Applied Surface Science 455 (2018) 455–464

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Polydopamine grafted on an advanced Fe_3O_4/lignin hybrid material and its evaluation in biosensing

Artur Jędrzak[a,b], Tomasz Rębiś[c], Marek Nowicki[d,e], Karol Synoradzki[f,g], Radosław Mrówczyński[b], Teofil Jesionowski[a,*]

[a] Institute of Chemical Technolwwwogy and Engineering, Poznan University of Technology, Berdychowo 4, PL-60965 Poznan, Poland
[b] NanoBioMedical Centre, Adam Mickiewicz University in Poznan, Umultowska 85, PL-61614 Poznan, Poland
[c] Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, PL-60965 Poznan, Poland
[d] Institute of Physics, Faculty of Technical Physics, Poznan University of Technology, Piotrowo 3, PL-60965 Poznan, Poland
[e] Centre for Advanced Technologies, Adam Mickiewicz University, Umultowska 89C, 61-614 Poznan, Poland
[f] Institute of Molecular Physics, Polish Academy of Science, Smoluchowskiego 17, PL-60179 Poznan, Poland
[g] Institute of Low Temperature and Structure Research, Polish Academy of Science, Okólna 2, PL-50422 Wroclaw, Poland

ARTICLE INFO

Keywords:
Magnetite
Lignin, polydopamine
Advanced (bio)hybrid
Glucose oxidase
Glucose biosensor

ABSTRACT

In this paper, a synthesis and physicochemical characterization of a novel magnetite/lignin (Fe_3O_4/Lig) and magnetite/lignin/polydopamine (Fe_3O_4/Lig/PDA) materials are presented as a novel and effective platforms for an enzyme immobilization or biosensing application. The hybrid has interesting features like improved thermal and mechanical stability, excellent adhesion for inorganic and organic materials, transferability of electrons and photothermal properties. In order to characterize features of the materials, carried out Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), thermogravimetry analysis (TGA), electrokinetic potential (zeta), and magnetic measurements (SQUID). From the TEM analysis, magnetite/lignin hybrid is proved to be covered by a 2–3 nm uniform layer of polydopamine.

In a further study, the resultant functional biomaterial Fe_3O_4/Lig and Fe_3O_4/Lig/PDA were used to immobilize glucose oxidase (GOx). The immobilization capacity of 26.92 and 29.24 mg/g were achieved for Fe_3O_4/Lig and Fe_3O_4/Lig/PDA, respectively.

After mixing of the materials with graphite and ferrocene, the modified carbon paste electrodes CPE/Fe_3O_4/Lig/GOx/Fc and CPE/Fe_3O_4/Lig/PDA/GOx/Fc were obtained and they were tested for application as bioelectrochemical glucose sensing system. The linear ranges of CPE/Fe_3O_4/Lig/GOx/Fc and CPE/Fe_3O_4/Lig/PDA/GOx/Fc were from 0.5 to 4.5 and 0.5–9.0 mM glucose, respectively. The hysteresis loops of the prepared materials show no coercivity and remanent magnetizations at room temperature, exhibiting typical superparamagnetic behavior.

1. Introduction

The dynamic development of the technology has contributed to the intensification of research into the creation of more innovative materials, characterized by enhanced properties than their original components. Such demands can be fulfilled by various organic–inorganic hybrid materials that were previously widely used as metal ion adsorbents [1], matrix for enzyme immobilization [2], catalysts [3] or materials for hydrogen storage [4] and biosensors constructions [5]. The development of new advanced materials for glucose biosensor have gained enormous attention due to the need for a cheap and effective blood glucose monitoring. Great efforts have been focused on the preparation of novel hybrid materials combined with glucose oxidase for amperometric glucose biosensors and immobilization process [6].

Immobilization is defined as a method of confining molecules or biomolecules like enzymes, microorganism, cells etc. on selected supports, including hybrid inorganic/organic materials [7,8]. According to the various method of enzymes' immobilization, the binding of the biomolecules may occur more or less permanently, influence on increasing the efficiency of catalytic processes, and improve the properties of enzymes [8–11]. In addition, the variable reaction parameters might affect enzymes' properties. Among the most significant

* Corresponding author.
E-mail address: teofil.jesionowski@put.poznan.pl (T. Jesionowski).

https://doi.org/10.1016/j.apsusc.2018.05.155
Received 20 February 2018; Received in revised form 15 May 2018; Accepted 20 May 2018
Available online 23 May 2018
0169-4332/

parameters are pH condition and temperature, which can cause protein denaturation process [9,12]. The application of immobilized enzymes might result in greater process efficiency compared with the use of native enzymes, due to the crucial changes of enzymes' condition (stable biocatalysts, prevention entering proteins to the process, easier and faster separation) immobilization processes are used in many industry fields, mainly in pharmacy, nanomedicine, food factories, chemical industries or in enviromental protection [8–12].

The novel hybrid materials due to the influence of the metallic oxides exhibited enhanced adsorption parameters as well as biocompatibility and bioactivity. For instance German et al. used gold nanoparticles (Au-NPs) on a carbon rod electrode modified with glucose oxidase. They are used colloidal Au-NPs applying electrochemical deposition on a graphite rod electrode. Then they immobilized and performed immobilization of GOx [13,14].

Hu et al., presented a synthesis of Fe_3O_4/g-C_3N_4/HKUST-1 composites as a novel biosensor platform for ochratoxin A and Li et al. published novel sensing platform assisted decoration of TiO_2 nanotube arrays with enzyme [15].

Another interesting application of Fe_3O_4 based hybrid material was proposed by Hoskins and co-workers. In their study, they used combination of magnetic particles of iron oxide and nanogold for biomedical application [16].

Zhao's team has been involved in the removal of arsenic(III) ions using CuO-Fe_3O_4 bifunctional magnetic material. In short time arsenic (III) ions were irradiated with light and oxidized to less toxic arsenic(V) ions and adsorbed on nanoparticle surfaces with high yield [17].

Zhang et al. were carried out a synthesis of silver nanoparticles (Ag) on functionalized nanoparticles of polydopamine-graphene (PDA-GNS) with uniform and high dispersion. The resulting Ag-PDA-GNS hybrid material exhibited strong antimicrobial properties [18]. Amirbandeh et al., conducted research on triazine-functionalized Fe_3O_4/graphene oxide nanocomposite. They used magnetite nanoparticles combined with graphene and checked its stability and reusability of glucoamylase immobilization [19].

In this work, we introduce synthesis of new hybrid materials based on magnetite/lignin (Fe_3O_4/Lig) and magnetite/lignin/polydopamine (Fe_3O_4/Lig/PDA) showing interesting physicochemical properties in results. The used component like magnetite [20,21], kraft lignin [22,23] and polydopamine [24,25] are characterized by well-known and sophisticated features. In next step, the immobilization of the glucose oxidase from *Aspergillus niger* [26] was effectively performed on the surface of newly prepared hybrid materials.

As a result, a second generation biosensor system with Fe_3O_4/Lig/PDA/GOx matrix and ferrocene as a redox mediator was proposed. The biosensor was then subjected to electrochemical analysis. The obtained results, (cyclic voltammetry, chronoamperometry), show that the constructed electrode system can be applied for the determination of glucose at a concentration range of 0.5–9.0 mM.

2. Experimental

2.1. Materials and chemicals

The reagents used in this work were iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ammonia solution (25%), citric acid, dopamine hydrochloride, kraft lignin, phosphate (PBS) buffer (pH 7.4; 10 mM), citric buffer (pH = 5.0; 10 mM), glucose oxidase from *Aspergillus niger* and glucose. To basic attempts to build biosensor, used carbon paste electrode (CPE) body with a hole (3 mm diameter), ferrocene, and commercial carbon paste. The chemical reagents were purchased from Sigma-Aldrich, except CPE and carbon paste (BASi, USA). All reagents and solvents were of reagent-grade quality.

2.2. Synthesis and modification of magnetite

Synthesis of the magnetite nanoparticles was carried out by the co-precipitation method by using hydrated iron chlorides (2 g of $FeCl_2{\cdot}4H_2O$ and 4 g of $FeCl_3{\cdot}6H_2O$). The iron chloride salts were dissolved in 8 mL of fresh deionized water and flow all mixture with nitrogen bubbling gas at a temperature of 80 °C. A 2 mL of $NH_3{\cdot}H_2O$ (25%) was dosed to receive the magnetite. The reaction time was 30 min, after that the temperature of the whole mixture increased to 90 °C. The magnetite were collected by an external magnetic field and raised by the deionized water to purified received magnetite. The magnetite was than dried and prepare to modification by (3-aminopropyl)triethoxysilane (APTES). In this case, uses a solution of APTES: water: methanol in ratio 1:4:16. In the crystallizer, a previously weighed 2 g of magnetite was added, to which were added small doses (several drops) of the previously obtained modifier of the solution. After adding the entire amount of the modifier solution, the magnetite was transferred to a dryer where it was dried for 24 h at 40 °C.

2.3. Magnetite/lignin preparation

The magnetite/lignin (Fe_3O_4/Lig) synthesis was initiated by mixing of 120 mL of dioxane and 14 mL of water were mix. Then 2 g of kraft lignin was weighed and added to a solution in a glass reactor where all the ingredients were subjected to a mechanical stirring by IKA WERKE stirrer at a rotational speed of 550 rpm. Then a solution of sodium iodide (3 g $NaIO_4$ + 60 mL H_2O) was prepared in the beaker, which was added to the mixture placed in the reactor with a peristaltic pump to activate lignin. In addition, the space that contained all the components was covered with aluminum foil so that the oxidation process would take place only under the influence of the added oxidant. The dosing rate was 6 mL/min. Upon completion of dosing of the lignin activating solution, 2 g of the previously modified magnetite was added. The synthesis of magnetite with lignin lasted 1 h. Upon completion of the synthesis, the contents of the flask were placed on a vacuum evaporator to evaporate the dioxane and water from the reaction system. The material was then placed in an oven at 40 °C for 24 h to completely dry the product. The dried Fe_3O_4/Lig carrier was crushed on a mortar, washed several times with distilled water and centrifuged on a centrifuge. This treatment was designed to remove unreacted ingredients.

2.4. Magnetite/lignin hybrid covering by polydopamine- (Fe_3O_4/Lig/PDA)

To cover the magnetite/lignin hybrid material, used 200 mg of Fe_3O_4/Lig, 200 mg of dopamine hydrochloride (DOPA·HCl) and 200 mL of 2-amino-2-hydroxymethyl) propane-1,3-diol (TRIS) at a concentration of 10 mM, pH 8.5. All components were transferred to a flask and subjected to a polymerization process using magnetic stirring, which was carried out for 5 h at a pH of 8.5. Then, the obtained product Fe_3O_4/Lig/PDA was isolated using an external magnetic field and washed several times with distilled water to remove the unreacted substrate. The resulting material was allowed to dry for 24 h in a dryer at 40 °C until completely dry. Then the resulting material was crushed on the mortar.

2.5. Physicochemical analysis

To determine functional groups presented in the structure of the precursors and obtained composite was subjected to Fourier transform infrared spectroscopy (FTIR). FTIR spectra were prepared using a Vertex 70 spectrometer (Bruker, Germany). Materials were analyzed in the form of tablets, made by mixing 250 mg of anhydrous KBr and 2 mg of the analyzed substance under a pressure of 10 MPa. The FTIR analysis were performed at a resolution of 0.5 cm^{-1} in the wavenumber range 4000–500 cm^{-1}. To determine the surface morphology of the obtained products scanning electron microscope (SEM), transmission