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Host-guest self-assembly toward reversible visible-light-responsive switching for bacterial adhesion

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ABSTRACT

Here we report a facile method to construct reversible visible-light-responsive switching from antibacterial to bioadhesion by host-guest self-assembly of β-cyclodextrin (β-CD) and azobenzene functionalized polycation/polyanion. The visible-light-responsible azobenzene functionalized polycation, poly{6-[(2,6-dimethoxyphenyl)azo-4-(2′,6′-dimethoxy)phenoxy]propyl dimethylaminoethyl methacrylate-random-poly(2-(*N*,*N*-dimethylaminoethyl) methacrylate) (Azo-PDMAEMA), was synthesized via quaternization reaction between 2,6,2′,6′-tetramethoxy-4-(3-bromopropoxy)azobenzene (AzoOMeBr) and poly(2-(*N*,*N*-dimethylaminoethyl) methacrylate) (PDMAEMA), and the polyanion, poly{6-[(2,6-dimethoxyphenyl)azo-4-(2′,6′-dimethoxy) phenoxy]hexyl acrylate-random-acrylic acid} (Azo-PAA), was synthesized via esterification reaction between 2,6,2′,6′-tetramethoxy-4-(6-hydroxyhexyloxy) azobenzene (AzoOMeOH) and poly(acryloyl chloride) (PAC) and subsequent hydrolysis reactions. The switch surface could be achieved via the alternate host-guest assembly of Azo-PDMAEMA and Azo-PAA onto a β-CD-terminated substratum (Sub-CD) through visible light irradiation. The positively charged Azo-PDMAEMA with quaternary ammonium groups exhibited antimicrobial properties and few bacteria were adhered on the surface, while the negatively charged Azo-PAA with carboxyl acid groups exhibited excellent bioadhesive properties and a large number of bacteria were adhered. Interestingly, the switch between antibacterial and bioadhesive could be realized upon visible light irradiation via alternate assembly of Azo-PDMAEMA and Azo-PAA. The proposed approach to manufacturing visible-light-responsive surface with reversible and alterable biofunctionality switching between antibacterial and bioadhesive is simple and efficient, which is promising for preparation of multifunctional polymeric surfaces to encounter multifarious demands for the biomedical and biotechnological applications.

Statement of Significance

Light has attracted great attention in building biointerfaces for its precise spatiotemporal control and convenient operation. However, UV light may damage to biological samples and living tissues, which will limit its applications. This study demonstrates a novel visible-light-responsive surface fabricated through reversible assembly of azobenzene functionalized polycations/polyanions on cyclodextrin (CD)-terminated substrate by host-guest interactions between the visible-light-responsive azobenzene mAzo and CD, which has not been examined previously. It is noted that the azobenzene functionalized polycations show strong antibacterial activities, while the polyanions show excellent bioadhesive properties, as can be switched through the alternate assembly upon visible-light irradiation. This facile and versatile approach to visible-light-responsive surfaces holds great potential for switching of bioadhesion.

1. Introduction

Bacterial adhesion on artificial material surfaces often gives rise to biocolonization, which has raised great concern in various fields such as biomedical and healthcare applications [1–7]. For instance,

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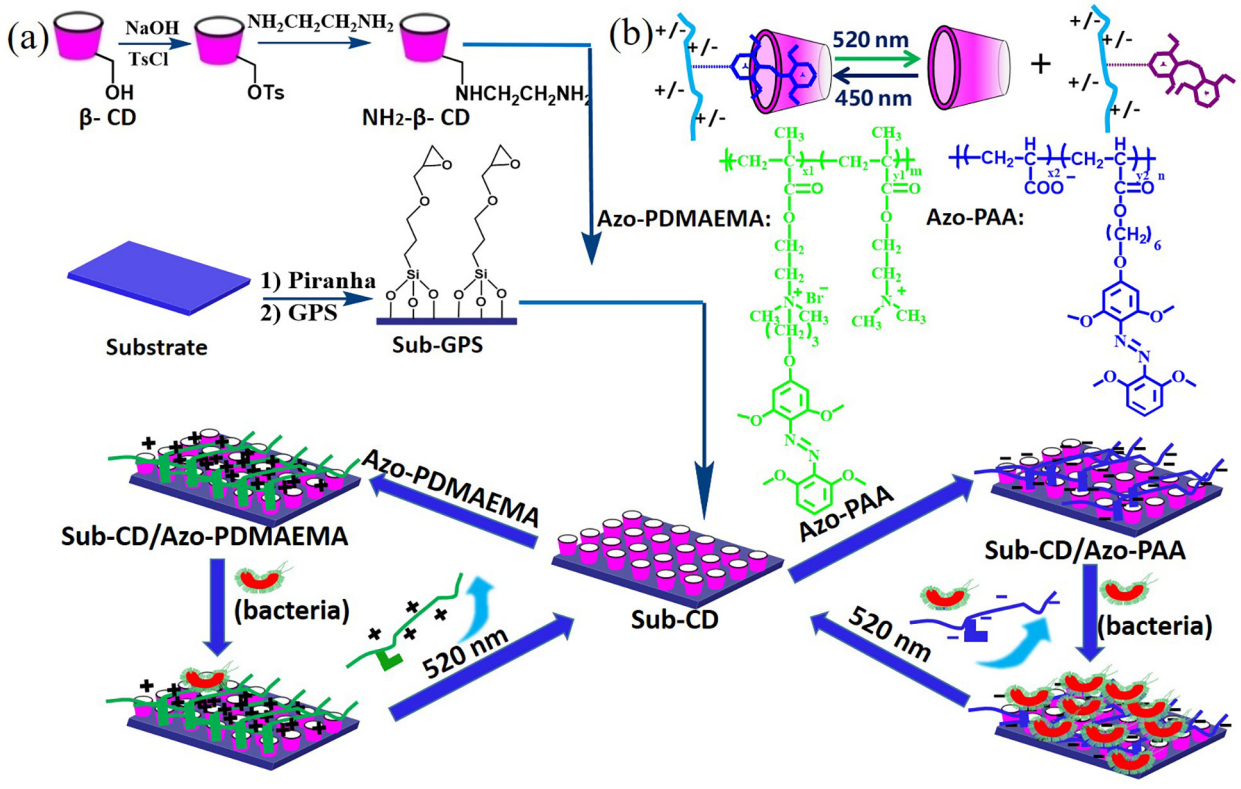
bacteria-induced biofouling of food-processing may affect food safety and quality [5]; bacterial contamination may also cause the failure of medical implants [6]; and pathogenic bacterial contamination on daily necessities may cause cross-infection [7]. Therefore, it is a significant task to design interfacial materials with the ability to control the bacterial adhesion. Stimuli-responsive interfacial materials, which have the capability to alter their chemical/physical interfacial properties in response to various external stimuli such as temperature [8,9], pH [10,11], light [13–15], or redox [16], have attracted great attention in constructing such versatile biointerfaces [6–16], which not only provide ideal platforms to study biological processes triggered by external stimuli but also hold the potential for applications such as biomolecular separation and detection. Among the above stimuli, light is an especially attractive external stimulus because of its possible achievement of spatial and temporal control [17–21]. Supramolecular self-assemblies through host-guest interactions have been paid more and more attentions in recent years due to their potential applications in biomedical and biotechnology fields [22,23]. A supramolecular platform consists of photo-responsive self-assembled monolayer containing azobenzene groups as guests and β-cyclodextrin-mannose conjugates as hosts was developed to capture and release bacteria via the host-guest interaction between azobenzene and cyclodextrin under UV light irradiation [14]. Combined of supramolecular host-guest chemistry between cucurbit[8]uril and azobenzene-mannose conjugate and supported lipid bilayers, a microfluidic device was fabricated to capture/release bacterial cells through UV light irradiation [15]. However, the UV light-induced damage to biological samples and living tissues may limit its applications *in vitro* or *in vivo* [24–27]. Compared with UV light, visible light is much less damaging to biological specimens and living tissues, which has been widely applied in developing drug delivery systems for the clinical applications [28–30]. Tetra-*ortho*-methoxy-substituted azobenzene (mAzo) is a novel visible-responsive chromophore [31–34]. Different from the conventional UV light responsive azobenzene, the azobenzene mAzo can be isomerized from the trans form to the cis form upon green light irradiation and the trans form can be recovered upon blue light irradiation [35,36].

Herein, we report a visible-light-responsive biofunctional surface fabricated by host-guest assembly of mAzo-functionalized polymers and cyclodextrins (CDs) for switching of bacterial adhesion. First, visible-light-responsive polycations, poly{6-[(2,6-dimethoxyphenyl)azo-4-(2′,6′-dimethoxy)phenoxy]propyl dimethylaminoethyl methacrylate-random-poly(2-(*N*,*N*-dimethylaminoethyl) methacrylate) (Azo-PDMAEMA), and visible-light-responsive polyanions, poly{6-[(2,6-dimethoxyphenyl)azo-4-(2′,6′-dimethoxy) phenoxy] hexyl acrylate-random-acrylic acid} (Azo-PAA), were synthesized. A β-CD-terminated surface (Sub-CD) was fabricated through a silane coupling reaction of (3-glycidyloxypropyl) trimethoxysilane (GPS) and subsequent ring-opening reaction with mono-6-dexoy-6-ethylenediamine-β-CD (NH_2-β-CD). The visible light responsive azobenzene functionalized polycations (Azo-PDMAEMA) and polyanions (Azo-PAA) were then alternately immobilized onto the Sub-CD surface to achieve the switchable biofunctional surfaces. The positively charged Azo-PDMAEMA with quaternary ammonium groups showed antimicrobial properties which could be applied as an antibacterial surface; while the negatively charged Azo-PAA with carboxyl acid groups showed excellent bioadhesive properties which could be applied as a unique surface for bacteria adhesion [13,16]. The fabrication of visible-light-responsive surfaces, the visible-light-triggered alternate assembly of Azo-PDMAEMA and Azo-PAA onto Sub-CD and their bacterial adhesion properties are illustrated in Scheme 1. This strategy for fabrication of visible-light-responsive biofunctional surface is facile and efficient, which can be recognized as a convenient method to switch between antibacterial and bioadhesive to satisfy different biomedical applications.



Scheme 1. (a) Chemical routes for preparation of Sub-CD, Sub-CD/Azo-PDMAEMA and Sub-CD/Azo-PAA, and schematic depiction of visible-light-triggered alternate and reversible switching between antibacterial and bioadhesive. (b) Schematic illustration of the supramolecular interaction between Azo-PDMAEMA/Azo-PAA and β-CD.

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