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Self-assembled and covalently linked capillary coating of diazoresin and cyclodextrin-derived dendrimer for analysis of proteins by capillary electrophoresis

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ABSTRACT

Self-assembled and covalently linked capillary coatings of cyclodextrin-derived (CD) dendrimer were prepared using photosensitive diazoresin (DR) as a coupling agent. Layer by layer (LBL) self-assembled DR/CD-dendrimer coatings based on ionic bonding was fabricated first on the inner surface of capillary, and subsequently converted into covalent bonding after treatment with UV light through a unique photochemistry reaction of DR. Protein adsorption on the inner surface of capillary was suppressed by the DR/CD-dendrimer coating, and thus a baseline separation of lysozyme (Lys), myoglobin (Mb), bovine serum albumin (BSA) and ribonuclease A (RNase A) was achieved using capillary electrophoresis (CE). Compared with the bare capillary, the DR/CD-dendrimer covalently linked capillary coatings showed excellent protein separation performance with good stability and repeatability. Because of the replacement of highly toxic and moisture sensitive silane coupling agent by DR in the covalent coating preparation, this method may provide an environmentally friendly and simple way to prepare the covalently coated capillaries for CE.

1. Introduction

As a powerful separation tool for biomacromolecule analysis, capillary electrophoresis (CE) has the advantages of high efficiency, high sensitivity, high speed, and low cost [1,2]. However, one of the major impediments for CE analysis is severe protein adsorption onto fused-silica capillary walls when analyzing proteinaceous samples [3–5]. Consequently, sample loss, poor resolution, peak broadening, long migration times, and unstable electroosmotic flow (EOF) were generated by the protein fouling [6]. In order to suppress protein adsorption onto capillary surface, the most efficient and commonly used approach is surface modification with capillary coatings [7,8]. Many kinds of coated capillaries [9–11] had been prepared to obtain better separation effect and succeed.

Generally, capillary coatings are classified into non-covalently and covalently bonded ones. The non-covalent coatings can be produced simply by flushing the capillary with coating solutions, and the coating molecules absorb on capillary surface by weak interactions such as electrostatic, van der Waals, and hydrogen bonding, etc. [12–15]. Furthermore, the layer-by-layer (LBL) self-assembly technique can also be used to prepare the non-covalently bonded capillary coatings, which provides the coating with new structures and functions [16–19]. For example, Haselberg et al. [20] prepared polybrene-dextran sulfate-polybrene (PB-DS-PB) triple layer coatings by the LBL self-assembly technique, and the coatings were fully compatible with mass spectrometry (MS) detection, causing no background signals and ionization suppression. The coatings were used for the analysis of α-chymotrypsinogen, ribonuclease A (RNase A), cytochrome c (Cyt-c) and lysozyme (Lys) by CE-MS, and the detection limits for them were 16, 11, 14 and 19 nM, respectively. Compared with the non-covalently bonded coatings, the covalently bonded coatings are very stable and robust. For example, Xu et al. [21] prepared chemically bonded PVA coatings that were used for high-efficiency separation of Cyt-c, Lys, myoglobin (Mb) and trypsin inhibitor. Timperman et al. [22] prepared chemically bonded PEG coatings which were used for high efficiency separation of BSA, alcohol dehydrogenase, carbonic anhydrase and trypsin inhibitor. PVA and PEG covalently linked coatings not only showed very good anti-protein fouling properties, but also demonstrated excellent stabilities for

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repeatable separations. However, the preparation process of covalently bonded capillary coatings is usually complicated which includes multi-steps such as capillary pretreatment, introducing coupling agents, and inserting target coating reagents, etc. [23–26]. Moreover, highly toxic and moisture sensitive silane coupling agents are traditionally used in the covalent coatings, which often cause environmental and quality problems during the manufacture and application [27,28]. In the fabrication process of capillary coatings with high quality and performance, how to combine the advantages of the non-covalently and covalently bonded coatings together, and avoid their disadvantages, is becoming one of the main development directions.

Dendrimers are highly branched macromolecules characterized by monodispersity, uniform and controlled sizes, copious surface functionalities [29,30], and low intrinsic viscosity in solution [30–32]. For example, Shou et al. [33] prepared a capillary coating based on 2,4,6,8-tetravinyl-2′,4′,6′,8′-tetramethyl cyclotetrasiloxane (D_4^{Vi}) for high efficiency CE separation of adenine. Kabir et al. [34] used sol–gel dendrimer coatings for capillary microextraction, and found the dendrimer coatings had excellent thermal and solvent stability. In this study, we developed a new method to fabricate the covalently linked cyclodextrin-derived (CD) dendrimer capillary coatings using the LBL self-assembly technique combined with photochemistry reactions. The fabrication, structure and property of the coatings were studied and discussed preliminarily.

2. Experimental

2.1. Reagents and solutions

Diazoresin (DR) (Mn=2500) was synthesized according to the method described elsewhere [35]. Lysozyme (Lys), cytochrome c (Cyt-c), bovine serum albumin (BSA), amyloglucosidase (AMG), myoglobin (Mb) and ribonuclease A (RNase A) were purchased from Sigma (St. Louis, USA). N,N-Dimethyl formamide (DMF) was purchased from Yongda Chemical Reagent Company (Tianjin, China). Phosphoric acid (H_3PO_4) was purchased from Fuyu Fine Chemical Company (Tianjin, China). Monosodium orthophosphate ($NaH_2PO_4 \cdot 2H_2O$) and dibastic sodium phosphate ($Na_2HPO_4 \cdot 2H_2O$) were bought from Shunqiang Chemical Reagent Company (Shanghai, China). Acetone was obtained from Sanhe Chemical Reagent Company (Tianjin, China). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Hongyan Reagent Company (Tianjin, China). Phosphate buffer was used

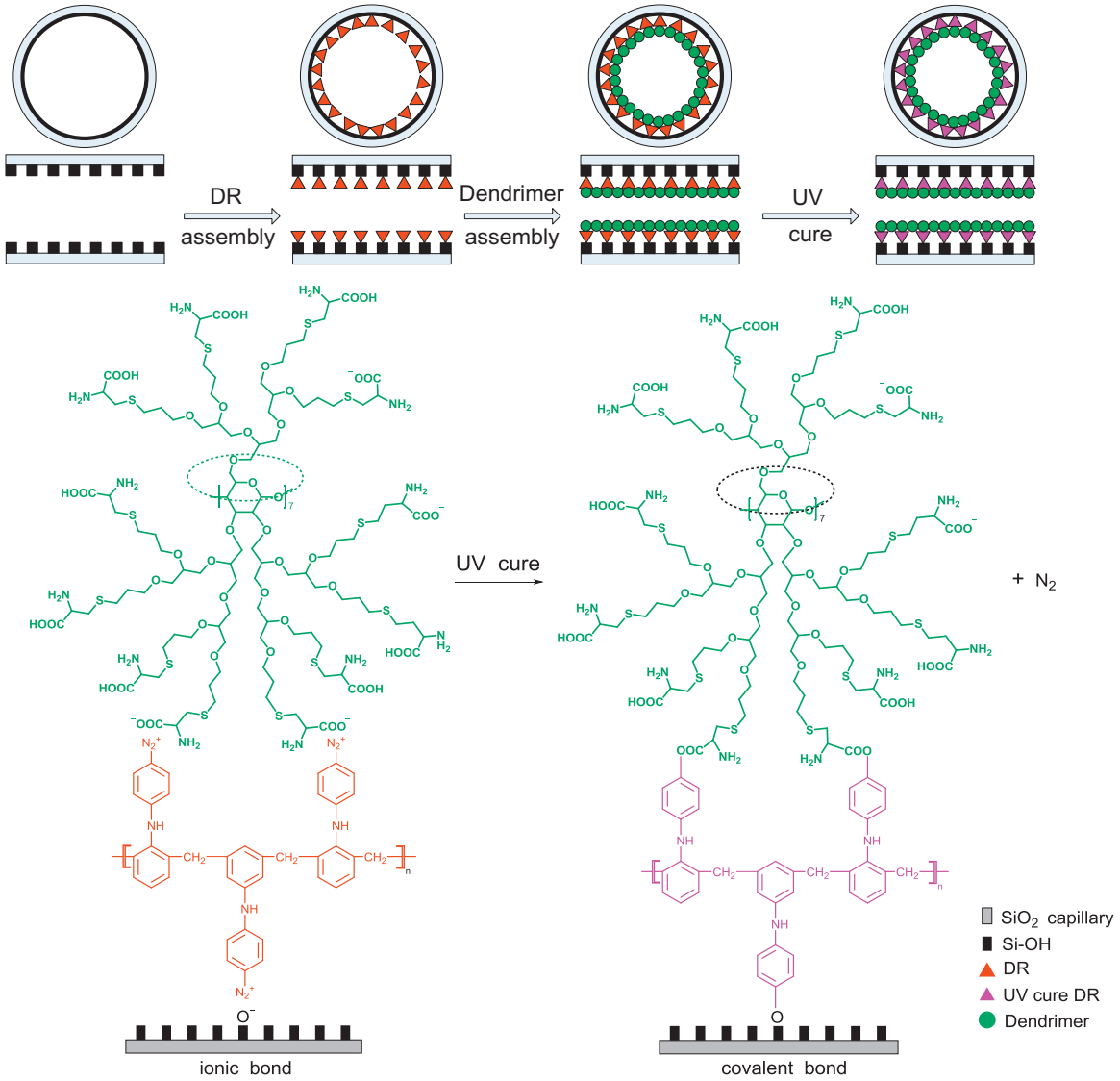

Fig. 1. Schematic illustration of preparation process of covalently bonded DR/CD-dendrimer coatings on capillary surface.