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Transparent silica thin films prepared from sodium silicate and bovine serum albumin with petal effect

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Abstract

A variety of advanced functions such as hydrophilicity and hydrophobicity are required for transparent glass plates recently. This paper reports a new procedure to produce transparent silica thin films on glass plates obtained from sodium silicate as inexpensive silica source by its dip coating and subsequent deposition of silica with $(NH_4)_2SO_4$ solution. When the thin films were prepared using bovine serum albumin (BSA), the resulting transparent films became more hydrophobic than that obtained without BSA and had good adhesion with water droplet, the so-called "petal effect". Water droplet on the silica thin film did not slide down even when the substrate turned vertically and upside down. Although no BSA was included in the silica thin film, BSA contributed to the formation of nano-sized asperity structures in the film, producing more hydrophobic (less hydrophilic) property and the petal effect.

Keywords: Silica; Transparent thin film; Sodium silicate; Bovine serum albumin; Petal effect

1. Introduction

Transparent plates of ceramics and glass are very useful materials, which are commonly used in our everyday life. Recently, these plates are often required to have characteristic functions for water such as hydrophilicity and hydrophobicity [1,2]. Especially, hydrophobic surface contributes to a variety of practical applications, for example, to front windshield of vehicle [3]. In a number of procedures for the preparation of hydrophobic transparent thin films on glass materials, the most representative one is the coating of organosilane compounds onto the surface [4–6]. However, these organic substituents are generally unstable to require repetitive coating with these expensive organosilanes. Thus, new preparation methods of hydrophobic transparent thin films on glass surface are desired. Silica is a desirable component for the thin film on glass materials because of high compatibility between them. However, the preparation of transparent silica thin films using sodium silicate as the most economical silica source has been scarcely reported [7–9].

It is well known that the surface hydrophobicity is controlled by the chemical property of surface component and the geometries of surface [10,11]. In the latter case, fine and ordered roughness often increases the hydrophobicity of the surface [12,13]. High water repellency and self-cleaning property found in lotus leaves referred to as "lotus effect" are created by the unique asperity microstructure of the surface [14]. On the other hand, "petal effect" as another character of materials surface to water observed in red rose petal is an emerging research agenda [15–19]. Water droplet on red rose petal is stopped from slipping down by the petal effect even when the petal surface is turned upside down [15]. At the beginning of the study on the petal effect, films are prepared by molding processes of the surface structures of rose petal [15] and lycopodium particle [16]. A two-layer polymer sheet formed by initiated chemical vapor deposition on molded rose petal surface is also reported [17]. Recently, fully artificial surfaces with the petal effect are also fabricated by mimicking the structure of natural rose petal using copper alkyl-thiolate [18] and polystyrene particle [19]. These new materials are expected to develop the use of the

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petal effect such as the analysis of a small amount of water [19]. Since silica is generally more stable than those organic materials, silica thin films having the petal effect will provide new practical applications in a variety of circumstances.

We have intensely studied the preparation of silica materials using sodium silicate as silica source. Using water/oil/water (W/O/W) emulsion, hollow silica particles are readily prepared from sodium silicate by a single step procedure [9,20–23]. When some water-soluble salts are added to sodium silicate, hollow particles with unique silica shells are obtained [22,23]. We also succeeded the preparation of silica thin films on glass substrate by the coating of sodium silicate solutions and the following deposition of silica on the glass [9]. In this thin film preparation, it was found that the addition of water-soluble materials to sodium silicate controlled asperity textures in the silica thin films. In this paper, we report a new preparation method of transparent silica thin films with the petal effect, which were prepared from the mixed solution of sodium silicate and bovine serum albumin (BSA) as a water-soluble protein.

2. Experimental

2.1. Materials

The sodium silicate employed in this study was water glass No.3 as Japanese Industrial Standards, JIS K1408, obtained from Kishida Chemical Co., Ltd. Bovine serum albumin (BSA; albumin from bovine serum as Cohn Fraction V, pH 7.0), papain, pepsin and lysozyme (lysozyme from egg white) were obtained from Wako Pure Chemical Industries. A special grade of $(NH_4)_2SO_4$ and (3,3,3-trifluoropropyl)trimethoxysilane were purchased from Kishida Chemical Co., Ltd. or Tokyo Chemical Industry Co., Ltd., respectively. Biuret reagent and Folin reagent were bought from Sigma-Aldrich Co. LLC. All other chemicals used here were commercial available and used without further purification.

2.2. Preparation of silica thin films

A typical experimental procedure of the preparation of silica thin films is described with the case of BSA mixing as follows. 16.67 g of sodium silicate was mixed with described amounts of BSA in Table 1 and 28 g of deionized water. These apparently-homogeneous solutions were dip coated onto a slide glass substrate (75 mm × 25 mm × 1 mm, common soda glass substrate purchased from AS ONE Corporation). Prior to the dip coating, all glass substrates were soaked in 1 M NaOH solution of methanol and dried at 100 °C for 30 min. These glass substrates were drawn down at the rate of 2.0 mm/s, and were withdrawn up at the rate of 0.1 mm/s using a dip coating machine (TD-1501; SATUMA Communication Industry Co., Ltd.). After drying at room temperature for 3 min, these dip coated thin films were immersed into 2 M aqueous solution of $(NH_4)_2SO_4$ in petri dish for 60 min. The glass substrates thus obtained were thoroughly rinsed with deionized water, and dried at 60 °C for 30 min.

The modification of the silica thin film with (3,3,3-trifluoropropyl)trimethoxysilane $[CF_3CH_2CH_2Si(OCH_3)_3]$ was carried out as follows. Approximately 0.1 mL of the silane was spread onto the one side of a glass substrate and heated at 150 °C for 24 h in a sealed vessel. After washing with acetone twice, the glass substrate was dried at room temperature.

2.3. Sample characterization

The contact angles of the thin films were measured by a contact angle meter of EXCIMER Inc., the Model Simage mini, using ATAN1/2θ method, where 3.6 μL of deionized water was used. The morphologies of the silica thin films were monitored with secondary electron image by a scanning electron microscopy (JEOL JSM-6390 scanning electron microscope). For the SEM observation, the glass substrates were cut to proper size, and gold was deposited by an ion sputtering device (JEOL JFC-1500). The visible spectra of aqueous solutions were recorded by a JASCO V-530 spectrometer, and diffuse reflectance UV and visible spectra were obtained with a JASCO V-550 spectrometer equipped with an integrating sphere (JASCO ISV-469), where Kubelka–Munk functions were plotted versus the wavelength. UV absorption of BSA (around 280 nm in wavelength) in the silica thin films on glass substrate was unmeasurable directly because of the strong absorption of the soda glass substrate below 320 nm. Alternatively, Lowry method [24] was used for BSA detection by a common protocol using commercially available Biuret reagent and Folin reagent. Due to the strong absorption of Lowry reagent in UV range (<400 nm), only the visible spectra of the solutions used for Lowry method were monitored for BSA detection. The pH values of aqueous solutions were estimated by a pH meter (Horiba PH-METER D-21). The determination of the petal effect was carried out by the following method. When a water droplet (14.4 μL) did not move at least for 30 s on a vertically placed substrate, the thin film on the substrate was considered to have the petal effect.

3. Results and discussion

3.1. Preparation of silica thin films from sodium silicate and proteins

Silica thin films were prepared by a two-step procedure, dip coating of a sodium silicate solution and subsequent deposition of silica using $(NH_4)_2SO_4$ solution. $(NH_4)_2SO_4$ was ascertained as the most efficient precipitant for the preparation of silica thin films having the petal effect in our preliminary examination. Moreover, since the fast withdrawal rate of dip coating process produced opaque thin films due to the formation of thicker silica layer on glass substrate, the withdrawal rate was fixed to 0.1 mm/s that is the slowest one for our dip coater. Table 1 summarizes the silica thin films produced from the mixed solutions of sodium silicate and proteins. A transparent silica thin film was successfully prepared from a sodium silicate solution without protein (**F-0**). As this thin film was hard to be pared, an alternate material picked from an opaque thin film obtained by a fast withdrawal rate (1 mm/s) was used for composition analysis. The IR spectrum and the XRD pattern of the material (not shown) indicated the formation of an amorphous silica thin film. This thin film was