$ and the detection limit was $1.1\,\mu M$. Gan et al. [10] demonstrated a graphene (GN) layer-wrapped phosphotungstic acid (PTA) hybrid electrode for the simultaneous determination of SY and tartrazine (TT), the linear detection range was $2.2\,nM – 0.66\,\mu M$ and the detection limit was 1.1 nM. Ghoreishi et al. [7] constructed a carbon-paste electrode (CPE) modified with gold nanoparticles for the simultaneous determination of SY and TT, and a linear detection range of $0.10\,\mu M – 2.0\,\mu M$ was obtained. These electrochemical detection methods were quite sensitive, but their selectivity was not enough good.

To improve the selectivity of electrochemical methods, recognition elements should be introduced [12,13]. Among multifarious recognition elements, molecularly imprinted polymers (MIPs), called as 'plastic antibody', are biomimetic recognition materials. They have advantages of high stability, low cost and good selectivity [14,15]. These properties make MIPs attractive in many fields such as sensors [16], antibody mimics [17] and solid phase extraction [18]. However, current technology often generates MIPs for the recognition of target compounds by using methacrylic acid (MAA) or 4-vinyl pyridine (4-VP) as functional monomer, and aprotic or low polar organic solvents as porogen [19]. When polar solvents are present, the interaction between the template and the monomer will be inevitably weakened or disrupted [20]. Thus the recognition

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capacity of MIPs to strong hydrophilic target molecules is generally poor. In addition, when MIPs are prepared in organic solvents, they usually show 'solvent memory' in aqueous media [21]. To overcome the shortcoming, water-compatible MIPs should be synthesized.

Ionic liquids (ILs) are molten salts, consisting of relatively large asymmetric organic cation and inorganic or organic anion. They have many unique characters such as non-volatility, non-flammability, high ion density and high ionic conductivity [22,23], hence they are very useful in many fields including solid-phase microextraction [24] and polymers [25]. Recently, a few molecularly imprinted ionic liquid polymers were reported [19,20,26,27]. As some IL monomers can interact with hydrophilic template molecules, IL-based water-compatible MIPs could be prepared. Thus, the recognition capacity of MIPs to hydrophilic target molecules in aqueous environment could be enhanced.

In general, MIPs are nonconductive. To fabricate MIPs based electrochemical sensors, conductive materials should be introduced. Graphene (GR) displays superior electronic and chemical properties, hence it is suitable for preparing electrochemical sensors [28,29]. Further more, when IL is combined with GR, the resulting composite material presents improved conductivity, compatibility and stability [30]. Thus, GR-IL hybrid is expected to show good performance in constructing electrochemical sensors.

In this paper, a novel IL-based water-compatible MIP and IL-functionalized GR are used to construct a SY sensor. Owing to their synergic effect, the resulting electrochemical sensor exhibits good selectivity, high sensitivity and fast response towards SY. The sensor has been applied to the detection of SY in soft drinks.

2. Experimental

2.1. Reagents and materials

Sunset yellow, Amaranth, Brilliant blue G, Allura red and Tratarzine (Fig. 1) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China) and their stock solutions (0.010 M) were prepared with water and stored in a refrigerator. 2,2'-Azobis-(isobutyronitrile) (AIBN) was obtained from Shanghai Shisihewei Chemical Industry Limited Company (China) and employed after twice recrystallization. Methacrylic acid (MAA) came from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ethyleneglycol dimethacrylate (EDMA) was purchased from Energy-Chemical Company (Shanghai, China). MAA and EDMA were distilled under reduced pressure to remove inhibitors. The ionic liquid 1-(3-aminopropyl)-3-methylimidazolium bromide ($IL-NH_2$) (purity: 99%) was provided by Lanzhou Institute of Chemical Physics (Lanzhou, China) and used as received; hydrazine hydrate (85%) and N-hydroxy succinimide (NHS) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China); 1-ethyl-3-(3-dimethylaminopropyl)-carbodimide hydrochloride (EDC) was from Shanghai Medpep Co. Ltd. 1-(α-Methyl acrylate)-3-allylimidazolium bromide (1-MA-3AI-Br) was synthesized in our laboratory and its structure was confirmed by ^1H NMR, ^{13}C NMR and IR analysis (see Supporting Information). All other chemicals used were of analytical reagent grade. The water used was redistilled.

2.2. Apparatus

Cyclic voltammetric and differential pulse voltammetric experiments were performed with a CHI 620D electrochemical workstation (CH Instrument Company, Shanghai, China). A conventional three-electrode system was adopted. The working electrode was a modified GCE (diameter: 2 mm), and the auxiliary and reference electrodes were a Pt wire and a saturated calomel electrode (SCE), respectively. The scanning electron microscope (SEM) images were obtained using a Hitachi X-650 SEM (Hitachi Co., Japan). Ultraviolet visible (UV-Vis) absorption spectra were recorded by a U-3900 spectrometer (Hitachi Co., Japan). The Fourie transform infrared (FTIR) absorption spectra were recorded with a model Nexus-670 spectrometer (Nicolet, USA). Atomic force microscopy (AFM) images were obtained using a digital Nanoscope IIIa atomic force microscope in tapping mode. Transmission electron microscopy (TEM) images were obtained using JEOL Ltd. All experiments were carried out at room temperature.

2.3. Preparation of ionic liquid functionalized graphene (rGO-IL)

rGO-IL was synthesized according to the literature with minor modification [31]. Briefly, 20 mg graphene oxide (GO) was dispersed in 20 mL water by sonicating for 1 h, then 25 mg EDC and 7 mg NHS were added in the suspension. After sonication for 30 min, 10 mg $IL-NH_2$ was introduced and the mixture was stirred for 24 h at room temperature. The resulted mixture was centrifuged
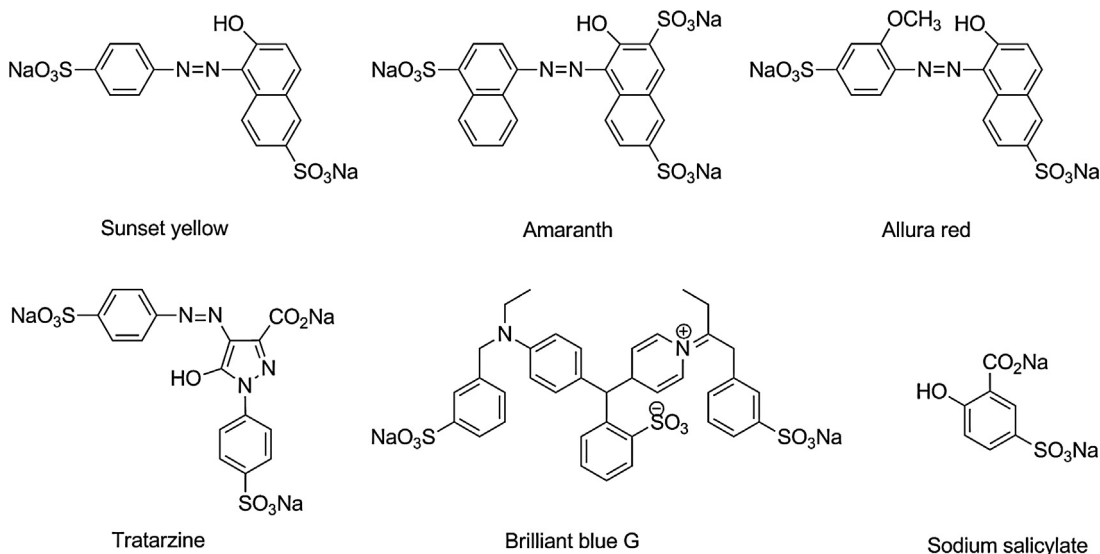

Fig. 1. Molecular structure of sunset yellow and some analogues.