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Mussel-inspired chitosan-polyurethane coatings for improving the antifouling and antibacterial properties of polyethersulfone membranes

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ABSTRACT

A straightforward mussel-inspired approach was proposed to construct chitosan-polyurethane coatings and load Ag nanoparticles (AgNPs) to endow polyethersulfone (PES) membranes with dual-antibacterial and antifouling properties. The macromolecule *O*-carboxymethyl chitosan (CMC) was directly reacted with catechol in the absence of carbodiimide chemistry to form the coating and load AgNPs *via in situ* reduction; while lysine (Lys) was used as a representative small molecule for comparison. Then, PEG-based polyurethane (PU) was used for constructing Lys-Ag-PU and CMC-Ag-PU composite coatings, which substantially improved the protein antifouling property of the membranes. Furthermore, the CMC-Ag-PU coating exhibited superior broad-spectrum antibacterial property towards *E. coli* and *S. aureus* than Lys-Ag-PU coating. Meanwhile, the CMC-Ag-PU coating showed sustained antifouling property against bacteria and could reload AgNPs to be regenerated as antibacterial and antifouling coating. This approach is believed to have potential to fabricate reusable antifouling and antibacterial coatings on materials surfaces for aquatic industries.

1. Introduction

Biofouling that caused by accumulation of bacteria on materials surfaces is a worldwide issue that affected aquatic industries. To address the issue, various antibacterial reagents such as chitosan, quaternary ammonium salts and metal ions are employed to enhance the antibacterial properties of membranes (Arsalan, 2014; Luo et al., 2017; Zhang et al., 2016); while hydrophilic macromolecules such as polyethylene glycol (PEG), polyvinylpyrrolidone (PVP) and zwitterionic polymers are usually introduced into membranes to decrease the adhesion of either live or dead bacteria (Dang, Quan, Xing, Wang, & Gong, 2015; Venault et al., 2016; Wang, Xiang, Zhao, & Zhao, 2016; Wang, Yuan et al., 2016). Till now, diverse methods have been applied for substrate modifications. Surface modifications by coating, grafting, UV irradiation, and plasma treatment are effective ways to confer substrates with desired properties and minimize the impact on inherent properties of substrates like mechanical and thermal properties (McCloskey et al., 2012; Revanur, McCloskey, Breitenkamp, Freeman, & Emrick, 2007; Theapsak, Watthanaphanit, & Rujiravanit, 2012). Since many surface modification methods are still restricted by harsh conditions or requirements for the specific properties of substrates, mussel-inspired method shows its superiority due to the broad applicability to various kinds of substrates and mild preparation conditions (Lee, Dellatore, Miller, & Messersmith, 2007; Liu, Ai, & Lu, 2014; Zhu & Edmondson, 2011). The method generally utilizes the adhering capacity of catechol moieties and the reactivity between the catechol and $-NH_2$ groups to form uniform coatings in aqueous solutions. Meanwhile, the catechol moieties also exhibit reductibility, and Ag^+ ions can be reduced into Ag nanoparticles (AgNPs) by the catechol moieties for antibacterial property (Wu et al., 2015).

Based on the mechanism of mussel-inspired method, it is reasonable to deduce that this method could be extended to various combinations of polyphenols and amines. Natural product, chitosan, contains abundant $-NH_2$ groups and has

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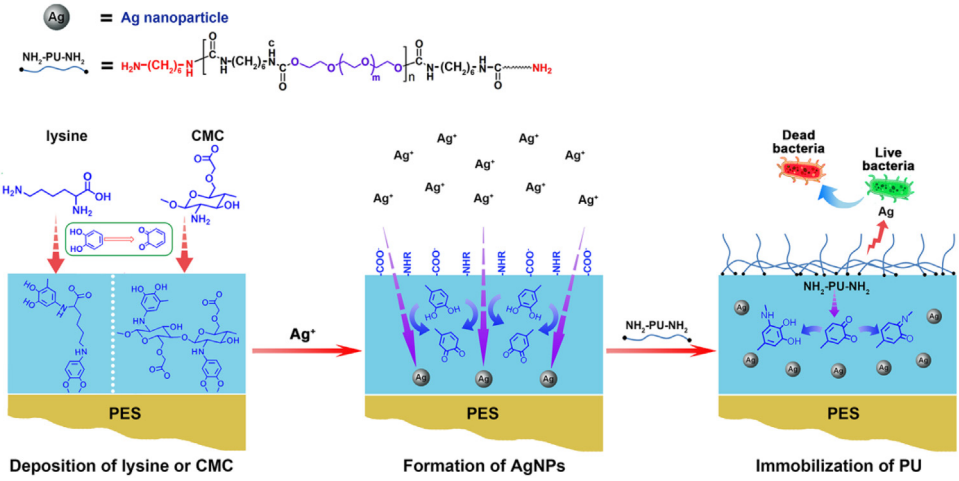

Scheme 1. Schematic diagram for the preparation of Lys-Ag-PU and CMC-Ag-PU membranes.

broad-spectrum antibacterial property. Conventional mussel-inspired chitosan generally requires carbodiimide reagents to link amino and carboxyl groups. For example, Kim et al. had reported that the coupling between hydrocaffeic acid and chitosan by adding *N*-(3-dimethylaminopropyl)-*N′*-ethyl-carbodiimide/*N*-hydroxysuccinimide (EDC/NHS) resulted in mucoadhesive or hydrogel (Kim, Kim, Ryu, & Lee, 2015; Kim, Ryu, Lee, & Lee, 2013).

Herein, a straightforward mussel-inspired approach was proposed to construct chitosan-polyurethane coatings and load Ag nanoparticles (AgNPs) to endow polyethersulfone (PES) membranes with dual-antibacterial and antifouling properties. The immobilized chitosan could kill the bacteria adhered on material surface; while the AgNPs could release Ag^+ to kill the bacteria in the environment. Meanwhile, the polyurethane (PU) contained PEG segments confers the membranes with antifouling property against protein and bacteria adhesions.

In the work, *O*-carboxymethyl chitosan (CMC) was directly reacted with catechol and subsequently deposited onto PES membranes, which eliminated the introduction of carbodiimide reagents and tedious purifications. Then the carboxyl and amino groups in CMC chains captured Ag^+, and the residual catechol moieties reduced Ag^+ into AgNPs without additional reductants such as $NaBH_4$ and ascorbic acid (Choi et al., 2016; Xia et al., 2015). Subsequently, the synthesized polyurethane (PU) containing PEG segments and terminal $-NH_2$ groups was anchored onto the oxidized coatings to attain CMC-Ag-PU composite coating (Lee, Scherer & Messersmith, 2006; Ma et al., 2015). Additionally, it was presumed that the macromolecular chitosan could form crosslinking sites at a large scale and provide more stable coatings than small molecules. Thus, lysine (Lys) was utilized as a representative small molecule to construct Lys-Ag-PU composite coating for comparison. The protein antifouling property in ultrafiltration process was firstly assayed. Then *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were used to evaluate the broad-spectrum antibacterial property and antifouling property against bacteria adhesion. To assay the reusability of the coating, the catechol moieties in the coating were regenerated by $NaBH_4$ to reload AgNPs, and the antibacterial property was investigated again.

2. Experimental section

2.1. Materials

Commercial polyethersulfone (PES, Ultrason E6020P, BASF), Chitosan (CS, deacetylation degree ≥90%, JinQiao. Number-average molecular weight (Mn) = 5.40×10^3 Da, weight-average molecular weight (Mw) = 1.04×10^4 Da and polydispersity index (PDI) = 1.93, measured by gel permeation chromatography(GPC)), L-lysine (Lys, 98%, Aladdin), chloroacetic acid (98%, Aladdin), catechol (99%, Aladdin), hexamethylene diisocyanate (HDI, 99%, Aladdin), hexanediamine (99%, Aladdin), bovine serum albumin (BSA, Aladdin), sodium hydroxide (NaOH, 99%, Kelong), isopropanol (99%, Kelong) and ethanol (99%, Kelong) were used as received. Polyethylene glycol (PEG1000, Aladdin. Mn = 1.12×10^3 Da, Mw = 1.16×10^3 Da and PDI = 1.04, measured by GPC) was dried under vacuum at 100 °C for 2 h before use. Micro BCA™ Protein Assay Kit and LIVE/DEAD® BacLight™ Bacterial Viability Kit were purchased from Thermo Fisher Scientific. Deionized (DI) water was used throughout the study.

2.2. Preparation of O-carboxymethyl chitosan (CMC)

O-carboxymethyl chitosan (CMC) was prepared by the method as mentioned in a previous study (Poon, Zhu, Shen, Chan-Park, & Ng, 2007). Briefly, 8.0 g CS was dispersed into 50 mL NaOH (50 wt.%) aqueous solution and stored at −20 °C overnight. Then the alkalized CS was warmed to room temperature and dispersed in 100 mL isopropanol. Followed by adding 14.0 g chloroacetic acid, the mixed solution was kept at 30 °C for 4 h with stirring. After neutralizing by HCl, the product was precipitated and washed with ethanol to obtain CMC.

2.3. Synthesis of polyurethane containing PEG segments and terminal-NH_2 groups

The reaction between HDI and PEG1000 was carried out *via* a green strategy without toxic solvents (Xiao et al., 2016). Firstly, 10.00 g (0.01 mol) PEG1000 was charged in a flask and melted at 70 °C. Then 2.52 g (0.015 mol) HDI was added with mechanical stirring. After 2 h, the precursor was cooled down to 25 °C and poured into 200 mL hexanediamine alcoholic solution (0.2 mol/L) to accomplish the chain extension for 30 min under stirring. Finally, the solution was filtered, dialyzed against water (Mw cut-off 3.50×10^3 Da) and freeze-dried to obtain the polyurethane (PU).

2.4. Preparation of Lys-Ag-PU and CMC-Ag-PU coatings on PES membranes

PES ultrafiltration membranes were fabricated by a conventional phase inversion method (Xue, Zhao, Nie, Sun, & Zhao, 2013).