



Research Paper

Molecular imprinting polymer with polyoxometalate/carbon nitride nanotubes for electrochemical recognition of bilirubin

Mehmet Lütfi Yola^{a,*}, Ceren Göde^b, Necip Atar^c^a *Iskenderun Technical University, Faculty of Engineering and Natural Sciences, Department of Biomedical Engineering, Hatay, Turkey*^b *Pamukkale University, School of Denizli Vocational Technology, Program of Machine, Denizli, Turkey*^c *Pamukkale University, Faculty of Engineering, Department of Chemical Engineering, Denizli, Turkey*

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ABSTRACT

In this work, a new molecular imprinted sensor based on polyoxometalate ($H_3PW_{12}O_{40}$, POM) functionalized carbon nitride nanotubes (C_3N_4 NTs) nanocomposite was prepared for bilirubin (BR) analysis. The structures of prepared surfaces based on the nanocomposite were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray analysis (EDX). After that, BR imprinted electrode on $H_3PW_{12}O_{40}/C_3N_4$ NTs nanocomposite was developed by cyclic voltammetry (CV) in 100 mM pyrrole containing 25 mM BR. The linearity range and the detection limit of the developed method were calculated as 1.0×10^{-12} – 1.0×10^{-10} M and 3.0×10^{-13} M, respectively. In addition, the imprinted sensor was applied to human plasma samples with high recovery and selectivity.

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1. Introduction

BR is yellow pigment and poorly soluble in water. The breakdown of old red blood cells causes BR which is in low concentrations [1]. BR is present in the body as two ways. (i) conjugated, (ii) unconjugated. Because of its poorly soluble, it passes to the liver. Its abnormal amounts cause the decomposition of eye and skin. Generally, BR can not include in human urine. If it is present, the significant health problems may form in the body. Owing to this situation, the monitoring of BR concentration is very important by using sensitive analytical methods [2–4]. Up to now, several methods such as the diazo coupling and the oxidase enzymatic methods were developed for the determination of BR [5,6]. In addition, several spectrophotometric methods were employed in the literature [7]. Nevertheless, the crucial interference problems are present in these methods. Due to these reasons, more sensitive, favorable portability, low-cost, simple and selective sensors based on nanomaterials are needed in terms of health safety. Hence, the highly selective methods for sensitive sensor applications have been presented. Molecular imprinting technology (MIT) is a method based on the formation of molecular imprinted polymer (MIP). It is the polymerization method by using monomer and target molecule [8]. In the development of

electrochemical nanosensor, the nanomaterials such as graphene/graphene oxide, carbon and carbon nitride nanotubes are utilized to improve the sensitivity. These nanomaterials have important advantages such as high surface area, electrical conductivity, thermal and mechanical stability [9,10].

Among nanomaterials, graphitic carbon nitride ($g-C_3N_4$) and ultra-thin graphitic carbon nitride ($utg-C_3N_4$) are one of the most stable carbon nitride materials. They have layered structures. There are van der Waals interactions between C–N layers. Like graphene/graphene oxide, they are utilized for nanotechnology applications such as photocatalysis or biosensing [11–13]. Especially, C_3N_4 NTs can increase electron transfer and reduce mass transfer resistance due to the active sites [14,15].

Polyoxometalates (POMs) have the anionic ion clusters including d-block transitional metal-oxides. They have both of redox behavior and photo-electrochemical behavior [16,17]. In addition, they are frequently used in homogeneous/heterogeneous processes. Especially, the reduced forms can facilitate the electron and proton transfer. Hence, they act as efficient donors and effective reducing agents [18].

In this study, the molecular imprinting technique was used for formation of selective active sites relating to BR. Firstly, polyoxometalate/carbon nitride nanotubes nanocomposite was prepared by hydrothermal treatment. After that, BR imprinted electrodes were formed on polyoxometalate/carbon nitride nanotubes modified electrode by using CV for 5 cycles. Finally, the

* Corresponding author.

E-mail address: mehmetyola@gmail.com (M.L. Yola).

prepared electrode was applied to human plasma samples for BR detection. According to the results, minimal waste formation in preparation of polyoxometalate/carbon nitride nanotubes nanocomposite is seen. The prepared MIP sensor is sensitive, selective, fast and cheap. In addition, BR analysis with high recovery in human plasma samples is firstly performed by MIP/H₃PW₁₂O₄₀/C₃N₄ NTs/GCE. We can say that the analytical method in this report can be preferred in comparison with the other methods.

2. Experimental

2.1. Materials

BR, ascorbic acid (AA), uric acid (UA) galactose (GAL) and dopamine (DOP) were obtained from Sigma–Aldrich. The stock solutions of BR (1.0 mM) were prepared by acetonitrile and the stock solution was diluted with 0.1 M phosphate buffer (pH 4.0). H₃PW₁₂O₄₀, pyrrole, melamine, acetonitrile (MeCN), ethanol, isopropyl alcohol (IPA), trichloroacetic acid (TCA) and activated carbon were purchased from Sigma–Aldrich (USA).

2.2. Instrumentation

Square wave voltammograms (SWVs) and cyclic voltammograms were carried out by IviumStat (U.S) equipped with C3 cell stand. PHI 5000 Versa Probe (Φ ULVAC-PHI, Inc., Japan/USA) was utilized for XPS analysis with monochromatized Al K α radiation (1486.6 eV) as an x-ray anode operated at 50 W. JEOL 2100 HRTEM (JEOL Ltd., Tokyo, Japan) and ZEISS EVO 50 SEM (GERMANY) analytic microscopies were utilized for the characterization of nanocomposites.

2.3. Preparation of utg-C₃N₄, C₃N₄ NTs and H₃PW₁₂O₄₀/C₃N₄ NTs

The utg-C₃N₄ and C₃N₄ NTs were prepared according to our previous report [9]. 0.1 g of H₃PW₁₂O₄₀ was dissolved in 20 mL HCl (2.0 mol L⁻¹). The 0.1 g solution of H₃PW₁₂O₄₀ added into 1.0 g of utg-C₃N₄. After the stirring for 1 h, the suspension was subject to hydrothermal treatment at 150 °C. The suspension was dried at 60 °C and H₃PW₁₂O₄₀/C₃N₄ NTs (1:10) was obtained [19].

2.4. Procedure for the electrode preparation

The used electrodes in this study such as bare GCE, utg-C₃N₄/GCE, H₃PW₁₂O₄₀/GCE, C₃N₄ NTs/GCE and H₃PW₁₂O₄₀/C₃N₄ NTs/GCE

were cleaned and developed according to the our previous report [20].

2.5. Preparation of BR imprinted voltammetric sensor

The BR imprinted sensor (MIP/H₃PW₁₂O₄₀/C₃N₄ NTs/GCE) was prepared by cyclic voltammetry for 5 cycles in 100 mM pyrrole containing 25 mM BR in 0.1 M phosphate buffer (pH 4.0) (Scheme 1). In addition, for a control experiment, non-imprinted voltammetric sensor without BR (NIP/H₃PW₁₂O₄₀/C₃N₄ NTs/GCE) was prepared.

2.6. BR removal from electrode surface

The 1.0 M NaCl was used as desorption solution for eliminating electrostatic interactions between pyrrole and BR molecules. BR imprinted electrode was dipped into 25 mL NaCl solution. After 15 min, the electrode was dried with nitrogen gas.

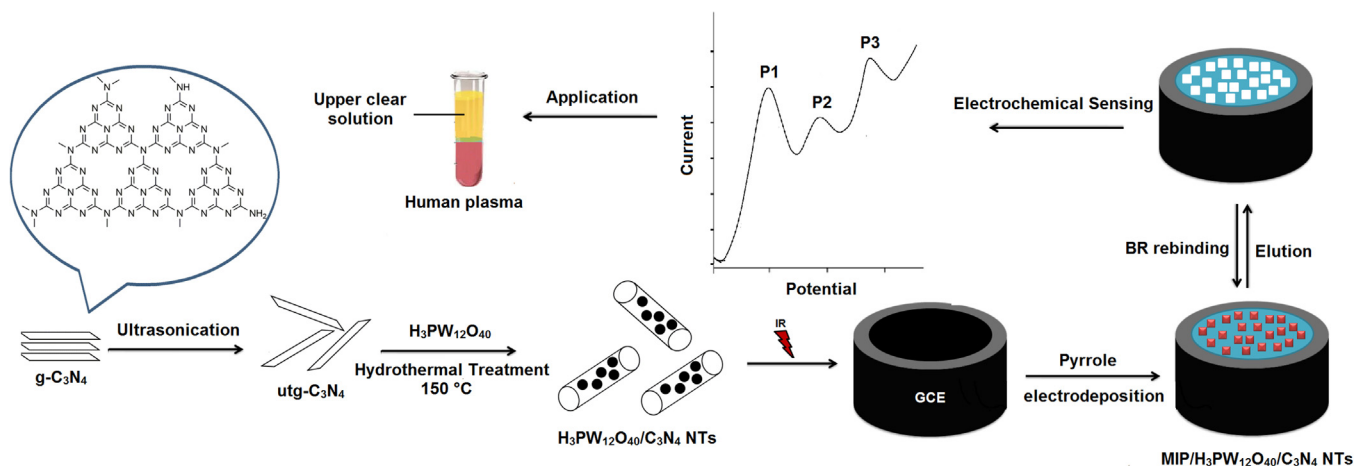
2.7. Sample preparation

The sample was prepared according to our previous report [21]. The upper clear solution was diluted with 0.1 M phosphate buffer (pH 4.0).

3. Results and discussion

3.1. Characterization of nanostructures

Fig. 1A demonstrates the bulk structure of graphitic carbon nitride. After the ultrasonication, the utg-C₃N₄ was successfully formed (Fig. 1B). After the hydrothermal treatment of utg-C₃N₄ at 150 °C, the formation of tubular carbon nitride occurred. Fig. 1C confirms the carbon nitride nanotubes. Fig. 1C also showed that C₃N₄ NTs had open ends. These C₃N₄ NTs had diameters ranging from 150 to 200 nm. Fig. 1D shows the TEM image of H₃PW₁₂O₄₀/C₃N₄ NTs nanostructure. According to the TEM image, the clouds of POM stick to the inner and outer surfaces of carbon nitride nanotubes. Fig. 1D shows nanojunction structure (diameters ranging from 150 to 200 nm) with cross-linking and the nanopore structure formed by cross-linked sheets. Hence, we can say that the interfacial interaction between H₃PW₁₂O₄₀ and C₃N₄ NTs provides the formation of H₃PW₁₂O₄₀/C₃N₄ NTs nanostructure. In addition, EDX analysis confirms the formation of H₃PW₁₂O₄₀/C₃N₄ NTs nanostructure. The C, N, O, P and W elements in the nanocomposite



Scheme 1. The preparation of MIP/H₃PW₁₂O₄₀/C₃N₄ NTs/GCE.

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