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Physico-chemical characterization of ferrocenyl-modified hyperbranched poly(ethylenimine) self-assembled multilayers



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ABSTRACT

In this work, we characterize the electrochemical behavior of a new ferrocenyl-modified, hyperbranched poly(ethylenimine) (HBPEI-Fc). The effects of the ionic strength, pH and the nature of the anion of the supporting electrolyte on the electrochemical behavior of the redox polymer were studied using cyclic voltammetry and an electrochemical quartz crystal microbalance. The interactions of the polymer with the anions of the supporting electrolyte, which was incorporated during the redox process, determined the electrochemical behavior that was observed. The polymer was employed for the construction of layer-by-layer-assembled multi-composite films using thiolated gold surfaces with HBPEI-Fc as the polycation and citrate-stabilized gold nanoparticles or glucose oxidase (GOx) as the negative polyelectrolyte. The self-assembled multilayers were characterized using UV-Vis spectrophotometry and electrochemical techniques to follow the signal of the ferrocene groups of the polymer. The adsorption of the polymer and GOx was analyzed using surface plasmon resonance to determine the surface coverage and the kinetic properties of the process. The results demonstrated that the ferrocenyl-modified polymer is an efficient platform for the immobilization of both inorganic materials, such as metallic nanoparticles, and biomolecules.

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1. Introduction

Redox polymers are characterized by functional groups in their backbones that can be reversibly reduced or oxidized. Charge transport in these polymers occurs through electron hopping between neighboring redox sites, physical diffusion of redox sites or a combination of these two mechanisms [1]. The movement of counter ions is associated with charge transfer during the electrochemical reaction to maintain electroneutrality. Consequently, the conditions of the medium, such as the nature of the supporting electrolyte, pH and ionic strength, as well as the polymer properties (e.g., conformation, chain and segmental motions and morphology), play a fundamental role in their electrochemical response [1].

Redox polymers have been extensively employed in the construction of layer-by-layer (LbL) self-assembled structures. Several examples of structures containing redox groups, such as viologen [2], Prussian blue [3], poly(thiophene) [4] and osmium bipyridyl complex (Os-bpy) [5], have been reported for potential applications in mechanical actuators, sensors, photochromic

devices and, more recently, for surface-mediated controlled drug release [6].

Specifically, ferrocene-modified polymers have been extensively studied because of their interesting reactivity and redox behavior, among other properties [7]. Two strategies have been attempted to obtain ferrocene-derivatized polymers: substitution of functional groups in polymers without redox behavior, such as poly(4-vinylpyridine) [8], chitosan [9], poly N-isopropylacrylamide [10] and poly(allylamine) [11], and the synthesis of redox copolymers in which ferrocene was covalently attached, such as poly(vinylferrocene-co-2-hydroxyethyl methacrylate) [12], poly(N-acryloylpyrrolidine-co-vinylferrocene), acrylamide copolymers [13], ferrocene-based peptide/amides [14] and poly(glycidyl methacrylate-co-vinylferrocene) [15].

Due to ferrocene's standard redox potential, ferrocene-modified polymers are appropriate as mediators for glucose oxidase in amperometric glucose biosensors [16,17].

Schmidtke and co-workers have studied a series of redox polymers based on linear poly(ethylenimine) and ferrocene (Fc-C6-LPEI) for use in glucose biosensors [18,19] and biofuel cell anodes [20]. Recently, they studied layer-by-layer assembled structures of Fc-C6-LPEI with poly(acrylic acid), poly(glutamic acid) or glucose oxidase, demonstrating that the formation of the film was dependent upon the nature of the anionic polyelectrolyte [21].

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Xu and co-workers have reported the fabrication and characterization of multilayer films based on layer-by-layer assembly of ferrocene poly(ethylenimine) and gold nanoparticles. The multilayers were applied to analyze its electrocatalytic response towards the oxidation of ascorbic acid and the reduction of oxygen [22].

All the cited examples show that the synthesis and application of ferrocenyl-functionalized polymers are of interest to many fields, such as electrochemistry, materials science, organic synthesis and catalysis. The development of novel redox polymers continues to be an important area of research in the field of bioelectronics [23].

In this work, we present the synthesis and characterization of a new ferrocenyl-modified polymer obtained from hyperbranched poly(ethylenimine) (HBPei), named HBPei-Fc. The goal of this work was to study the electrochemical behavior of the polymer and evaluate the effect of the anion of the supporting electrolyte, pH and ionic strength on the electrochemical response. Based on the interesting molecular structure and resulting high charge density, the second goal of our work was to evaluate the construction of multi-composite films built using electrostatic layer-by-layer assembly of HBPei-Fc as the polycation and citrate-stabilized gold nanoparticles or glucose oxidase as the negative polyelectrolytes. The resulting structures were characterized using UV–Vis spectrophotometry, scanning electron microscopy, surface plasmon resonance, electrochemical-quartz crystal microbalance and cyclic voltammetry.

2. Materials and methods

2.1. Reagents

Citrate-stabilized gold nanoparticles (Au-NPs) with a 15-nm average diameter were synthesized using the Turkevich method. The diameter of the Au-NPs was determined using the Khlebtsov method [24] (considering the experimentally determined value of the maximal absorbance, $\lambda_{\text{max}} = 520 \text{ nm}$). The glucose oxidase (GOx) (Type X-S, *Aspergillus niger*, EC 1.1.3.4, 210,000 units per gram of solid, Mw = 160 kDa) and hyperbranched polyethylenimine (HBPei, average Mw = 750 kDa) were from Sigma. The sodium 3-mercaptopropylsulfonate (MPS), ferrocenecarboxaldehyde and sodium borohydride were from Aldrich. Other chemicals were reagent grade and were used without further purification. All solutions were prepared with ultra-pure water (18 M Ω cm) from a MilliRO–MilliQ system.

2.2. Synthesis and characterization of ferrocenyl-modified hyperbranched polyethylenimine

The synthesis of HBPei-Fc was performed as described in [25]. The presence of ferrocenyl groups in the synthesized polymer was corroborated using UV–Vis experiments (see Fig. S1 of Supporting information). The substitution degree (SD) of amine hydrogen by ferrocenylmethylene moieties was determined using ^1H Nuclear Magnetic Resonance spectra from the integration ratio of the ferrocenyl proton to the polymer methylene backbone signals (Fig. S2 of Supporting information). The value was 28.4%, which is in good agreement with the value reported for linear polyethylenimine (av. MW = 86,000) and branched polyethylenimine of low molecular weight (av. MW = 200,000) [25].

2.3. Equipment

UV–Vis experiments were performed with a Shimadzu UV1601 Spectrophotometer using a quartz cuvette with a 1.0 or 0.1 cm path length. Cyclic voltammetry (CV) was performed with an

Autolab PGSTAT 128N potentiostat (Metrohm Autolab B.V.). Gold disk electrodes (Au) of 2 mm diameter (Model CHI 101) were used as the substrates. A platinum wire and an Ag/AgCl, 3 mol dm $^{-3}$ NaCl electrode (Model RE-5B, BAS) were used as the counter and reference electrodes, respectively. All reported potentials are referred to this reference electrode. Electrochemical-quartz crystal microbalance (EQCM) measurements were conducted with a CHI 400 Time-Resolved EQCM System (CHI). Quartz disks coated with gold (Model CHI 125A, 0.196 cm 2 of area) were used as substrates. The experiments were performed at room temperature. Surface plasmon resonance (SPR) measurements were conducted with a single channel Autolab SPRINGLE instrument (Metrohm Autolab B.V). SPR sensor disks (Model BK 7) were mounted on a hemi-cylindrical lens through index-matching oil to form the base of a cuvette. Sample solutions (100 μL) were injected automatically into the cuvette. The measurements were conducted under non-flow liquid conditions with the cuvette thermostated at 25 $^{\circ}\text{C}$.

2.4. Surface modification

Clean gold surfaces were immersed in a fresh $2.00 \times 10^{-2} \text{ M}$ MPS solution prepared in $1.60 \times 10^{-3} \text{ M}$ sulfuric acid solution, followed by careful rinsing with deionized water. Adsorption of HBPei-Fc was performed over 15 min from a 3.0 mg mL^{-1} polymer solution prepared in a 0.200 M acetate buffer solution pH 5.00. After the adsorption step, surfaces were copiously rinsed with acetate buffer solution. The resulting electrodes are indicated as Au/MPS/HBPei-Fc.

Adsorption of Au-NPs was performed by immersion of the Au/MPS/HBPei-Fc surfaces in the colloidal Au-NPs solution for the specified time. After each adsorption step, surfaces were copiously rinsed with deionized water. Multilayered films were constructed by alternate immersion of Au/MPS substrates in HBPei-Fc and Au-NPs solutions for the selected time. These structures are named Au/MPS/(HBPei-Fc/Au-NPs) $_n$, with n being the number of HBPei-Fc/Au-NPs adsorption steps.

For UV–Vis measurements, the internal surface of the quartz cuvette (Quartz) was treated by sonication for 20 min in an ethanolic solution of NaOH 1.0% w/v to expose negative charges. Adsorption of HBPei-Fc and Au-NPs was performed by filling the cuvette with each solution for a predetermined time. Then, the solutions were removed, and the cuvette was repeatedly washed with deionized water. UV–Vis measurements were performed in deionized water to avoid modification by surface drying. These structures are named Quartz/(HBPei-Fc/Au-NPs) $_n$, where n is the number of HBPei-Fc/Au-NPs adsorption steps.

Adsorption of GOx was performed by immersion of Au/MPS/HBPei-Fc surfaces in 1.0 mg mL^{-1} GOx solution prepared in 0.050 M phosphate buffer solution at pH 7.40 for 30 min, followed by copiously rinsing with phosphate buffer solution. The structures are denoted as Au/MPS/(HBPei-Fc/GOx) $_m$, where m is the number of HBPei-Fc/GOx adsorption steps.

3. Results and discussion

3.1. Electrochemical response of HBPei-Fc

3.1.1. Adsorption of HBPei-Fc

We evaluate the adsorption process using SPR to determine the concentration and adsorption time of HBPei-Fc for further construction of self-assembled multilayers. Fig. 1 presents the sensorgram obtained during the adsorption of the polymer at the Au/MPS surface. The experiment starts recording a baseline in a 0.200 M acetate buffer solution at pH 5.00. Next, a 3.0 mg mL^{-1} HBPei-Fc solution is injected into the cuvette, and a fast increase in the

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