Biosensors and Bioelectronics 64 (2015) 277–284

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

2,6-Diaminopyridine-imprinted polymer and its potency to hair-dye assay using graphene/ionic liquid electrochemical sensor

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ARTICLE INFO

Article history:
Received 1 July 2014
Received in revised form
31 August 2014
Accepted 4 September 2014
Available online 8 September 2014

Keywords:
Molecular imprinting-electrochemical sensor
Graphene
Ionic liquid
Diaminopyridine derivatives detection
Multiple hydrogen bonding
Hair dyes

ABSTRACT

A new analytical approach for detecting diaminopyridine derivatives has been constructed using a molecular imprinting-electrochemical sensor. Opposed to the conventional strategy of employing diaminopyridine as the functional monomer and uracil derivatives as the target analyte, in the current study, the 2,6-Diaminopyridine-imprinted core–shell nanoparticles were synthesized with 2,6-Diaminopyridine as the template molecule and 6-aminouracil as the functional monomer. Graphene and ionic liquid which can assist 2,6-Diaminopyridine-imprinted core–shell nanoparticles in electrochemical reaction kinetics by increasing conductivity have been introduced to form one of the electrode modified layers. The proposed analytical method has been applied in 2,6-Diaminopyridine detection in hair-dyes and demonstrated appropriate sensitivity and selectivity, with a linear range of 0.0500–35.0 mg kg^{-1} and a detection limit as low as 0.0275 mg kg^{-1}.

1. Introduction

For fashion pursuit or practical purpose, more and more people choose to change their hair color or cover their gray hair. Hair dyes with many variations in color tone and brightness become popular among these people. However, hair dye products containing dye intermediates are known to be mutagenic and carcinogenic to animals (Ames et al., 1975; Watanabe et al., 1990). Because of the toxicity of their components, the coloring paste composition is under control of the European Council Directive (76/768/EEC) (Gioia et al., 2005). 2,6-Diaminopyridine (2,6-DAP), based on its good dyeing capacity, is also used as a coupler agent for the hair dye synthesis (Xue et al., 2009). Since the mutagenicity and carcinogenic properties of the components in hair dye is still complicated, the determination of 2,6-DAP, one of the components of hair dye is of significant for human health. Many analytical methodologies such as high-performance liquid chromatography (HPLC) (Wang and Huang, 2005; Zhou et al., 2004), gas chromatography–mass spectrometer (GC/MS) (Tanada et al., 1991; Tanada et al., 1994) and micellar electro kinetic capillary chromatography (MEKC) (Lin et al., 1999) have been introduced to monitor dye intermediates in hair dyes. However, these methods usually require expensive equipments, laborious and time expensive extractions of hair dye components, which make them unsuitable for routine analysis.

Molecularly imprinted materials have attracted considerable research interests due to their ability of selectively recognizing a chemical species through specific binding between a functional monomer and a target molecule. The integration of molecularly imprinted materials into chemical/biological sensors and biomedical materials is considered as a promising strategy (Haupt and Mosbach, 2000; Stephenson and Shimizu, 2007; Alexander et al., 2006; Takeuchi et al., 2000; Shi et al., 1999; Hayden et al., 2006; Hayden and Dickert, 2001). Multi-hydrogen bonding between templates and functional monomers is a valuable tool to stabilize the template-functional monomer complexes during polymerization. Numerous researches about the synthesis and application of molecularly imprinted polymers (MIPs) based on multi-hydrogen bonds have been reported (Kugimiya et al., 2001; Li et al., 2005, 2006; Manesiotis et al., 2005; Tanabe et al., 1995; Yano et al., 1998). Those studies provide us with an inspiration of developing a different molecularly imprinted polymer, acting in a diametrically opposite way, a new molecularly imprinted polymer in which uracil derivative was used as the functional monomer and 2,6-DAP as the template molecule for recognition of diaminopyridine derivatives has been established.

Due to advantages such as high sensitivity, rapid response, ease of control and can realize real-time detection, the electrochemical sensor was chosen to be the analytical method in the proposed paper (Ratautaite et al., 2014; Li et al., 2012a). Since MIPs are

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http://dx.doi.org/10.1016/j.bios.2014.09.016
0956-5663/

generally nonconductive, which limits their application in sensoring, it is necessary to introduce conductive materials to improve the conductivity (Zhang et al., 2012; Matsui et al., 2004; Lakshmi et al., 2009; Li et al., 2012b). Graphene, a single layer of sp^2 hybrid carbon atoms tightly packed into a two-dimensional (2D) lattice (Zhou et al., 2010a) has many superior properties including outstanding electric conductivity, large specific surface area, good mechanical strength and high mobility of charge carriers (Park and Ruoff, 2009; Geim and Novoselov, 2007; Li et al., 2008) and graphene modified electrodes have great potential in designing new electrochemical sensors (Sun et al., 2013). Meanwhile, ionic liquids (ILs), a new class of solvent made of molten organic cations and various anions, due to its unique physical properties of wide electrochemical windows, commendable chemical and thermal stability, high ionic conductivity and low toxicity (Pandey, 2006), can be used not only as the supporting electrolyte but also as the modifier in chemically modified electrode (Sun et al., 2012). Fluids formed from graphene sheets and ILs which increases the applicability of these nanomaterials will open up possibilities for new applications in different fields. For example, The gels formed by ILs and graphene have been studied as potential electrolytes for dye sensitized solar cells by Ahmad et al. (2011). The method proposed by Han and co-workers proved that the dispersion of a small amount of graphene sheets in [bmim][PF_6] could enhance the conductivity of the IL considerably (Zhou et al., 2010b). Zhao and Hu demonstrated that collective Van der Waals forces between ionic liquids and graphene are able to describe both the short-ranged cation-π interaction and the long-ranged dispersion interaction, through a combination of a quantum mechanical calculation on the level of density functional theory (Zhao and Hu, 2013). More recently, it was found that ILs could improve the dispersion of graphene by shielding the π–π stacking interaction among graphene sheets.

In this paper, 2,6-DAP-imprinted core–shell nanoparticles (DICSNs) has been synthesized. A molecular imprinting-electrochemical sensor based on graphene–IL composite has been constructed and applied to the 2,6-DAP detection in hair dyes. Compared with HPLC method, the present sensor showed advantages such as high sensitivity and wide linearity range.

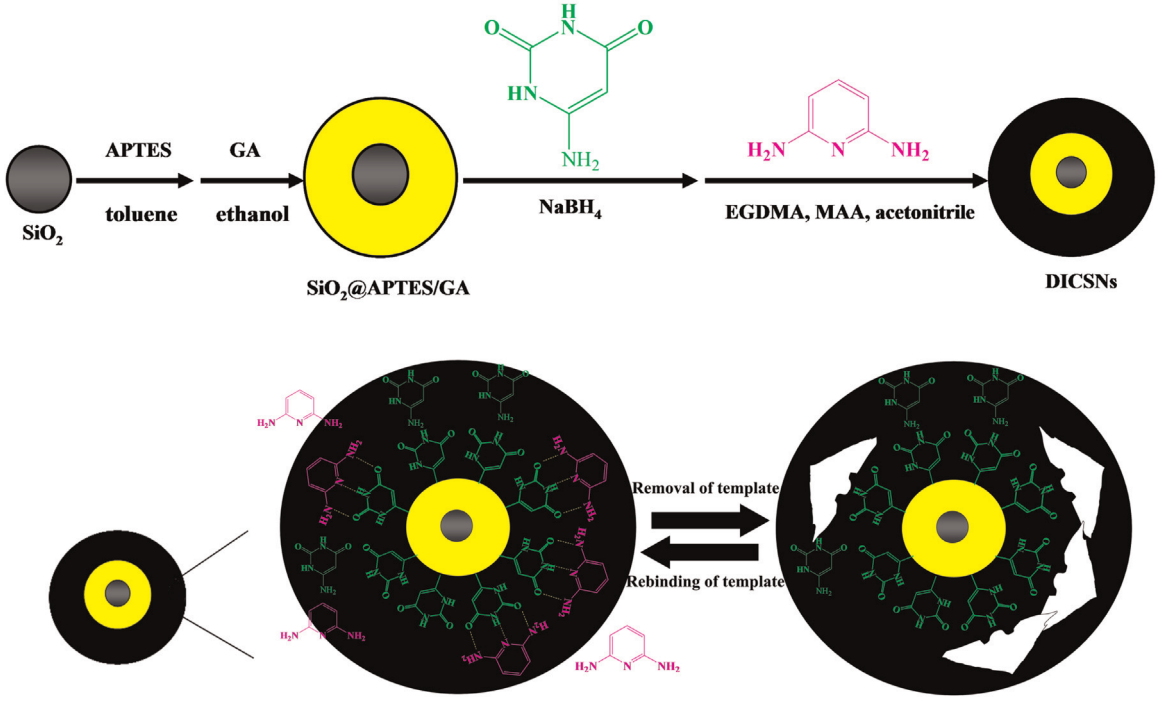
2. Experimental section

2.1. Reagents and materials

2,6-Diaminopyridine (2,6-DAP), 2-Aminopyridine (2APY), 3,4-Diaminopyridine (3,4-DAP), and 3-Aminopropyltriethoxysilane (APTES), were supplied by J&K Scientific Ltd. The ILs, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), 1-propionitrile-3-methyl-imidazolium tetrafluoroborate ([pmim]BF_4), ≥99%, were offered by the Center for Green Chemistry and Catalysis (Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences). 6-aminouracil (6AU), ethylene glycol dimethacrylate (EGDMA), and potassium ferricyanide ($K_3[Fe(CN)_6]$), were obtained from Aladdin Chemistry Co., Ltd. Hydrazine solution (50 wt%) was obtained from Tianjin Guang-cheng Chemical Reagent Factory (Tianjin, China) and glutaraldehyde (GA, 50 wt%) from Damao Chemical Reagent Factory (Tianjin, China). All other chemicals were analytical reagent grade. Ultrapure water, with a resistivity of 18.25 MΩ cm, was obtained from a UPH-IV ultrapure water purifier (Chengdu Ultrapure Technology Co., Ltd. China). Three hair dyes (L'Oréal, HUYO and Zhanghua) for real sample determination were bought from supermarket.

2.2. Synthesis of 2,6-DAP-imprinted core–shell Nanoparticles (DICSNs)

The detailed preparation procedure of DICSNs is illustrated in Scheme 1. The monodispersed silica spheres (SiO_2) were prepared by hydrolysis of TEOS with aqueous ammonia referring to the modified Stöber method reported in our previous work (Zhao and Hao, 2013). The synthesized monodispersed SiO_2 (0.30 g) was mixed with APTES (7.0 mL) and anhydrous toluene (50 mL) in a flask. The mixture was refluxed for 10 h under dry nitrogen. The



Scheme 1. Illustration of the construction of the 2,6-DAP-imprinted core–shell nanoparticles (DICSNs).