



Reversible molecular adsorption of free-standing nano-composite film made from boehmite and poly(acrylic acid)



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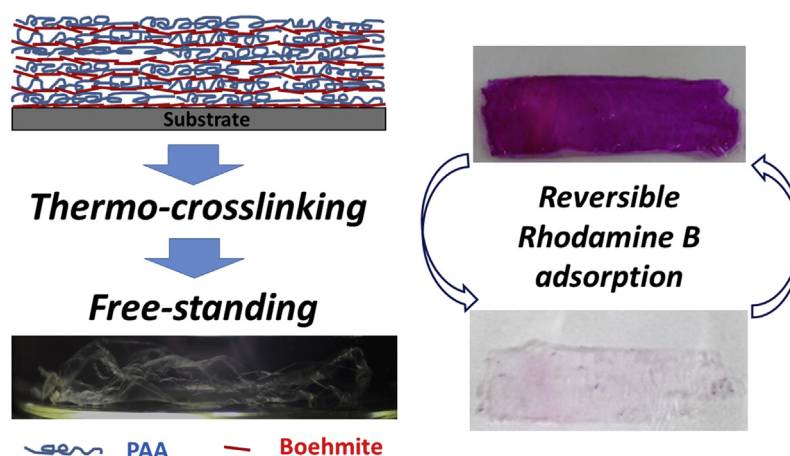
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HIGHLIGHTS

- A nano-composite film with reversible molecular adsorption behavior was fabricated.
- With thermal cross-linking, the film can wholly detach from the substrate.
- The free-standing film remains stable in a wide pH range for a considerable period of time.
- Dynamic hydrogen bonding and electrostatic interaction endowed the free-standing film reversible swelling/shrinking ability.

GRAPHICAL ABSTRACT



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ABSTRACT

A nano-composite film with reversible small molecules adsorption behavior was fabricated via layer-by-layer (LbL) assembly of boehmite nano-particles and weak polyelectrolyte poly(acrylic acid) (PAA). Both electrostatic force and hydrogen bonding interaction were involved to fabricate the nano-composite thin film. Boehmite/PAA nano-composite thin film was further cross-linked with thermal treatment, which enhanced the stability of the film. When immersed into the basic solution, the thermal cross-linked film wholly detached from the substrate. And the dynamic cross-links such as hydrogen bonding and electrostatic interaction endowed the free-standing film reversible swelling/shrinking ability in response to pH variations at least five times. Furthermore, the free-standing Boehmite/PAA film showed reversible rhodamine B (RB) adsorption behavior, which could be utilized for controlled loading and releasing.

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1. Introduction

Nano-composite thin films have drawn considerable attention due to important applications in various areas, such as optical

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devices [1], sensors [2], gas barrier [3], nanofiltration [4], catalyst [5], solar cell [6], flame retardance and protective coating [7,8]. Layer-by-layer (LbL) assembly technique, developed by Decher in the early 1990's, is a versatile method to prepared thin film and coating with well-defined structure [9,10]. According to different demands, various species, such as synthetic polymers, protein, DNA, inorganic colloids, metal clusters, and even virus are utilized for LbL assembly [11].

The fabrication of LbL nano-composite film is usually implemented by alternately depositing inorganic nano-items and oppositely charged organic polyelectrolytes. Many inorganic nano-items, such as nanosheets [12], nanotube [13], metal [14], magnetic [15], semiconductor nanoparticles [16,17] have been successfully used to prepare nano-composite films. For example, graphene oxide nanosheet and poly(allylamine hydrochloride) (PAH) have been LbL assembled to prepare membrane for water purification [12]. A bio-sensor for cholesterol fabricated by LbL assembly of positively charged nano-composite (PAH-MCNTs-GNPs) and the negatively charged enzyme (horseradish peroxidase) has been achieved [13]. TiO₂ amphoteric colloidal charged particles and polyelectrolytes have been used to fabricate a dye-sensitized solar cell [6]. Besides electrostatic interaction, hydrogen-bonding is utilized as attractive force to construct nano-composite thin films. Based on hydrogen-bonding interactions in aqueous solution, the LbL assembly of poly(vinylpyrrolidone) (PVPON) and a spherical polymer brush with a poly(methylsilsesquioxane) (PSQ) core and PAA hair chains have been realized [18]. And Irmukhametova et al. also have reported that PEGylated organosilica nanoparticles are capable of forming hydrogen-bonded LbL film with PAA in acidic solution [19].

LbL assembled films are usually integrated together through non-covalent bonds, and hence the stability of the film is relatively weak [20–22]. Generally, LbL assembled systems are attached on the substrate and it is difficult to get free standing films. For practical applications, stability enhancement and free-standing state are required [23,24]. Cross-linking is an effective way to improve the stability of LbL films. Many chemical methods have been applied to cross-link LbL assembled thin films, including photo-induced reaction [25], thermal-induced reaction [26], disulfide coupling [27] and catechol oxidation reaction [28]. In order to get free-standing film, different approaches have been developed, such as dissolving substrates [29], sacrificial layers [30], or neutral substrate [31].

In this work, we constructed LbL nano-composite thin films using Boehmite and PAA. The stability of Boehmite/PAA nano-composite film was enhanced by thermal cross-linking. The cross-linked film can be completely detached from the substrate when immersed into the basic solution (pH > 10.0). The free-standing film showed reversible molecular adsorption behavior which was tuned by pH value.

2. Experimental

2.1. Materials

Poly(acrylic acid) (PAA, M_w = 450,000) was purchased from Sigma-Aldrich. Aluminum isopropoxide (Al(C₃H₇O)₃) was bought from Ling Feng Shanghai Chemical Reagent Co., Ltd. Rhodamine B (RB) was obtained from Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid, nitric acid, sulfuric acid, hydrogen peroxide were of analytical grade. All chemicals were used as received.

2.2. Boehmite sol preparation

The sol was prepared according to the Yoldas process [32]. Nitric acid (0.01 mol) mixed with water (10 mol) was stirred 30 min

at room temperature, then 0.1 mol aluminum isopropoxide was added into the system, and further stirred 24 h at 90 °C to get the pristine sol.

2.3. Film fabrication

PAA was dissolved in deionized water at a concentration of 0.5 mg/mL. Boehmite sol was diluted 100 times. The pH values of PAA solution and Boehmite sol were adjusted through adding hydrochloric acid or sodium hydroxide solution under the monitoring of a pH meter (Mettler Toledo, SevenMulti). When diluted under alkaline conditions, rapid precipitation of boehmite sol was observed (Fig. S1). Because PAA begins to ionize at pH 2.0 [21], LbL assembly of PAA and Boehmite was conducted in the pH region from 2.0 to 6.0.

Silicon or quartz slides, the substrates for depositing nano-composite film, were cleaned by immersing into the boiling H₂SO₄/H₂O₂ mixture (v/v, 7/3) for 30 min (*caution: this solution is extremely corrosive*). They were rinsed with deionized water thoroughly, and finally dried with nitrogen flow. An automatic machine (Kejing Auto-Instrument Co. Ltd., Shenyang, China) was utilized to perform LbL assembly. The machine alternately dipped the substrates into Boehmite sol and PAA solution, with the interval of three rinsing steps in the same pH solvent. The assembling time and the rinsing time were set to 4 and 1 min, respectively. After assembling, the wet film was dried in the ambient and then preserved in the desiccator. The prepared film expressed as (Boehmite/PAA)_n means the film assembly of Boehmite and PAA solutions through *n* assembling cycle(s).

2.4. Cross-linking

(Boehmite/PAA)_n nano-composite film was vacuumed heated at 175 °C for 24 h to obtain the thermally induced chemical crosslinks.

2.5. Film detachment

The cross-linked (Boehmite/PAA)_n nano-composite film was immersed into pH 11.0 aqueous solution. After immersion for 24 h, the film completely detached from the substrate.

2.6. Dye loading and releasing

The pH values of RB solutions were adjusted under the pH-meter monitoring. Temperature of RB solution was controlled by a thermostat. For dye loading, the cross-linked (Boehmite/PAA)₆₀ nano-composite films were immersed into RB solutions (1.0 μg/mL with different pH values) for 24 h at 30 °C. The free-standing (Boehmite/PAA)₂₀₀ films were used to load RB at acidic pH value and release it at basic pH value repeatedly.

2.7. Characterization

The growth of the film was monitored in situ by a Quartz Crystal Microbalance with Dissipation (QCM-D) (Siju Biological Material, Suzhou, China). For all measurements, quartz crystal chips ~ 5 MHz with a gold coated surface were rinsed in thioglycolic acid ethanol solution (5 mmol/L) for 24 h, then the chips were washed by ethanol and pure water in high speed, alternately for 3 times at least and finally dried with nitrogen flowing. The system was under injection with a 50 μL/min flow rate. All solutions were ultrasonic dealt for 30 min to remove bubbles. For the film fabricating, the assembling solution flowed through the crystal for 15 min, which followed by a flushing for 10 min with pH 2.0 water. All solutions were adjusted to pH 2.0 previously. Boehmite sol was pumped into the QCM chamber to deposit the first layer.

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