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Palladium nanoparticles functionalized graphene quantum dots with molecularly imprinted polymer for electrochemical analysis of citrinin

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ABSTRACT

Citrinin (CIT) is mutagenic and resistant to decomposition. In addition, it is founded in many foods and causes the significant diseases in human body. In this report, an imprinted electrochemical surface based on glassy carbon electrode (GCE) modified with palladium nanoparticles (PdNPs) involved in 5-(4-Hydroxybenzylidenamino)-2-mercaptobenzimidazole (BZ) functionalized graphene quantum dots (GQDs) was formed for CIT analysis. The formation of the surfaces was characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS). CIT imprinted electrochemical surface was formed in the presence of 80.0 mM pyrrole as monomer and 20.0 mM CIT as template. The linearity range and the detection limit (LOD) of the developed nanosensorwere calculated as 1.0×10^{-9}–5.0×10^{-9} M and 2.0×10^{-10} M, respectively.

1. Introduction

CIT, 4,6-dihydro-8-hydroxyl-3,4,5-trimethyl-6-oxo-3H-2-benzopyran-7-carboxylic acid, is isolated from *Penicilliumcitrinum*. It is mutagenic and resistant to decomposition. Thus, it is in many foods (cheese and red yeast rice) [1,2]. Abundant CIT causes important diseases such as liver and kidney and has nephrotoxic and hepatotoxic effects [3,4]. Owing to these effects, CIT is one of the most dangerous chemicals in terms of World Health Organization. In the literature, high-performance liquid chromatography-fluorescence, [4] and micellar electrokinetic capillary chromatography (MEKC) [5] were presented as analytical methods for CIT detection. Nonetheless, these methods have troublesome steps for real sample analysis. In addition, there is much material consumption. Thus, the fast and sensitive analytical methods based on nanocomposite are urgent needed in the literature.

Especially, the significant developments are performed in the production of nanocomposite-supported materials for sensitive and selective nanosensors [6–13]. Nonetheless, there are negative catalytic performances in many sensor systems and electronic devices. To overcome this problem, carbon-based nanomaterials as graphene/graphene oxide (GO) are frequently used in terms of important electronic properties [14,15].

The molecular imprinting technique is based on polymerization around template. The specific cavities related to analyte molecule are easily formed in the polymerization process. Thanks to this method, we can create selective and sensitive sensor systems based on molecularly imprinting polymer (MIP) [16].

Up to now, there is no study on the electrochemical detection of ATR by palladium nanoparticles/molecular liquids/graphene quantum dots nanocomposite with molecularly imprinted polymer. Firstly, palladium nanoparticles/molecular liquids/graphene quantum dots nanocomposite was prepared and characterized by SEM, TEM, EIS and XPS. After that, MIP/PdNPs/BZ/GQDs/GCE were developed in the presence of 80.0 mM pyrrole and 20.0 mM CIT. 1.0×10^{-9}–5.0×10^{-9} M and 2.0×10^{-10} M were calculated for linearity range and LOD, respectively. In addition, the prepared electrode was applied to chicken egg samples for CIT detection with high selectivity and recovery in presence of ochratoxin A (OCH A) and ochratoxin B (OCH B). Finally, the present sensor was stable for 60 days.

2. Experimental

2.1. Materials

CIT, OCH A and OCH B were obtained from Sigma–Aldrich. The stock solutions of CIT (1.0 mM) were prepared according to the literature [17]. Pyrrole, graphite powder, disodium tetrachloropalladate (Na_2PdCl_4),

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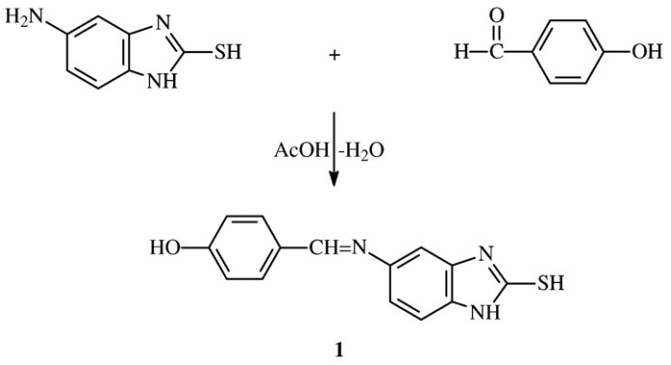

Scheme 1. Synthesis route of compoundBZ (1).

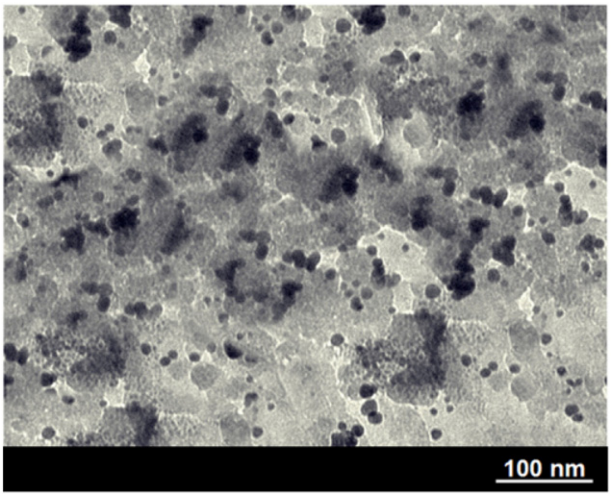

Fig. 1. TEM image of PdNPs/BZ/GQDs.

acetonitrile (MeCN), isopropyl alcohol (IPA), hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$) and N-(3-dimethylaminopropyl)-N-ethylcarbodiimidehydrochloride (EDC) were purchased from Sigma–Aldrich (USA).

2.2. Instrumentation

IviumStat (U·S) equipped with C3 cell stand was used for obtaining differential pulse voltammogram (DPV), cyclic voltammogram and electrochemical impedance curves. XPS and TEM characterizations were applied via PHI 5000 Versa Probe (F ULVAC-PHI, Inc., Japan/USA) and JEOL 2100 HRTEM, respectively. ZEISS EVO 50 analytic microscope (Germany) model was performed for SEM images.

2.3. Synthesis of BZ, GQDs and BZ/GQDs

5-Amino-2-mercaptobenzimidazole (0.01 mol) was dissolved in acetic acid (20 mL) and treated with4-hydroxybenzaldehyde (0.01 mol). After that, evaporated at 50–55 °C in vacuo. After several re-crystallization, the compound BZ was formed (Scheme 1).GQDs was prepared according to our previous literature [18]. GQDs suspension was interacted with 0.2 M EDC solution for 4 h for activation of carboxylate groups. After that, activated GQDs was mixed with 1.0 mM BZ at a 1:1 volume ratio for 2 h (BZ/GQDs).

2.4. Synthesis of Pd NPs and Pd NPs/BZ/GQDs nanocomposite

PdNPs were prepared according to our previous literature [19]. To prepare Pd NPs/BZ/GQDs nanocomposite, 1.0 mg mL^{-1} of PdNPs solution was mixed with 0.1 mg mL^{-1} of BZ/GQDs nanocomposite at volume ratio of 1:1. Finally, the Pd NPs/BZ/GQDs nanocomposite was stored at room temperature.

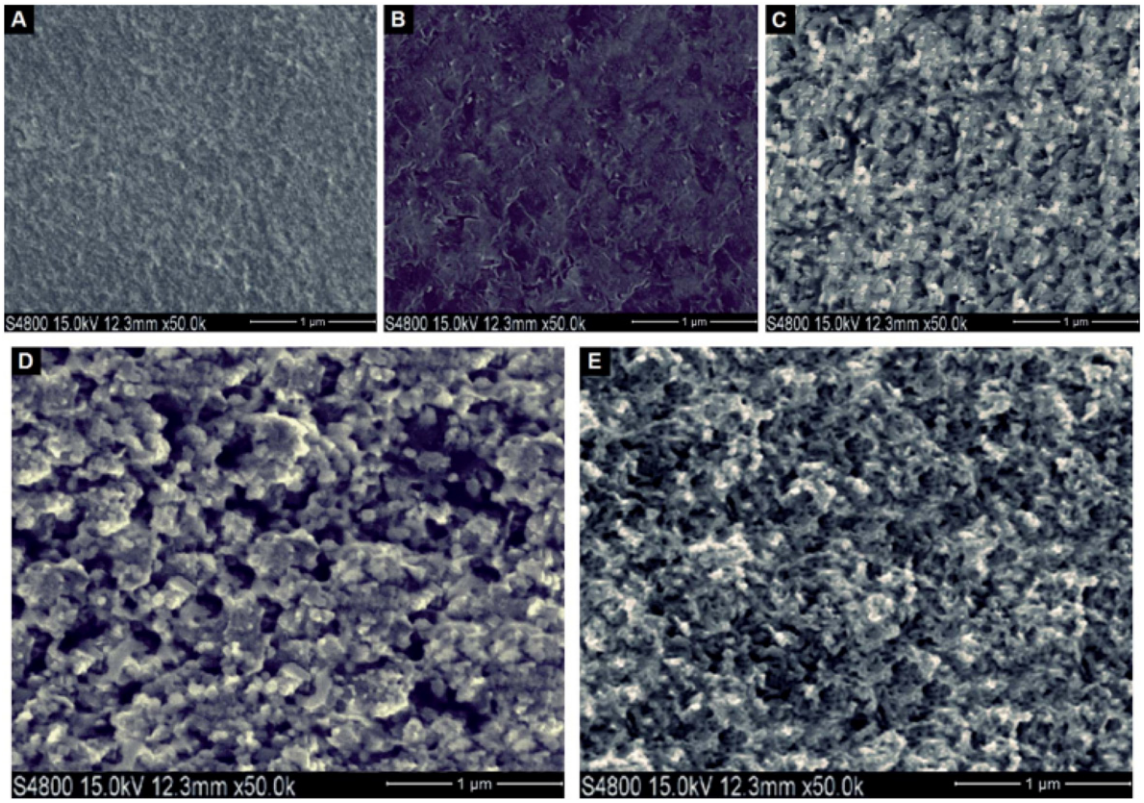

Fig. 2. SEM images of (A) bare GCE, (B) GQDs/GCE, (C) BZ/GQDs/GCE, (D) PdNPs/BZ/GQDs/GCE and (E) MIP/PdNPs/BZ/GQDs/GCE.