Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Journal of Colloid and Interface Science 315 (2007) 396–399

JOURNAL OF
Colloid and
Interface Science

www.elsevier.com/locate/jcis

Note

Effects of hydrogen peroxide on the electrochemical decomposition of layer-by-layer thin films composed of 2-iminobiotin-labeled poly(ethyleneimine) and avidin

Katsuhiko Sato, Yukihisa Naka, Jun-ichi Anzai [*]

Graduate School of Pharmaceutical Sciences, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan

Received 15 May 2007; accepted 19 June 2007

Abstract

The effects of hydrogen peroxide on the electrochemical decomposition of layer-by-layer thin films composed of 2-iminobiotin-labeled poly(ethyleneimine) (ib-PEI) and avidin were studied. An ib-PEI/avidin thin film prepared on the surface of a platinum (Pt) film-coated quartz resonator was electrochemically decomposed in the presence of hydrogen peroxide (H_2O_2) in the solution. The resonant frequency of the thin-film-deposited quartz resonator was increased upon application of electric potential (0.4–0.6 V vs Ag/AgCl) to the Pt layer, suggesting that the mass on the quartz resonator was decreased as a result of decomposition of the ib-PEI/avidin film. It was found that decomposition of the film is highly accelerated in the presence of H_2O_2 compared to the decomposition in the same buffer solution without H_2O_2, due to a pH change originating from electrochemical oxidation of H_2O_2 on the Pt surface. The rate of electrochemical decomposition of the ib-PEI/avidin film was highly dependent on the concentration of H_2O_2, buffer capacity, and pH of the solution.

Keywords: LbL thin film; Layered film; Avidin; Electrochemical decomposition; Quartz crystal microbalance

1. Introduction

The development of nanometer-sized layered assemblies has been a focus in surface sciences and technologies. Among techniques for preparing nanoassemblies, a layer-by-layer (LbL) deposition technique developed by Decher and Hong [1] has been widely used for developing layered thin films by taking advantages of an electrostatic force of attraction [2,3], hydrogen bonding [4,5], and biological affinity [6–8]. The layered films have found applications in magnetic nanodevices [9], biosensors [10,11], perm selective membranes [12], encapsulation and controlled release [13], etc.

Recently much attention has been devoted to developing stimulus-sensitive LbL thin films that decompose in response to pH changes, dithiol, and electrical potential [14–16]. In this context, we have reported that LbL assemblies composed of concanavalin A and glycogen are sensitive to sugars and degradable in response to sugars [17]. We have found also that LbL thin films composed of avidin can be disintegrated by changing the environmental pH [18,19]. The avidin-containing films were prepared using 2-iminobiotin-labeled poly(ethyleneimine) (ib-PEI) and avidin through biological affinity between 2-iminobiotin and avidin. Avidin is a glycoprotein (molecular weight 68,000) found in egg white and is known to contain four identical binding sites to biotin (binding constant; ca. 10^{15} M^{-1}) [20]. It is also known that avidin binds 2-iminobiotin less strongly than biotin and the affinity is pH-dependent (the binding constant of 2-iminobiotin to avidin is 2.9×10^{10} M^{-1} in a basic solution, while the value of the protonated form in acidic media is ca. 10^3 M^{-1}) [21]. It is thus reasonable to assume that the LbL thin films prepared using avidin and ib-PEI are sensitive to the environmental pH. In fact, the ib-PEI/avidin films could be decomposed by changing the environmental pH from basic to weakly acidic [18]. It has been further found that ib-PEI/avidin LbL films prepared on the

---

[*] Corresponding author.
E-mail address: junanzai@mail.pharm.tohoku.ac.jp (J. Anzai).

0021-9797/$ – see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2007.06.028

surface of a platinum (Pt) electrode can be disintegrated upon applying an electric potential to the electrode due to acidification of the local pH around the Pt surface [22]. The present paper reports that the electrochemical decomposition of ib-PEI/avidin films can be greatly accelerated in the presence of H_2O_2 in solution.

2. Experimental

2.1. Chemicals

Avidin was purchased from Calzyme Laboratory Inc. ib-PEI was prepared by the reaction of poly(ethyleneimine) (PEI, from Nakalai Tesque Co., Japan, molecular weight 60,000–80,000) and 2-iminobiotin *N*-hydroxysuccinimide ester hydrobromide (Sigma Co.) according to the reported procedure (the content of 2-iminobiotin residues in the ib-PEI is ca. 2 mol% based on the total amino groups in PEI) [19]. All other reagents were of the highest grade available and used without further purification.

2.2. Preparation of ib-PEI/avidin LbL films

The ib-PEI/avidin LbL films were prepared on a Pt film-coated quartz resonator as reported in [19]. Briefly, a quartz resonator was immersed in an avidin solution ($0.1\ \mathrm{mg\,ml^{-1}}$) for 15 min at room temperature to deposit the first layer of avidin. After being rinsed in the working buffer for 5 min, the quartz resonator was immersed in an ib-PEI solution ($0.1\ \mathrm{mg\,ml^{-1}}$) for 15 min to deposit the ib-PEI. The deposition was repeated in order to build up the multilayer assemblies. A 10 mM borate buffer containing 100 mM KCl (pH 11) was used for preparing the avidin and ib-PEI solutions.

2.3. Decomposition of ib-PEI/avidin LbL films

The decomposition of the ib-PEI/avidin films was studied by monitoring a resonance frequency of the ib-PEI/avidin film-deposited quartz resonator with a quartz crystal microbalance (QCM) in borate buffer solutions containing 100 mM KCl. Changes in the resonance frequency were monitored upon applying electrical potential to the Pt layer on the resonator. A Ag/AgCl electrode (3 M KCl) was used as a reference electrode. All measurements were carried out at room temperature (ca. 20 °C).

2.4. Apparatus

A QCM (QCA 917 system, Seiko EG & G, Japan) was employed for monitoring the deposition and decomposition of LbL films. A 9-MHz AT-cut quartz resonator coated with a thin Pt layer (surface area $0.2\ \mathrm{cm^2}$) was used as a probe, in which the adsorption of 1 ng of substance induces a -0.91 Hz change in the resonance frequency. A conventional potentiostat was used for applying electric potential to the quartz resonator.

3. Results and discussion

We have previously reported that ib-PEI/avidin layered films deposited on the surface of a Pt-coated quartz resonator can be

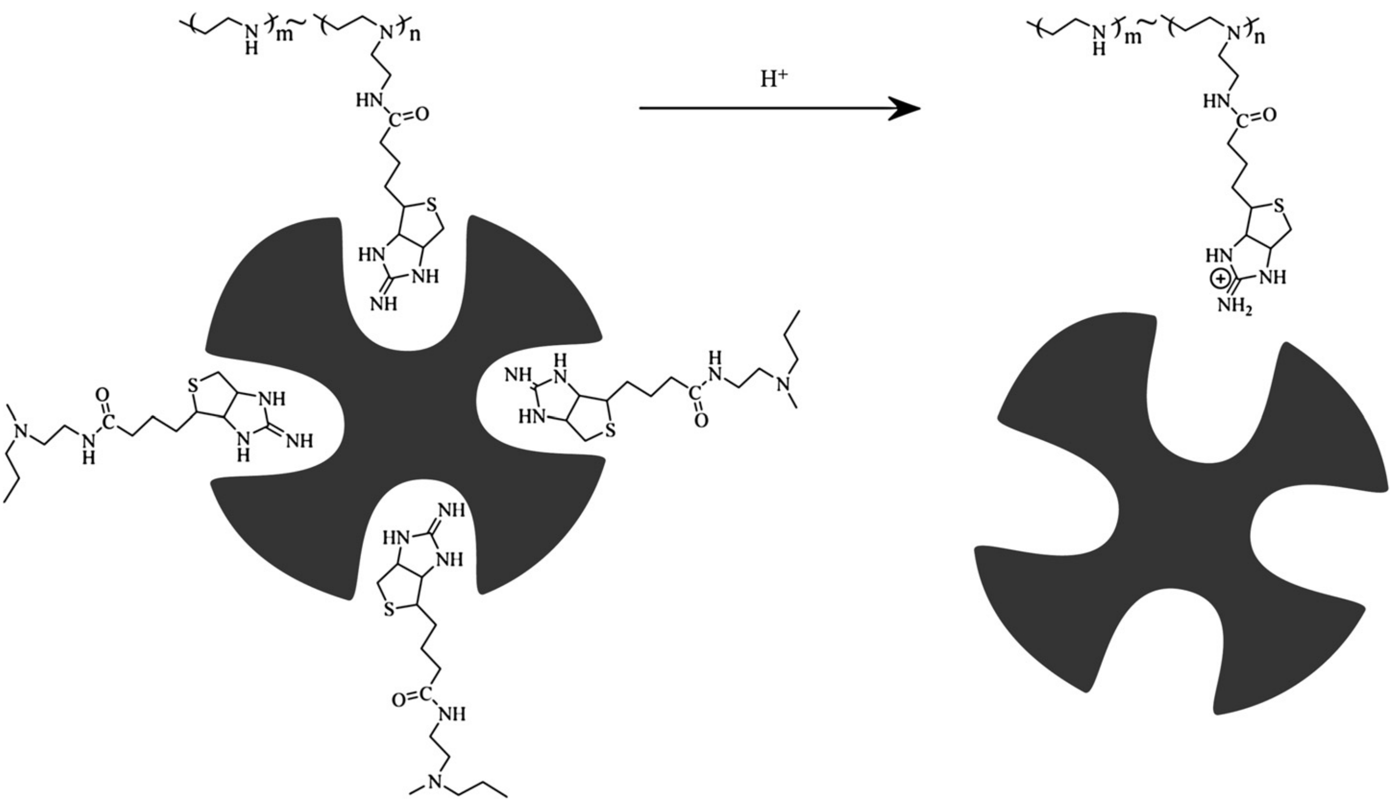

Fig. 1. A schematic illustration of ib-PEI/avidin complexation and dissociation induced by protonation to 2-iminobiotin moieties in ib-PEI upon pH change.