



## Advanced electroactive materials based on lignosulfonates

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Lignin is an abundant biopolymer on earth, present in all woods and grasses. In its native form, it is insoluble in any solvent and therefore useless for solution chemistry, in spite of its documented antioxidant properties. On the other hand, chemical derivatives of lignin (technical lignins) are produced in the quantities of millions of tons per annum as a by-product in the production of cellulose from wood or other plant materials. Depending on the technology used, technical lignins differ in molecular weight, chemical composition and the structure of chemical moieties that make them soluble in organic solvent or even in water. Of particular interest are lignosulfonates that exhibit both poly-electrolyte and poly-phenol character due to the presence of ionizable and hydrophilic sulfonic moieties and substituted phenol groups responsible for their reducing properties. In this report, we demonstrate that technical lignosulfonates can be used as both reducing and stabilizing agents for cost-effective synthesis of various nanoparticles including noble metal nanoparticles and transition metal hexacyanoferrates that show valuable multifunctional electrochemical properties. The obtained hybrid materials show multiple redox activity due to the presence of lignin-derived quinones. Therefore, such materials can be used as energy storing materials or sensing platforms for electrochemical sensors (Fig. 1). Lignosulfonates and lignosulfonate-stabilized nanoparticles can be also introduced into chemically or electrochemically polymerized conducting polymers e.g. polyaniline, polypyrrole and poly-ethylenedioxythiophene. Lignosulfonic acid (LS1) and partially desulfonated lignosulfonic acid (LS2) were oxidatively deposited on a preactivated glassy carbon (GC) electrode, giving rise to redox active films showing three distinct redox couples at midpeak potentials ( $E^{\circ}$ ) of 0.22, 0.44, and 0.53 V (vs Ag/AgCl in 0.1 M H<sub>2</sub>SO<sub>4</sub>). The redox activity was assigned to quinone moieties of different degrees of substitution, formed upon the oxidation of electroactive groups in the lignosulfonate structure. The most predominant couple ( $E^{\circ} = 0.44$  V) shifted negatively with pH at a rate of 59.5 mV per pH unit. In neutral electrolytes, the LS1- and LS2-modified electrodes behaved as anionic coatings, showing an increase in the charge transfer resistance ( $R_{ct}$ ) for the ferrocyanide/ferricyanide redox couple. The change in  $R_{ct}$  was highly dependent on the LS sulfonation degree, and in comparison, to an unmodified electrode it increased by ca. 490% for LS1-modified electrodes and by only 53% for LS2-modified electrodes. The LS-modified electrodes showed high electrocatalytic activity toward oxidation of reduced nicotinamide adenine dinucleotide (NADH). Electrocatalysis was studied in TRIS-HNO<sub>3</sub> buffers having pH of 5.0, 7.5, and 8.5 in the absence and presence of 20 mM Mg<sup>2+</sup>, using the rotating disk electrode technique. Determined kinetic constants revealed that the impact of electrocatalysis depended strongly on the pH, the LS sulfonation degree, and the presence of bivalent metal ions. At fixed pH, the observed oxidation rate constant was lower for LS1-based electrodes than for LS2-based electrodes. On the other hand, the relative enhancement of this constant caused by the presence of Mg<sup>2+</sup> ions was much higher for LS1-based electrodes than for LS2-based electrodes. This phenomenon was explained by the participation of sulfonic groups in the formation of a ternary complex between quinone moiety, metal ions, and NADH. The values of other kinetic constants, including the Michaelis-Menten constant ( $K_M$ ), suggested that the formation of such a complex is preferred in alkaline pHs. The growing adoption of biobased materials for electronic, energy conversion, and storage devices has relied on high-grade or refined cellulosic compositions. Herein, lignocellulose nanofibrils (LCNF), obtained from simple mechanical fibrillation of wood, are proposed as a source of continuous carbon microfibers obtained by wet spinning followed by single-step carbonization at 900 °C. In this study, advanced multifunctional silica/lignin composite materials have been prepared. The main focus of this study includes the chemical modification of Kraft lignin, and its interaction with silica matrix, thereby providing the possibility of applying the obtained systems in a number of areas, including electrochemistry. Analysis of dispersive-morphological properties revealed that the samples containing 10–20 parts by weight of lignin had the best parameters. The elemental analysis of the final composites, thus, obtained indicated an increase in the contents of carbon, hydrogen and sulphur with increasing quantity of lignin used. Spectrophotometric evaluation of the products obtained, proves the successful synthesis of silica/lignin composites which is manifested by the presence of characteristic bands of appropriate functional groups. The increasing intensity of these bands with increasing content of lignin in the silica matrix conforms entirely with the expectations. Thus, obtained composite powders were blended with multiwalled carbon nanotubes at the mass ratio of 1:2 with the aid of ultrasound. The blends were cast-deposited on glassy carbon electrode and the electrochemical activity was assessed by cyclic voltammetry. It revealed the presence of a redox system assigned to lignin-derived quinone/hydroquinone couple.

**Bottom Note:** This work is partly presented at 3rd International Conference on Electrochemistry July 10-11, 2017, Berlin, Germany