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Structural and electrochemical properties of multifunctional silica/lignin materials

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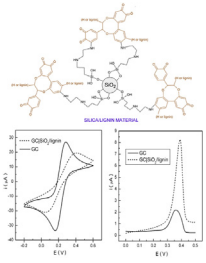
HIGHLIGHTS

- Synthesis of silica/lignin materials.
- Materials characterisation applying NIBS, SEM, FT–IR, and XPS techniques.
- Electrophoretic deposition of the silica/lignin material on the electrode surface.
- Electrochemical properties of the silica/lignin-modified electrode.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis and characterisation of silica/lignin materials is described. Silica was synthesised by the modified Stöber method and its surface was functionalised with aminosilane. The organic matrix was the activated Kraft lignin (KL). The materials obtained were subjected to thorough characterisation (physicochemical, dispersive, morphological and electrochemical) by the NIBS, SEM, FT–IR, and XPS methods. Results of the characterisation permitted evaluation of the application possibilities of the products and the choice of the best ones for specific applications. Because of high negative ionic charge the material particles could be effectively deposited on positively polarised glassy carbon electrode by electrophoretic deposition. The silica/lignin modified electrode showed enhanced charge transfer resistance for anionic redox probe (ferrocyanide/ferricyanide couple) and an enhanced capability to the adsorption of silver cations. The latter property could be exploited in anodic striping voltammetry of silver.

1. Introduction

Lignin is a complex aromatic biopolymer composed mainly of *p*–coumaryl, coniferyl and sinapyl alcohols as three fundamental monomers differing in methoxylation degree [1–5]. It is one of the most frequently met renewable substances in the world after cellulose and natural oils [4]. This natural biopolymer makes about 30% of organic carbon in the biosphere [2], e.g. in plant cells. There are different processes permitting isolation of lignin from plants and obtaining lignin materials of specific properties like e.g. Brauns lignin [6], dioxane acidolysis lignin [7], Klason lignin [8] or Kraft lignin [9,10]. Lignin is an important initial material in many chemical syntheses and in production of biocomposites of target properties. Some lignin derivatives interact with living organisms. For instance Kraft lignin shows a high anti-oxidation activity of human red blood cells [11]. Other derivatives of lignin dissolved in

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water show antiviral activity [12]. Lignin has been found to play an important role in absorption of bile acids so affect the metabolism of lipids [13]. Moreover, lignin extracted form black lye in the Kraft process shows a high adsorption ability of heavy metal ions (1587 mg g^{-1} for Pb and 73 mg g^{-1} for Zn at 30 °C) [14].

A very popular material applied in many branches of science and industry is silica, which is characterised by a number of desirable properties such as high hardness, chemical resistance, chemical reactivity and highly developed surface area. There are many mechanisms of silica syntheses; the most popular are flame method [15,16], hydrolysis and condensation of silicon alkoxides (Stöber method) [17,18], precipitation from a water solution of sodium silicate [19–21], as well as synthesis from emulsion systems [22,23]. Silica of the best properties and most popular for applications is obtained by the method proposed by Stöber and others. This method gives a colloidal silica of spherical particles obtained by hydrolysis and polycondensation of tetraalkoxysilanes catalysed by a mixture of water, ammonia and alcohol [24–26]. Because of their specific physicochemical and electrochemical properties, silicas are applied in many branches of industry. They are the auxiliary products in pharmaceutical industry [27], supports of new and effective catalysts [28,29], fillers in paint and paper production, active fillers of plasto- and elastomers [30,31]. Walcarius [32,33] has shown that silica is also attractive for electrochemical applications as a matrix in chemically modified electrodes. According to the same author the nearest future will bring significant progress in development of syntheses of new mesoporous and ecological materials based on silica [34], which will permit implementation of new type of electrodes and stimulate development of electrochemical methods.

Also various technical lignins where found to be valuable electrode modifiers in the development of electrochemical sensors [35–37] and energy storing materials [38–40].

Recently, much attention has been directed to the search for new generation organic-inorganic biocomposites characterised by high quality and functionality. A natural consequence is the attempt at producing biocomposites of new type, based on lignin built in the silica matrix. However, so fare, the modification of silica with lignin has been undertaken by only few groups whose results have shown that the materials obtained in this way can be used for sorption of harmful and toxic organic compounds and heavy metal ions [41–43] or as polymer fillers [44,45]. The physicochemical, electrokinetic and electrochemical properties of this group of materials reported in this work suggest that they can be also applied for production of a new type of modified electrode materials.

2. Experimental

2.1. Reagents

The main substrates for the synthesis of silica by the modified Stöber method applied in this study were: 95% ethyl alcohol (analytical grade) made by CHEMPUR, Poland; 25% ammonia (analytical grade), POCh SA, Poland and tetraethoxysilane TEOS (analytical grade) purchased from Sigma–Aldrich, USA. *N*–2–(aminoethyl)–3–aminopropyltrimethoxysilane was used as a modifying agent and for activation of silica surface, Kraft lignin was the main component of the biocomposite and sodium periodate was the agent used for oxidation of functional groups of lignin, all these reagents were purchased at Sigma–Aldrich, USA. Another reagent used 1,4–dioxane (analytical grade) was made by CHEMPUR, Poland. Silver nitrate was purchased from POCh SA, Poland. Analytical reagent grade chemicals and double–distilled water were used to prepare buffers used for electrochemical studies.

2.2. Silica/lignin material synthesis

For the purpose of this study, silica was synthesised by the modified Stöber method. The silica was obtained in a few stages by hydrolysis and polycondensation from 50 cm^3 ethyl alcohol (95%), 11 cm^3 aqua ammonia $NH_3 \cdot H_2O$ (25%) and 17 cm^3 tetraethoxysilane (TEOS).

The substrates were placed in a reactor and intensely stirred (1800 rpm) by a high-speed stirrer Eurostar Digital IKA Werke GmbH, Germany. The synthesis duration was 1 h. The reaction gave white silica precipitate which was filtered off from the post-reaction mixture by filtering under reduced pressure. The product was three times washed with ethyl alcohol. Each time after addition of alcohol, the silica containing solution was subjected to sonification for about 5 min in an ultrasonic bath SONIC–3 made by Polsonic, Poland, and filtered off under reduced pressure. In the final stage of the process the silica was additionally washed with abundant amount of distilled water. To remove moisture, the sediment was subjected to convection drying in a stationary drier made by Memmert, Germany (105 °C, 24 h). The silica obtained was subjected to preliminary modification with *N*–2–(aminoethyl)–3–aminopropyltrimethoxysilane in order to activate the material (5 wt. parts of silane per 100 wt. parts of silica). The hydrolysed modifier dissolved in a mixture of water/methanol at the rate of 1:4 (v/v) was applied to the silica surface with the help of an atomiser, then the solvent was distilled off by vapour distillation.

At the next stage the silica modified with the silane was subjected to another modification with Kraft lignin. This process started with making two initial solutions: solution 1 was composed of lignin dissolved in a mixture of dioxane/water at the rate 9:1 (v/v) and was prepared in a three-necked flask, solution 2 (oxidising solution) was composed of sodium periodate dissolved in 30 cm^3 of water. Solution 2 was introduced in doses with the help of a peristaltic pump to solution 1 upon continuous stirring at (1000 rpm). The process of oxidation was performed with no access of light. After completion of solution 2 application, the system was stirred for about 30 min more. To thus obtained mixture the silane-modified silica was added, upon continuous stirring for 1 h. After this time, dioxane was distilled off (Büchi Labortechnik, Switzerland). The final product, which was the silica/lignin material, was filtrated, washed with water and next dried at 105 °C for about 24 h. Methodology of the silica/lignin materials production in Fig. 1 is presented.

In the above-described way, six samples were prepared which differed in the proportion of wt. parts of lignin to 100 wt. parts of silane-modified silica being the matrix of the material.

2.3. Physicochemical characterisation

Dispersive and morphological properties of the samples were characterised by their particle size determination using Zetasizer Nano ZS (0.6–6000 nm) and Mastersizer 2000 (0.2–2000 μm) made by Malvern Instruments Ltd., UK, whose operation is based on the non-invasive backscattering (NIBS) and laser diffraction techniques, respectively. To get the information on the dispersion, particles morphology and type of agglomeration in the samples, the images estimated by a scanning electron microscope (SEM) made by Zeiss EVO40, Germany, were analysed. Electrokinetic curves of the initial powders and the materials produced were determined by electrophoretic light scattering (ELS) on a Zatasizer Nano ZS instrument equipped with an autotitrator. Zeta potential was measured for the sample placed in a 0.001 M solution of NaCl. The percent contents of the elements N, C, H and S in the samples were determined by a Vario EL Cube analyser, Elementar Analysensysteme, Germany. The presence of desired functional groups