Journal of Colloid and Interface Science 510 (2018) 308–317

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Integrating zwitterionic polymer and Ag nanoparticles on polymeric membrane surface to prepare antifouling and bactericidal surface via Schiff-based layer-by-layer assembly

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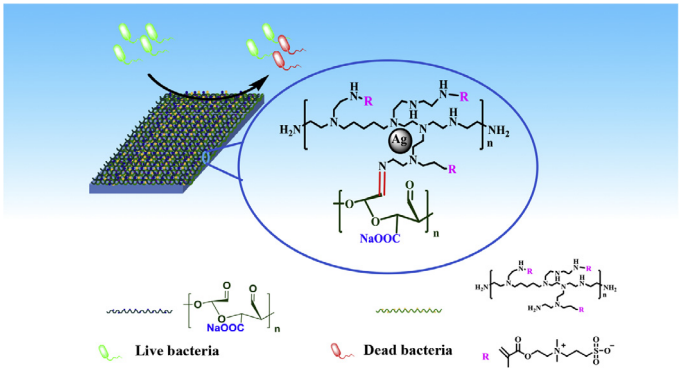
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 July 2017
Revised 19 September 2017
Accepted 20 September 2017
Available online 21 September 2017

Keywords:
Schiff-based LbL assembly
Long-term anti-fouling
Polyzwitterionic
Bactericidal
Ag nanoparticles

ABSTRACT

Development of antibacterial membranes is strongly desired for biomedical applications. Herein, we integrated antifouling and bactericidal properties on polymeric membrane surface via Schiff-based layer-by-layer (LbL) assembly. Zwitterionic polymers bearing plentiful amino groups (based on polyethylenimine (PEI) and sulfobetaine methacrylate (SBMA), and termed as PEI-SBMA) were utilized to prepare an antifouling membrane surface; then robust wide-spectrum bactericidal Ag nanoparticles (Ag NPs) were *in situ* generated on the surface. The as-prepared zwitterionic polymer surface showed excellent resistance to protein adsorption and bacterial adhesion. The Ag NPs could be tightly and uniformly distributed on the membrane surface by the chelation of PEI-SBMA, and endowed the membrane with bactericidal activity. Meanwhile, the Ag NPs loaded membrane could effectively resist bacterial attachment for a long time, even though the bactericidal activity lost. The proposed bactericidal and antifouling membrane was flexible, versatile and could be large-scale preparation; and this strategy would have great potential to be widely used to avoid undesired bacterial contamination of biomedical implants or biological devices.

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https://doi.org/10.1016/j.jcis.2017.09.071
0021-9797/

1. Introduction

Currently, zwitterionic polymers have been widely used to fabricate super-low fouling surface due to their significant hydration ability induced by electrostatic interactions as well as hydrogen binding [1–5]. However, after the modifications by zwitterionic polymers, the materials could not inhibit bacterial growth in environment and completely prevent the bacterial adhesion on material surfaces [6]. Therefore, endowing zwitterionic polymer modified materials surface with a bactericidal activity has been recognized as an efficient strategy to address these issues [6]. Throughout the related studies, embedding silver nanoparticles (Ag NPs) into polymer matrix is one of the most popular and useful approaches for inhibiting bacterial growth in environment due to their wide-spectrum bactericidal activity [7–10]. Hence, we anticipated that antifouling zwitterionic polymers and Ag NPs could be integrated on one material surface to achieve antifouling and bactericidal abilities.

In recent years, many techniques have been developed to anchor zwitterionic polymer onto materials surface, such as blending [11], surface-initiated atom transfer radical polymerization [12], surface-initiated reversible addition-fragmentation chain transfer polymerization [13], Layer-by-Layer (LbL) assembly [14], coating [15] and so on [2,16,17]. Among these methods, LbL assembly is admitted as one of the most flexible and versatile approaches, and allows various materials to be assembled into nano-scale films by using simple, controllable and inexpensive procedures [18–20]. The assembly processes are usually driven by non-covalent bondings, such as electrostatic interaction and hydrogen bonding. Nevertheless, it is difficult to construct multilayer films by using zwitterionic polymers via the usual noncovalent electrostatic interaction due to the inner salt structure. Compared with non-covalently bonded LbL assembly, covalently bonded assembly could significantly improve the robustness of multilayer films, and exhibit enormous advantages in practical applications [14,21–23]. In recent years, Schiff-base reaction, which refers to the reaction between a class of compounds containing aldehydes (or ketones) and amino groups, resulting in imine groups (—C═N—), was widely used in chemistry due to their mild reaction conditions and high reaction rates [24–26]. Meanwhile, numerous natural bio-macromolecules, synthetic polymers, and functional nano-materials have been applied to design or construct Schiff-based complexes. Thus, it was anticipated that the Schiff-based LbL assembly could be utilized to anchor zwitterionic polymer multilayer onto the surface of materials for constructing an antifouling coating.

Recently, a novel amino-riched zwitterionic polymer named as PEI-SBMA was reported and prepared based on polyethylenimine (PEI) and sulfobetaine methacrylate (SBMA), and it was used to easily prepare zwitterionic surface [27,28]. By using PEI-SBMA, Chang et al. [27] easily prepared antifouling hydroxyapatite surface via one-step dip-coating; and Jiang et al. [28] constructed elecrto-neutral membrane surface via interface polymerization. For the novel amino-riched zwitterionic polymer, it combined with the advantages of PEI and SBMA: (1) easily chelated metal ions, (2) widely adhered on material surface, (3) readily reacted with other functional groups (epoxy group, carboxyl, aldehyde and so on), and (4) specifically acted as an antifouling material due to the zwitterionic structure. Therefore, the amino-riched PEI-SBMA was anticipated to be employed for constructing antifouling surface via the Schiff-based LbL assembly and chelating Ag ions to *in situ* generate Ag NPs, which could endow the antifouling surface with bactericidal ability.

Herein, we designed a self-sterilizing surface for efficiently controlling the potential bacterial infections in biomedical implants or biological devices. The surface was composed of zwitterionic polymers and Ag NPs, so that it was estimated to exhibit both bulk bactericidal and surface anti-fouling properties. Firstly, amino plentiful zwitterionic polymers of PEI-SBMA and aldehydes-rich oxidized sodium alginate (OSA) were synthesized; then, a multilayer antifouling coating was prepared by using the two as-prepared macromolecules via the facile Schiff-based LbL assembly. After that, Ag ions were able to specifically bind with the obtained surface polymeric network and subsequently reduced to Ag NPs. Moreover, the surfaces were systemically characterized by attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Additionally, the antifouling properties and bactericidal activity were further evaluated via protein adsorption and bacteria experiments.

2. Experimental section

2.1. Materials

Polyethersulfone (PES, Ultrason E6020P) was obtained from BASF, Germany. Sodium alginate (SA, Aladdin), sodium metaperiodate (99%, Best), bovine serum albumin (BSA, fraction V, Aladdin), polyethyleneimine (PEI, M_W = 10,000, 98%, Aladdin), silver nitrate ($AgNO_3$, 99%, Best) were used as received. Sulfobetaine methacrylate (SBMA) was synthesized according to our previous papers [12,29]. Bovine serum fibrinogen (BFG) was obtained from Sigma Chemical Co. Micro BCA™ protein assay reagent kits were purchased from PIERCE. The LIVE/DEAD Baclight Bacterial Viability Kit L-7012 was purchased from Thermo Fisher Scientific Inc. Deionized (DI) water was used throughout the study. PES was selected as the model substrate, and the home-made PES ultrafiltration membranes were prepared as described in our previous paper [3,30].

2.2. Synthesis and characterization of the polymers

The oxidized alginate was prepared according to a reported procedure with a slight modification [24]. Briefly, 2.5 g sodium alginate was dissolved in 200 mL water, and then 4.8 g sodium metaperiodate was added and stirred in the dark for 24 h at room temperature. After that, the obtained mixture was precipitated in alcohol solution, filtered and dialyzed against water for three days with refreshing the water several times per day (cutoff: 8000–14,000). Finally, the product was dried by lyophilization and named as OSA.

The zwitterionic polymer of PEI-SBMA was synthesized via Michael addition reaction as reported previously [27,28]. A mixture of PEI aqueous solution (2 g) and SBMA (4 g) was solubilized in 12 g water and the reaction was performed at 80 °C for 12 h. Then, the resulting reaction solution was dialyzed for several days to completely remove the unreacted SBMA, followed by freeze-drying prior to characterization. The PEI-SBMA was characterized by the ^{1}H NMR using D_2O as solvent.

2.3. Preparation and characterization of the LbL assembly surface

Firstly, the home-made PES membranes were cut into specified dimension (1 × 1 cm^2), and then immersed into a PEI-SBMA aqueous solution (10 mg mL^{-1}) with shaking at room temperature overnight. Afterwards, the membranes were thoroughly rinsed for three times with DI water to absolutely remove the free polymers, named as PES/PEI-SBMA. As shown in Scheme 1, the substrates were immersed in the PEI-SBMA and OSA (10 mg mL^{-1}) solutions alternately, each for 10 min, washing for three times with DI water