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Effects of CO_2 bubbles on layer-by-layer assembled hybrid thin film

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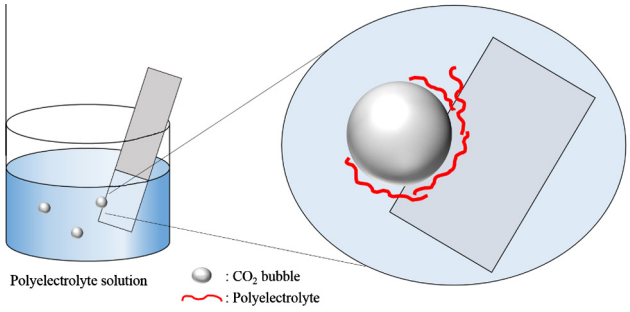
HIGHLIGHTS

- The effects of CO_2 bubbles on LbL assembled multilayer film were investigated.
- Bubble formation at the solid-water interface have physical effect on film deposition.
- The thickness and roughness of CO_2-treated film increased.
- No significant aggregation of polyelectrolytes on the surface was observed.
- CO_2 bubble method is proposed as an effective modification method of LbL film.

GRAPHICAL ABSTRACT



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ABSTRACT

In recent years, polyelectrolytes such as poly (diallyldimethylammonium chloride) and polystyrene sulfonate have been widely applied to hybrid thin films for industrial applications. In this paper, we report a method to modify the film by applying CO_2 bubbles during layer-by-layer (LbL) assembly. The differences in thickness, mass, and surface morphology between CO_2-treated hybrid LbL and pristine films were analyzed by quartz crystal microbalance, atomic force microscopy, scanning electron microscopy, and profilometry. The internal structure of the hybrid LbL films was investigated by analyzing the release of doxorubicin (DOX) incorporated in each film through photoluminescence. Upon CO_2 treatment, the thickness, mass, and surface roughness increased, while the amount of incorporated DOX decreased.

1. Introduction

The fabrication of nanofilms of various materials has attracted considerable interest due to the potential applications in many fields [1–5]. Although an accurate control of nanoscopic features in nanomaterials has already been achieved, the design of stacking structures and characteristics of nanoscale films is still a considerable challenge.

The layer-by-layer (LbL) self-assembly technique is one of the most effective methods to prepare nanofilms of various materials such as polymers, nanoparticles, carbon, and biomolecules [6–8]. This approach provides a precise control of the structure and film thickness through complementary interactions (i.e., covalent interactions, hydrogen bonding, electrostatic interactions, and hydrophobic interactions) [9–12].

Recently, LbL has attracted interest as a simple, versatile, and environmentally friendly method for diverse applications in biomedicine, nanoparticle-based catalysis [13], and energy storage [14]. At present, several kinds of polyelectrolytes (PEs) are used as building blocks for thin film fabrication. For examples, poly (diallydimethylammonium chloride) (PDAC), poly (4-vinylpyridiine) (P4VP), and linear poly (ethylene imine) (LPEI) are commonly used as cationic building blocks, while poly (sodium styrenesulfonate) (PSS), poly (acrylic acid) (PAA), poly (2-acryla mido-2-methyl-1-propanesulfonic acid) (PAMPS), and Nafion are utilized as anionic building blocks [15–18].

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However, although LbL is a powerful film deposition method, it presents some limitations in controlling with precision the internal structures and surface morphologies. Even though the nanoscopic features of the LbL film can be controlled by adding additional base, acid and salt buffer, there are some cases that cannot add buffers. Herein, to overcome the limitations of the conventional LbL assembly approach, we introduce the CO_2 bubble method, which allows controlling the internal structure and surface morphology of the LbL film.

Since CO_2 gas is well-known soluble molecule in water solvent, supersaturated CO_2 solution can be easily achieved without harsh conditions such as high pressure and low temperature. There are plenty of previous studies about the properties of CO_2 molecules dissolved in solution [19–22]. However, until now, there are no report about application of CO_2 in LbL assembly. We characterized the CO_2 bubble treated films by analyzing their variations in thickness, mass, and surface roughness, as well as their internal structure.

2. Material and methods

2.1. Materials

Poly (diallydimethylammonium chloride) (PDAC; MW 20,000–35,000) and poly (sodium 4-styrenesulfonate) (PSS; MW 70,000) were purchased from Sigma Aldrich. All solutions were prepared in distilled water with 1 mg/mL concentration, and 0.1 M sodium chloride (NaCl) was added to control the charge density. Phosphate buffered saline (PBS) was purchased from Biosolutions Inc.

2.2. Preparation of (PDAC/PSS) LbL film

2.2.1. Conventional LbL film

Multilayer films were fabricated on Si wafer and quartz glass substrates. The substrates were thoroughly cleaned in a piranha solution (sulfuric acid:hydrogen peroxide 70:30 v/v%) for 10 min, and then treated with O_2 plasma to produce negative charge. Next, the substrates were dipped into a positively charged PDAC (1 mg/mL, 0.1 M NaCl) solution for 10 min, and then subjected to three washing steps lasting 2 min, 1 min, and 1 min. Subsequently, the substrates were dipped in a negatively charged PSS (1 mg/mL, 0.1 M NaCl) solution for 10 min, and washed three times for 2 min, 1 min, and 1 min. This cycle provided one bilayer of the $(PDAC/PSS)_n$ film ('n' indicates the number of repeated cycles). The dipping cycles were repeated until the desired film was fabricated.

2.2.2. CO_2 Addition in the LbL process

The substrates were prepared following the same process adopted for the conventional LbL films with CO_2 bubble addition. When the substrate was dipped into the PDAC and PSS solutions, the CO_2 gas was continuously added throughout the full length of adsorption steps. The CO_2 gas was introduced by the gas flow from the CO_2 gas barrel. Furthermore, in order to facilitate dissolving CO_2 molecules into the solution, porous ceramic bubble generator was connected at the end of gas tube.

2.3. Incorporation and release of doxorubicin (DOX)

The CO_2-treated $(PDAC/PSS)_{15}$ and control $(PDAC/PSS)_{15}$ films were dipped into a DOX solution (0.2 mg/mL) for 20 h for incorporation. DOX-loaded $(PDAC/PSS)_{15}$ films were dipped into 10 mL of PBS (pH 7.4). Then, 1 mL of PBS was collected at different points of time and added to an equal quantity of fresh PBS. The incorporation and release mechanism of DOX molecule were simple diffusion.

2.4. Characterization

The thickness of the multilayer films was measured by a profilometer (Dektak 150, Veeco). Mass of the films was indirectly determined by quartz crystal microbalance (QCM, QCM200, Stanford Research Systems). Surface morphologies and roughnesses of the films were examined by atomic force microscopy (AFM, NX-10, Park Systems) in non-contact mode and field-emission scanning electron microscopy (FE-SEM, LIBRA 120 microscope, Carl Zeiss). All of the films images were taken in the dried state without post-treatment. The amount of released DOX was monitored by photoluminescence spectroscopy. The refractive indices of the multilayer films on Si wafers were measured by ellipsometry (Gartner Scientific Corp., L2W15S830) with 632.8 nm He Ne laser light. All measurements of samples were obtained after being dried by gentle nitrogen gas.

2.5. QCM analysis

The amount of adsorbed mass of polyelectrolytes was analyzed by QCM (QCM200, Stanford Research Systems). LbL films were fabricated on Au-chrome electrodes following same process as described earlier. The change in frequency of the QCM electrode was monitored from 1 layer to 12 layer of LbL films after being dried by gentle nitrogen gas. From the change of frequency, the mass of LbL film can be determined by using Sauerbrey equation.

$$\Delta F\ (\mathrm{Hz}) = -\frac{2F_0^2}{A\sqrt{\rho_q \mu_q}}\Delta m$$

F_0 is the fundamental resonance frequency of the crystal (approximately 5.0 MHz).
A is the area of the QCM electrode.
μ_q is shear modulus (2.95×10^{11} g/(cm·s^2)).
ρ_q is density of quartz (2.65 g·cm^{-3}).

The equation can be simplified as follows by applying numerical values:

$$\Delta F\ (\mathrm{Hz}) = -56.6 \times \Delta m_a$$

2.6. Nanoporosity analysis

The porosities of CO_2-treated film and control film were calculated using the Lorentz-Lorenz equation.

$$\frac{N_f^2 - 1}{N_f^2 + 1} = (1 - \mathrm{P})\frac{N_0^2 - 1}{N_0^2 + 1}$$

where N_f and N_0 are the refractive index of $(PDAC/PSS)_n$ multilayer film and the refractive index of PDAC (or PSS) film respectively. P represent the porosity of the film. N_0 is calculated to be about 1.385 because the refractive indices of single component PDAC and PSS film are 1.375 and 1.395 respectively.

3. Results and discussion

The CO_2 concentration could be determined by measuring the pH value of the solutions. When the CO_2 bubbles were added to the polyelectrolyte solution, the pH values changed, as the dissolved CO_2 gas promoted the release of hydrogen ions [22]. Therefore, upon addition of CO_2 bubbles, the acidity of the polyelectrolyte solution tended to increase; the pH value of the