Electrodeposition Assisted Dynamic Assemblies of Chitosan/Alginate Composite Multi-Membrane

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Abstract. Electrodeposition of natural polymer as an effective approach to improve bioactivity of the conductive substrate has received much attention in medical and other applications. In this work, we developed a novel chitosan/alginate (CS/ALG) multi-membrane on titanium plate via the electrodeposition assisted dynamic assembly approach. Specifically, the electrical signal induced CS coating can serve as a versatile platform for layer by layer assemblies of ALG into the multi-membrane through strong electrostatic interaction. The prepared multi-membranes exhibit great swelling performance and excellent mechanical properties at dried states, with the tensile stress and strain values reaching to 58.2 MPa and 4.25 % for the 10 layers sample. In summary, we believe such green, low-cost and rapid fabrication approach and mild processing environment would spur great potential for construction of multi-functional coating and smart drug elusion system on the conductive implants.

1. Introduction
Electrodeposition or Electrophoretic deposition (EDP) as one of the most promising approaches for the multi-functional composite coating construction has been extensively investigated for numerous applications [1, 2]. For the most cases, EDP was often involved with two fundamental states: electrophoresis and deposition processes. Specifically, electrophoresis is response to the electric field induced migration of charged particles that dispersed in a stable solvent while the deposition represents the coagulation and/or precipitation of charged particles into a thick coating on the electrode surface [3, 4]. In recent years, however, a similarly behavior of natural polymer has been observed, and which can be deposited on the working electrode as a polymeric hydrogel film [5]. These findings have motivated a widely investigation of polymer-based EDP for a variety of applications ranging from electrochemical sensing system [6] to the biomedical fields [7].

Various polymers can be electrochemically deposited on the electrode surface, such as chitosan (CS) [8, 9], alginate (ALG) [10] and gelatin [11, 12] and their composite films [13]. Among these polymers, CS as the second abundant amino biopolymers in nature has been widely used for a great variety of biomedical applications due to its excellent biocompatibility, biodegradability, and antibacterial activity [14, 15]. As previous reported, CS can recognize the localized electrical signal and self-assemble into a hydrogel coating on a conductive substrate [16-18]. However, the electrodeposited CS film often suffered with weak mechanical strength which is strongly limits its practical applications [19, 20]. Thus, in this study, we have developed a novel CS/ALG multi-membrane with great swelling performance and excellent mechanical properties on the titanium by combining a layer by layer assembly technique to the chitosan’s EDP process. The multi-membrane can be facilely constructed from dynamic
assemblies of ALG to the CS modified titanium plate. The surface and multilayer morphologies have been confirmed by using a scanning electron microscope (SEM). The hydrophilic properties are determined on a water contact angle (CA) system. The relationship between the complex structure and mechanical properties has also been revealed by a tensile stress strain measurement.

2. Materials
Chitosan from shrimp shells (CS, a degree of deacetylation of 90%, average molecular weight of 220 kDa and sodium alginate from macrocystis pyrifera (ALG) were both purchased from Sigma-Aldrich. The other chemicals, i.e., sodium hydroxide (NaOH), calcium chloride (CaCl2) were of analytical grade and used without further purification.

3. Methods

3.1. EDP of CS Modified Titanium Plate
The EDP process was performed by immersing a titanium plate electrode (1 cm × 2 cm × 100 µm) in a CS solution (1 wt%, pH ≈ 5.5) with a platinum wire serving as the counter electrode. Next, connected the two electrodes to an electrochemical workstation (624D, CHI instrument, Shanghai) and imposed with a constant current density of 0.2 A/m² for 60 seconds. After deposition finished, the plate was disconnected from workstation, removal from the solution, briefly rinsed with DI water and the then stored at room temperature for further use.

3.2. Dynamic Assemblies of The Multi-Membrane
The dynamic assembly process was performed according to the previously reported layer by layer technique [21]. In brief, firstly immersed the CS modified titanium plate into a solution that containing of 2% ALG and 0.1 M NaOH for 5 min. After the ALG layer formed, removed the titanium plate out from the ALG solution, briefly rinsed with distill water and then immersed in the CS solution (1 w/v%, pH≈5.5) for 2% ALG and 0.1 M NaOH for 5 min. After the ALG layer formed, removed the titanium plate out from the ALG solution, briefly rinsed with distill water and then immersed in the CS solution (1 w/v%, pH≈5.5) for another 5 min. Finally, the multi-membrane can be prepared by cyclic immersing the titanium plate into above two solutions for several times.

3.3. Characterizations.
The optical images were collected by using a stereomicroscope (Shunyu SZM45, Jiangsu, China) and the thickness of each layer was analyzed using Nano Measurer software. In some case, the hydrogel was gently peeled off from the titanium plate by using a tweezers and then fully dried via a vacuum dryer at 60 °C for 4 h to allow the microstructure to be observed via a scanning electron microscope (SEM; VEGA3 LMU, TESCAN). Water contact angle (CA) was conducted by the sessile drop method on a contact angle system (Dataphysics, Germany KRUS Co.). Mechanical properties were determined using a universal testing machine equipped with a 100 N load cell (H5K-S, Hounsfield). The films with an area of 1 × 1 cm² have been tested at a cross-head speed of 1 mm/min.

4. Results and Discussion

4.1. EDP of CS Coating on the Titanium Plate
Based on CS’s unique pH-dependent solubility (pKa~6.3) and great film forming properties, CS can recognize the localized electrical signal that triggered self-assembly into a hydrogel film on the cathode electrode surface [20]. As schematically showed in figure 1, when imposing with the constant current density of 0.2 A/m² for 60 s, a transparent and thick CS hydrogel film can be rapidly produced on the cathode electrode. Specifically, the applied electrical signal would induce a high pH microenvironment (e.g. electrolysis of water) that allows the amine groups rich in CS chains to be deprotonated and self-assembled into a hydrogel coating. This result indicates the EDP method could be used to modify the titanium plate electrode with a CS coating for improvement of its bioactivity.
4.2. Dynamic Self-Assembly of CS/ALG Multi-Membrane

Figure 2a demonstrates the multi-membrane hydrogel was constructed by repeat curing the CS modified titanium plate in the ALG/NaOH and CS/CaCl₂ solution sequentially. Step 1 shows the Ca²⁺ ions induced self-assembly of ALG layer while the excess OH⁻ ions are entrapped within the gel network. Step 2 shows the OH⁻ ions are freely diffuse out from the pre-existed ALG layer that allowing CS to undergo a sol-gel transition on the ALG layer surface while the loaded abundant Ca²⁺ ions can serve as a source of crosslinker for the later ALG layer formation [22]. Based on the opposite charges of CS (positive charge) and ALG (negative charge), strong electrostatic interaction would form between each layer and the cycle number is response to the number of layers. Figure 2b indicates the film thickness was progressively increased with increasing the of layer numbers in the multi-membrane hydrogel. This result reveals that the CS modified titanium plate could be used as a substrate for dynamic construction of CS/ALG composite multi-membrane.

4.3. Morphology Characterization

Figure 3 reveals the significant difference of surface microstructure between the CS and ALG membrane. The CS membrane showed with a very smooth surface while a rough surface could be observed from the ALG membrane. When switched the surface layer from CS to the ALG membrane resulting an obvious change of water contact angle from 106° to 71°. This result indicates the hydrophobic and hydrophilic properties of the multi-membrane can be facile adjusted by switching the surface layer membrane.
Figure 3. Surface morphologies and water contact angles of (a) CS and (b) ALG membrane.

Figure 4 reveals the multi-layer internal microstructure of the fabricated membrane with distinct layer numbers. Thickness of the multi-membrane at dried state was observed gradually increased with increasing the layer numbers, and which is consistent with film at wet state. However, the film thickness was showed remarkable difference compared to the hydrogel film suggesting the excellent swelling capabilities of such multi-membrane and great potential use in biomedical fields.

Figure 4. SEM images of the multi-membranes with (a) 2, (b) 4, (c) 6 and (d) 8 layers.

4.4. Mechanical Strength

Figure 5 reveals the relationship between mechanical properties and layer numbers of the multi-membranes. The tensile stress-strain measurements were performed on the different samples. As showed in figure 5, the mechanical properties are increased with increasing the layer numbers and exhibited the maximum stress-strain properties for the 10 layers membrane, with the tensile stress and strain values of 58.2 MPa and 4.25 %, respectively. This result can be attributed to the synergistic effect of the strong intermolecular interactions between the CS and ALG polymer chains, densely packed and layered architecture that contribute mostly to the higher tensile stress-strain performance of the multi-membrane.
5. Conclusion
Chitosan/alginate composite films with multilayered internal structure, tunable surface hydrophilic performance and superior mechanical properties were successfully prepared by dynamic assemblies of chitosan and alginate onto an electrochemically modified titanium plate. EDP approach allows the titanium plate to be modified with a CS coating that can be served as the substrate for dynamic layer by layer assemblies of ALG into the multi-membranes. The prepared multi-membranes exhibit great swelling performance and excellent mechanical properties at dried states, with the tensile stress and strain values reaching to 58.2 MPa and 4.25 % for the 10 layers sample. Coupling the excellent swelling performance and strong mechanical properties of the fabricated multi-membranes would suggest a great potential for future use in the conductive implant system.

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