



Core-shell hyperbranched chitosan nanostructure as a novel electrode modifier



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ABSTRACT

The present study reports, for the first time, the development and use of core-shell amino-terminated chitosan (Cs) hyperbranched nanoparticles (HBCs-NH₂ NPs) as a novel natural polymer-based electrode modifier for efficient electrochemical systems. The electrochemical activity of the developed HBCs-NH₂ NPs as compared to Cs NPs was identified by standard oxidation–reduction reactions of ferricyanide. The oxidation–reduction peaks height was about twofold higher than the response of Cs-modified electrode. On the other hand, NADH oxidation at the nanostructured surfaces confirmed the electrocatalytic activity where the oxidation of NADH appeared at a lower overpotential (from 805 mV to 635 mV vs Ag/AgCl). Eventually, a diffusion-controlled process was confirmed from the scan rate effect.

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1. Introduction

Chitosan (Cs), a polysaccharide composed of linearly linked D-glucosamine units, is produced by deacetylation of chitin (N-acetyl-D-glucosamine) which is the main constituent of cell wall in crustacean shells [1–3]. This natural polymer, Cs has many superior properties such as biocompatibility, biodegradability, high mechanical strength, low cost and high-quality film forming ability [4]. Cs-metal hybrid NPs were frequently employed in electrode modification due to their high surface area and the good electron transfer capability, however Cs itself showed a poor electrochemical activity [5–7].

Nicotinamide Adenine Dinucleotide (NAD) is an important coenzyme for most of the dehydrogenase enzymes in metabolic redox reactions. NAD is responsible for electron transfer as it can be changed between the reduced form (NADH) and the oxidized one (NAD⁺), and hence its determination is of a high importance [8]. One of the main difficulties in electrochemical determination of NADH is its high oxidation overpotential which may oxidize other electroactive species in the media, and consequently affects both sensitivity and specificity of the measuring system [9]. Thus, the usage of electrode modifiers, which are substances that enhance the redox reactions and the electron transfer to lower the working potential, helps in evading this obstacle [10].

In the present study, we introduce, for the first time, a new core-shell amino-terminated Cs-based hyperbranched nanostructure as a conductive natural polymer to be used as an electrode modifier. The hypothesis is that the decoration of Cs NPs surface with a large number of electron-rich groups such as amino groups would improve their electrical conductivity as well as the electrocatalytic activity. The oxidation of NADH coenzyme was chosen as a good model for studying the electrochemical responses of the newly developed HBCs-NH₂-modified carbon paste electrode.

2. Materials and methods

2.1. Synthesis of core-shell HBCs-NH₂ NPs

All reagents used in synthesis of HBCs-NH₂ NPs were obtained from Sigma-Aldrich (St. Louis, USA). The synthesis procedure and characterization of the HBCs-NH₂ were reported in details in our previous study [11]. Briefly, Cs NPs were first synthesized by nanospray drying (Buchi, B-90 nanospray dryer, Buchi Co., Switzerland) at air flow rate of 135 l/min with an inlet temperature of 120 °C and using the 0.7 μm cap. Dendritic polyamidoamine (PAMAM) branches were prepared using a modified procedure to that described by Tomalia et al. [12]. The as-prepared PAMAM branches were added to a predetermined concentration of Cs NPs aqueous suspension and dispersed by sonication for 5 min, then stirred for 5 days at room temperature. The obtained core-shell HBCs NPs were collected via centrifugation at 12,000 rpm for 10 min and washed three times. The resulting HBCs NPs with

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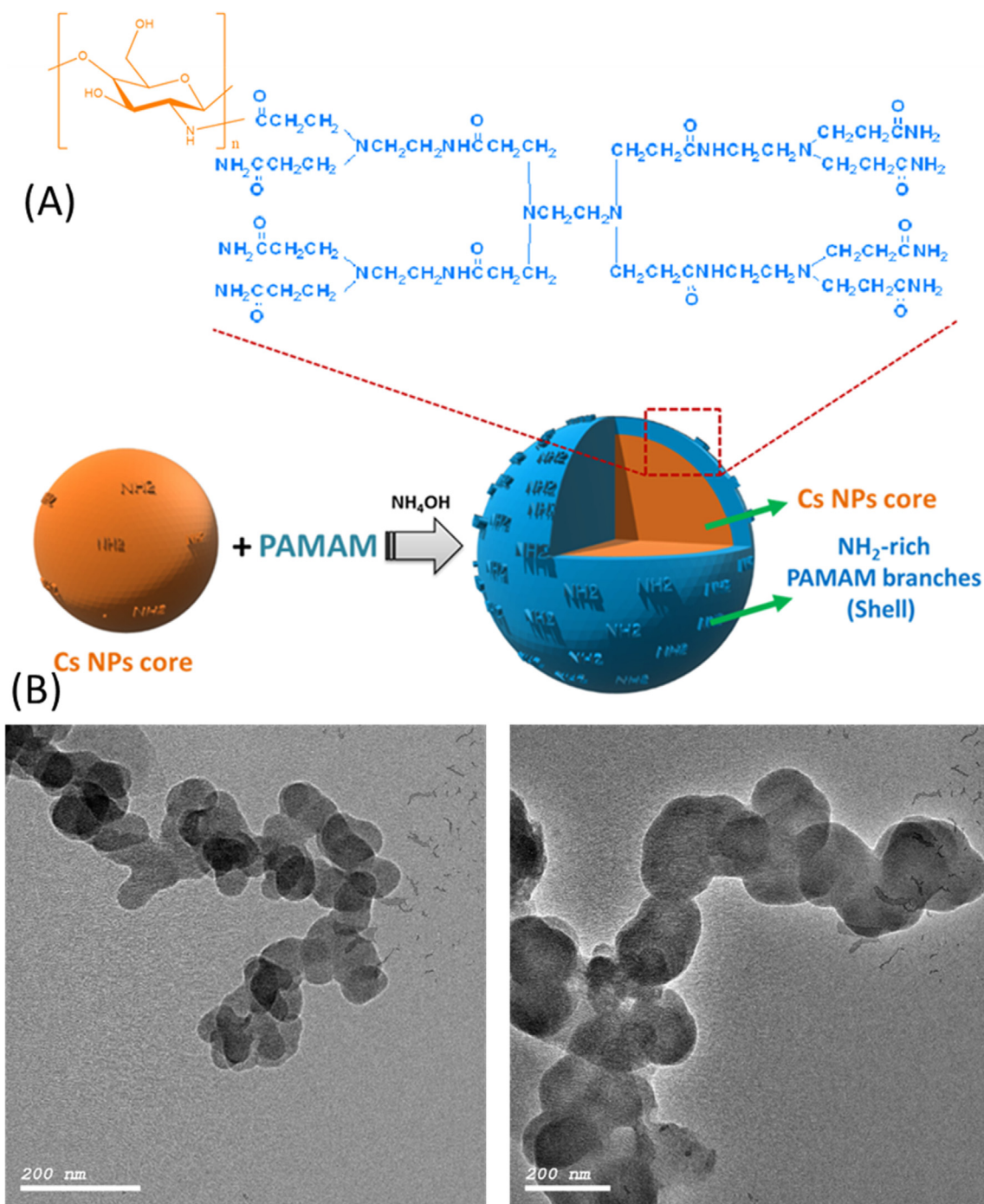


Fig. 1. (A) A schematic diagram of structure and synthesis of HBCs-NH₂ NPs, and (B) TEM micrograph of the developed HBCs-NH₂ core-shell NPs.

terminal methyl ester moieties were aminolyzed into HBCs-NH₂ NPs with the aid of an alcoholic NH₄OH solution (10 ml NH₄OH/30 ml methanol) with stirring at room temperature for 3 days.

2.2. Instrumentation

All electrochemical measurements were performed using a computer-controlled GamryPotentiostat/Galvanostat/ZRA G750 (Gamry, Pennsylvania, USA). The measurements were done using a three-electrode electrochemical cell containing a 4 mm diameter

CPE as the working electrode, a Pt disc as auxiliary electrode and a 3 M KCl Ag/AgCl reference electrode.

2.3. Electrochemical measurements

Cs NPs and HBCs-NH₂ NPs-based films were formed on the surface of CPEs through drop-casting of 2% w/v suspensions of each NPs for three times, followed by thermal treatment in an oven at 50 °C for 15 min. Cyclic voltammetry of the modified electrodes was first carried out in a 0.1 M KCl with different concentrations of FCN, followed by 0.1 M phosphate buffer saline solution (PBS) with different concentrations of NADH.

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