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In-situ fabrication of polyelectrolyte-CSH superhydrophilic coatings via layer-by-layer assembly

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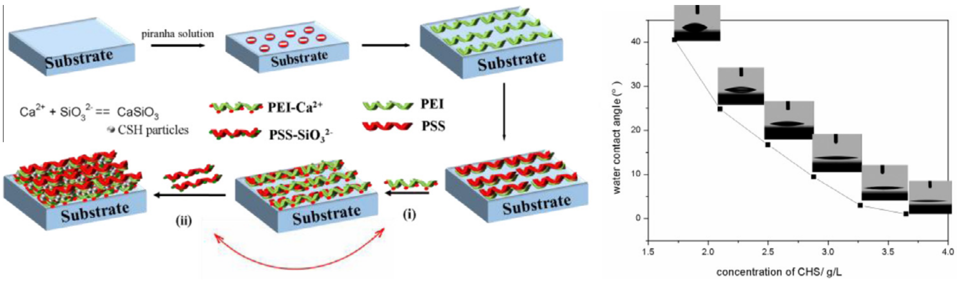
HIGHLIGHTS

- $(PEI–PSS/CSH)_n$ coating films were fabricated on either quartz or glass substrate.
- The water contact angles can be tuned by either the number of deposition cycles or the concentration of CSH.
- The films exhibited superhydrophilic, antireflective and antifogging characteristics.

GRAPHICAL ABSTRACT



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ABSTRACT

Superhydrophilic and antireflective coatings were fabricated via the layer-by-layer (LbL) assembly method with *in situ* precipitation of sodium silicate and calcium acetate on quartz or glass slide substrate. The influences of assembly conditions on the growth behavior, surface topologies, zeta potentials, wettability, antifogging behavior and transmittances of the multilayer coatings have been investigated in details. The results indicated that more than three deposition cycles with 3.27 g/L calcium silicate hydrates (CSH) solution were optimal condition for the fabrication of a superhydrophilic and antireflective coating structure of poly(ethyleneimine)/poly(sodium 4-styrenesulfonate) $(PEI/PSS–CSH)_3$ with 98.0% of transmittance, and even 99.4% of $(PEI/PSS–CSH)_4$ multilayer film. Additionally, the 3.0 bilayers of PEI–PSS/CSH coatings exhibited superior antifogging characteristics. This *in situ* formation of CSH nanoparticles in the LbL film offers a potential strategy to fabricate multifunctional films for a variety of technological applications.

1. Introduction

Surface wettability control has received much attention in both academics and practical applications [1–3]. Superhydrophilicity, a typical and special wettability with a water contact angle (WCA) closed to 0 degree, endows the surface a completely non-water-repellent property. Water would then lie on such a surface as a flat film rather than in form of droplets [4]. And the dirt and other staining materials on the surface can be readily washed away with this superspreading water layer. The superhydrophilic surface has thereby promising applications in industry and daily life such as self-cleaning antireflective optical coatings, selfcleaning and decontamination, antifogging, and biocompatibility [5–7].

Two basic approaches can be used to create superhydrophilic surfaces on substrates or materials. One way is to create photocatalytic particles-based surfaces, such as titania-based superhydrophilic surfaces first reported in 1997 [8]. On the basis of this method, metal oxide photocatalysts (TiO_2, ZnO, SnO_2, WO_3 and

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V_2O_5) have been developed for creating superhydrophilic surfaces by exposing them to UV light radiation [9–14]. Even without UV radiation, the superhydrophilicity can also be achieved by suitable chemical modifications [15–17]. A second approach is to introduce a textured structure of the surface in order to promote its superwetting behavior [18–20]. It is well known that the wettability of a solid or flat surface depends mainly upon its surface composition and roughness [21–24]. Construction of the hierarchical structures on films has been demonstrated as a versatile approach to create a defined surface roughness and thereby enhance their water wettability [25–27].

Methods for the fabrication of robust nanoparticle-based thin films with enhanced superwetting behavior have been recently reported. The methods were domain-selective treatment by etching or lithography [28], laser microfabrication [29], electrochemical deposition [30,31], sol–gel self-assembly-based deposition of nanoparticles [32,33], *in situ* synthesis of polymeric-thin-films-templated nanoparticles [34,35], hydrothermal treatment [36], spin and spray coating [37,38], as well as layer-by-layer (LbL) assembly [39,40]. Among these techniques, LbL assembly has been demonstrated as a versatile, feasible and inexpensive way to fabricate large-area films with well-tailored composition and architecture. Since the SiO_2 nanoparticles-based multilayer thin films were first prepared via LbL assembly method by Lvov and co-workers [41], a number of hierarchically structured surfaces have been fabricated, such as the hierarchically porous TiO_2/SiO_2 superhydrophilic thin films fabricated by alternate assembly of positively charged TiO_2 nanoparticles and negatively charged SiO_2 nanoparticles [42], the porous SiO_2 and TiO_2 hollow spheres-based superhydrophilic films [43,44], and superhydrophilic mesoporous silica thin films prepared by combining the template method and the LbL assembly technique [45–47]. Moreover, raspberry-like or mulberry-like silica nanospheres-based hierarchically structured coatings were produced by LbL of dual-size particles to create superhydrophilic coatings [48–50]. More recently, the superhydrophilic thin films fabricated by highly porous ZnO nanoparticles and poly(acrylic acid) (PAA) via LbL technique displayed a broadband antireflection in the visible region, and thus provide selective opacity in the UV region and enhanced transmittance in the visible region up to the near-infrared region [51]. However, on the basis of the reviews mentioned above, all building blocks are just limited to metal oxide or SiO_2 particles, and have to be prepared before the assembly process. This greatly limited the possible applications. Hence a facile and cost-effective approach should be developed for large-scale film productions. Recently, Sun and co-workers developed this method for the fabrication of mechanically stable antireflection and antifogging silica coatings by LbL deposition of poly(diallyldimethylammonium chloride)–silicate complexes with poly(acrylic acid) on quartz substrates. However, the SiO_2 inorganic phases can be only obtained by calcinations of its precursor [52].

Calcium silicate hydrates (CSH) are the main constituents of the hydrated cement systems, which are responsible for most of important engineering properties of concrete such as strength and permeability [53], and was widely explored in constructive industry and academics due to low cost-effect and high strength [54–56]. Many efforts have been attempted to exploit the excellent bioactivity, stability, and biocompatibility of CSH [57–59]. CSH has been synthesized by chemical precipitation in solutions or solid-state reaction with controlled structures and morphologies [60–63]. Moreover, the nanolayered CSH can be used as inorganic templates for the intercalation of polymers and polyelectrolytes [64,65], as powerful reinforcing agents to prepare nanocomposites with excellent bioactivity [64,66]. However, how to use CSH as an inorganic unit is still a challenge in LbL self-assembly process. Herein we report the preparation of the polyelectrolytes-CSH films with controlled thickness, and tunable wetting behavior as well as surface structures (roughness, morphology) using a controlled number of deposition cycles and various initial concentrations of CSH. These films were fabricated by LbL assembly accompanied by *in situ* precipitation of CSH. The surface structures (morphology, roughness and thickness) and wetting ability of the films were investigated by SEM, AFM, profilometer, and water contact angles (WCAs) methods. Moreover, the anti-fogging and antireflection behaviors of the films were also explored without further post-treatment such as calcinations. The usage of *in situ* fabrication of cost-effective CSH during LbL assembly process would greatly simplify the synthetic procedure and reduce the cost of the multifunctional coatings. Also the subsequential assembly of analogous inorganic/polymer composite films using synthetic polymer and a wider range of inorganic phases would spur the quest to emulate natural hierarchical structured composites [26].

2. Experimental section

2.1. Materials

Poly(ethyleneimine) (PEI, $M_w = 750{,}000$) and poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70{,}000$) were purchased from Sigma–Aldrich (USA). Sodium silicate ($NaSiO_3$) and calcium acetate [$Ca(CH_3COO)_2$] with A.R grade were obtained from Tianjin Fu Chen Chem. Reagents Ltd., Co., (Tianjin, China). Concentrated sulfuric acid (98%) and hydrogen peroxide (30%) were provided by Tianjin Fine Chemicals (Tianjin, China). Deionized water (conductivity of 18.0 MΩ cm) was used in all experiments. Unless otherwise described, all reagents were used as received, and all aqueous polymer solutions were used without pH adjustment or the addition of ionic salts. The quartz slices were provided by Beijing Xingshida Ltd., Co., (Beijing, China).

2.2. Synthesis procedure

The polyelectrolyte multilayer (PEM) of PEI/PSS–calcium silicate hydrate (CSH) was deposited on the flat quartz or glass substrates according to Scheme 1. Both substrates were treated with hot piranha solution (3:1 mixture of 98% H_2SO_4 and 30% H_2O_2), followed by washing with deionized water thoroughly. Prior to the assembly of the nanoparticle-based multilayers, the PEI/PSS bilayer was firstly assembled onto the substrate as the cap layer. The concentrations of the PEI and PSS solutions were 2.0 g/L. The *in situ* fabrication of the multilayer films of PEI/PSS–calcium silicate hydrate (CSH) were performed according to the following protocol: (i) the substrate covered by PEI/PSS bilayer was dipped into a transparent solution of 2.0 g/L PEI–calcium acetate for 20 min, followed by rinsing with deionized water for 1 min; (ii) The film from step (i) was then introduced into a transparent solution of 2.0 g/L PSS–sodium silicate for 20 min, followed by rinsing with deionized water for 1 min. Herein, the molarity of the calcium acetate and sodium silicate with molar ratio of Ca/Si of 1.0 in the two polyelectrolyte solutions were ranged from 1.72 to 3.65 g/L. The CSH cluster was formed by the reaction of cationic Ca^{2+} with anionic SiO_3^{2-} during LbL deposition (Herein, we postulate that the Ca^{2+} and SiO_3^{2-} reacted completely in the polyelectrolyte solution and the equimolar amounts of CSH nanoparticles were formed as the reaction equation in Scheme 1 [67]. The hydrophilic-to-superhydrophilic transition of the (PEI/PSS–CSH) was carried out. Steps (i) and (ii) were then repeated until the desired number of deposition cycles was reached. Multilayer films of PEI/PSS–calcium silicate hydrate (CSH) with *n*-cycle deposition are noted as $(PEI/PSS–(CSH))_n$. The similar procedure was applied for the deposition of the same composite PEM onto a glass substrate.