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Detection of allura red based on the composite of poly (diallyldimethylammonium chloride) functionalized graphene and nickel nanoparticles modified electrode

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ABSTRACT

A novel and sensitive electrochemical sensor for allura red determination was developed based on poly (diallyldimethylammonium chloride) (PDDA) functionalized graphene (Gr) and nickel nanoparticles (Ni) composite (PDDA-Gr-Ni). Allura red displayed remarkably increased electrochemical activity on PDDA-Gr-Ni composite modified electrode due to the synergistic effect of the large surface area and improved electron transfer efficiency of both Gr and Ni nanoparticles, which offers the feasibility for highly sensitive determination of allura red by electrochemistry method. The electrochemical properties of allura red on the modified electrode were investigated by cyclic voltammetry and differential pulse voltammetry. Under the optimum experimental conditions, the peak current of allura red was proportional to its concentration in the range of 0.05–10.0 μmol L^{-1} and the limit of detection (LOD) was 8.0 nmol L^{-1}. This simple and sensitive sensor was successfully applied to determine allura red in real sample, which provides an operational access to allura red detection in the field of food safety control.

1. Introduction

Recent food safety events have attracted numerous attention on the food security, especially on the addition of food additives. As one typical family of food additive, low cost and highly stable synthetic dyes are widely used in food industry to increase the food appearance and attraction [1]. However, the excessive consumption of synthetic dyes might bring side effects in human health, such as allergies and asthma [2,3]. Therefore, the content of the synthetic dyes must be strictly controlled. One of the mostly used synthetic dyes is allura red (Fig. 1), which could be found in many commercial food products such as soft drinks, candies, ice cream and bakery products. In spite of its extensive application, its health risk could not be neglected because its azo and aromatic ring groups might potentially damage human beings, hence the detection of its content is extremely important in food industry. In China, its maximum limit in soft drinks is 0.1 g/kg (GB2760-2014). Many analytical methods have been established to detect allura red, such as spectrophotometry [4,5], differential pulse polarography [6–8], cloud point extraction [9,10], high performance liquid chromatography [11,12], capillary electrophoresis [13,14] and electrochemical method [15]. Among them, electrochemical methods are more preferable and have attracted increasing attention because of their high sensitivity, low cost, simple operation, fast response and small size requirement, hence it is feasible to miniaturize instrument for on-site detection. In this work, we fabricated a new and facile electrochemical sensor by the composite of poly (diallyldimethylammonium chloride) (PDDA) functionalized graphene and nickel nanoparticles to sensitively determine the content of allura red.

As one of the most promising materials, graphene (Gr) has attracted considerable attention since its first discovery. The unique single-atom-thick sheet of carbon atoms arrayed in a honeycomb pattern has endowed graphene with excellent properties, such as stiff mechanical strength, large specific surface area and high thermal and electric conductivity, and makes it possible to be applied in various fields such as supercapacitors, batteries, and sensors [16–22]. However, the highly hydrophobic nature of graphene also greatly limits its application because graphene tends to agglomerate irreversibly or restack due to strong π–π stacking interaction and van der Waals forces [17,23–25]. To weaken the hydrophobic interaction between single-atom sheets, various protective reagents and surfactants are introduced to

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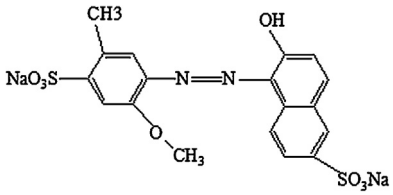


Fig. 1. The structure of allura red.

functionalize the graphene surface and enhance its dispersibility in aqueous solution [26–28]. In this work, we are using poly (diallyldimethylammonium chloride) (PDDA), a strong cationic polymer electrolyte to disperse the hydrophobic graphene and improve electric conductivity. Beside, we also introduce metal nanoparticles to graphene because of their high catalytic activities for many chemical reactions, especially for Co and Ni nanoparticles [29]. The selected metal nanoparticle is nickel nanoparticles (Ni NPs) which have comparable catalytic activity with conventional noble metal catalysts such as Pt and Pd, but lower cost, and has been widely applied in the fields of fuel cells, biosensors and automotive industries [30]. More importantly, the strong catalytic activity of Ni NPs could improve the sensitivity of electrochemical sensors towards some weak electroactive substances. Therefore, by combining the properties of Ni NPs and the PDDA dispersed Gr, it is feasible for electrochemical sensor made by PDDA-Gr-Ni composite modified glassy carbon electrode (GCE) to offer high sensitivity for the detection of allura red.

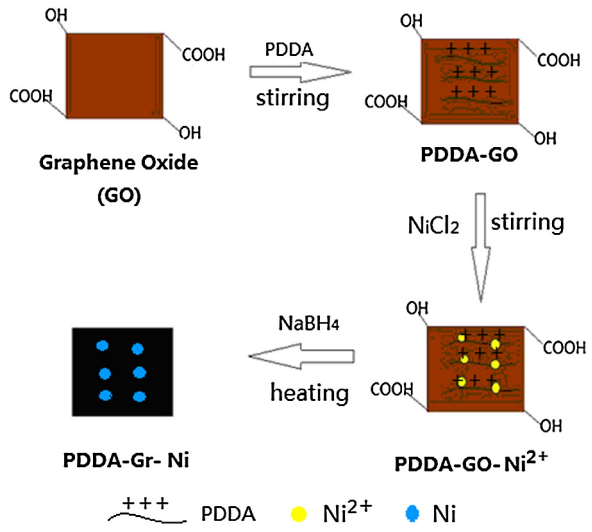
2. Materials and methods

2.1. Reagents

Allura red was purchased from Aladdin Chemistry (Shanghai, China) and dissolved into distilled water to prepare 1.0 mmol L^{-1} standard solution. Poly (diallyldimethylammonium chloride) (PDDA, MW = 200,000–350,000, 20 wt% in water) was purchased from Aladdin Chemistry (Shanghai, China). Ni, Pd, Pt and Co NPs were prepared from nickel chloride ($NiCl_2$), palladium chloride ($PdCl_2$), chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) and cobalt nitrate ($Co(NO_3)_2$), respectively, which were all received from Aladdin Chemistry (Shanghai, China). Phosphate buffer solution (PBS) of 0.1 mol L^{-1} was prepared by mixing of 0.1 mol L^{-1} Na_2HPO_4 aqueous solution and 0.1 mol L^{-1} NaH_2PO_4 aqueous solution and adjusting to a required pH value by HCl or NaOH before using. All the chemicals were of analytical grade and used without further purification. All the aqueous solutions were prepared in distilled water and the experiments were carried out at room temperature (about 25 °C).

2.2. Apparatus

Transmission electron microscope (TEM) images were obtained on JEM-2100 (Japan) with a 200 kV accelerating voltage. UV–vis absorption spectra were acquired on Shimadzu UV-2550s spectrophotometer. X-ray diffraction (XRD, Shimadzu) study was conducted by Cu Ka radiation source (λ = 1.54056 Å). All the electrochemical measurements were performed on RST5000 electrochemical system (Suzhou, China) with a three-electrode system, including a bare glassy carbon electrode (GCE) (3 mm in diameter) as working electrode, a saturated calomel electrode (SCE) as reference electrode, and a platinum wire electrode as auxiliary electrode. The pH values were measured by PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was daily calibrated with standard buffer solution.



Scheme 1. The proposed scheme of the formation of PDDA-Gr-Ni composite.

2.3. Synthesis of PDDA-Gr-metal nanoparticles composite

Graphene oxide (GO) was synthesized from natural graphite powder according to a modified Hummers and Offemans method [31]. Typically, 10 mg GO powder was dispersed in 20 mL water to form a 0.5 mg mL^{-1} GO dispersion after ultrasonication for 1 h. After mixing with 5 mL PDDA, 5 mg $NiCl_2$ was slowly added into the GO dispersion under constantly stirring and stirred for 0.5 h. Then, 20 mg reducing reagent $NaBH_4$ was added and the mixture was allowed to react for 6 h at 80 °C (with constantly stirring). Finally, the mixture was centrifuged at 12,000 rpm for 10 min and washed by water for several times to get a black precipitation of PDDA-Gr-Ni composite, which was later dried in vacuum. The preparation of PDDA-Gr and PDDA-Ni was similar to PDDA-Gr-Ni without addition of $NiCl_2$ or graphene, respectively. The preparation of PDDA-Gr-Pt, PDDA-Gr-Pd and PDDA-Gr-Co composite followed in a similar way but with the addition of $H_2PtCl_6{\cdot}6H_2O$, $PdCl_2$ and $Co(NO_3)_2$ instead of $NiCl_2$. The detailed preparation procedure of PDDA-Gr-Ni composite modified GCE could be found in Scheme 1.

2.4. Fabrication of the electrochemical sensor

The bare GCE was carefully polished by alumina slurry, washed successively by anhydrous alcohol and distilled water in an ultrasonic bath for 3 min, and dried in N_2 blowing. 1.0 mg PDDA-Gr-Ni was added into 5 mL distilled water and sonicated for 1 h to get homogeneously dispersed solution (0.2 mg mL^{-1} PDDA-Gr-Ni). Afterwards, the PDDA-Gr-Ni dispersion was dropped on the freshly prepared bare GCE surface and dried under the infrared lamp. For comparison, PDDA-Gr/GCE, PDDA-Ni/GCE, PDDA-Gr-Pt/GCE, PDDA-Gr-Pd/GCE and PDDA-Gr-Co/GCE were fabricated under the similar procedures.

2.5. Sample preparation and measurement procedures

The allura red solution with concentration of 10 μmol L^{-1} is prepared by diluting dye standard solution with PBS (0.1 mol L^{-1}, pH 3.0). Then the prepared PDDA-Gr-Ni modified GCE was immersed in the above solution. After 5 min accumulation, the CV responses were recorded at the scan rate of 100 mV s^{-1}. Before or after every measurement, the electrode was cleaned by distilled water and the potential scan was repeated successively in triplicate in a blank solution to regenerate the electrode surface. The real