



In-situ pore filling of TiO₂ nanoparticles in honeycomb patterned porous films: A modified breath figure method

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ABSTRACT

Polystyrene (PS) honeycomb patterned porous films filled with titanium dioxide (TiO₂) nanoparticles were prepared by a modified breath figure method. The honeycomb patterned porous films filled with TiO₂ nanoparticles were obtained by pouring titanium butoxide over partially dried PS solution during the fabrication of the PS films under humid conditions. TiO₂ nanoparticles were obtained by the hydrolysis of titanium butoxide in the condensed micro water droplets at the PS solution/air interface. Morphology, elemental mapping, X-ray diffraction (XRD), X-ray photoelectron spectroscopy, and UV–Visible analysis support the formation of TiO₂ nanoparticles in the honeycomb patterned pores. XRD studies showed that the formed TiO₂ nanoparticles are anatase. Photo-activity of the incorporated TiO₂ nanoparticles was examined by the change of the water contact angle of the films before and after UV irradiation. Water contact angles was decreased by UV irradiation, implying the transformation of the surface from hydrophobic to hydrophilic due to the photo-induced wettability by TiO₂.

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1. Introduction

Patterned porous films have attracted substantial attention because of their potential applications in numerous fields such as tissue engineering, optoelectronic devices, size-selective separation, adhesion, sensors, polymer electrolytes, stretchable electrodes, and so on [1–7].

The breath figure (BF) method is an easy and convenient process used for the fabrication of patterned micro-porous films. BF was first reported by Widawski et al. for the fabrication of polystyrene-*b*-polyparaphenylene honeycomb-patterned porous (HCP) films [8]. In the BF method, polymer solution taken in volatile organic solvent was fabricated under high humid conditions resulting in the condensation of water droplets which arrange to regular hexagon like structures to obtain HCP films. BF technique has been extensively practiced and continuously modified to investigate its mechanism, and to control the pore size, shape, two- or three-dimensional pore array, effect of various substrates, solvent, polymer concentration, vapors, and airflow, etc [3,6]. The possibility of BF method was also examined in spin coating, dip coating, along

with solution casting techniques [3,6].

Functionalized HCP films have broader and specific applications compared with pristine un-functionalized HCP films. For the functionalization, most of the previous reports focused on the bulk functionalization of the films by employing polymer composites/blends and surface modification by step-by-step or in situ procedure [9–12]. However, selective functionalization of HCP films can be more attractive depending on the applications and for the consideration of nano-science and technology in the future. Selective functionalized HCP films such as either top [13], bottom surface [14,15] only functionalized, pore decorated [16–19], or pore filled [20–24] HCP films can have unique properties and specific applications.

Only few reports are available on either the selective pore decoration or pore filling of HCP films. Self-assembly or Pickering emulsion were applied for the pore decoration of HCP films [18,19]. A more complex functionalization procedure is involved when pore (filled) specific functionalization is considered. Few reports on pore-filled HCP films have been reported. Tang et al. and Colombo et al. have directionally electrodeposited gold nanoparticles into pores of the HCP films [21,22]. Li et al. reported the in-situ formation of TiO₂ micro-particle within the pores of polystyrene (PS) HCP films using TiCl₄ in PS solution [20]. Leon et al. reported the pore-filling of PS-HCP films with cobalt ferrite by pouring pre-

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synthesized cobalt ferrite dispersion onto HCP films, with the filling step assisted by a magnetic field or gravity [23].

Titanium-based materials have recently enticed much research interest because of its photo activity, corrosion resistance, biocompatibility, and good machinability, making it a material of choice in artificial bones, dental implants, photo catalysis, separations, photovoltaics, pigment, sensors, energy storage, and waste water treatment applications [25–27]. Thus, incorporation of TiO₂ in the HCP film is a strategy to combine the advantages of both HCP films and TiO₂ [28–30]. For the incorporation of TiO₂ in the HCP films, polymer composites or blends with TiO₂ nanoparticles can be considered. However, the selective filling of pores with TiO₂ in PS HCP films will show better performances because PS and TiO₂ are present in their pristine states. Whereas in composites/blends, the activity of TiO₂ is decreased because the TiO₂ is partially buried/covered by polymer making it un-available for application.

In the present work, PS HCP films with TiO₂ nanoparticles filled pores (PS-*pf*-TiO₂) were fabricated using condensed water droplets formed at the PS solution/air interface during BF method for the hydrolysis of titanium butoxide. Firstly, we report in-situ pore-filling method in the fabrication of HCP porous films using micro-water droplets as a reactive template. The strategy consists the pouring of titanium butoxide onto the partially dried PS solution during the BF process, wherein titanium butoxide reacts with micro-water droplets and form TiO₂ nanoparticles in the pores. By employing the present strategy, PS-*pf*-TiO₂ HCP films contain PS and TiO₂ nanoparticles in their pristine forms and can confer the benefits of both components. The obtained films are specifically TiO₂ nanoparticles pore-filled PS-HCP films.

2. Experimental

2.1. Materials

Polystyrene (PS, Mn = 170,000), titanium butoxide (Ti(OBu)₄, 97%), and other reagents were purchased from Sigma Aldrich, USA and used without any further purification.

2.2. Fabrication of PS-*pf*-TiO₂ and PS films

PS (250 mg) was dissolved in a 5 mL of chloroform. Then the PS solution was cast in a glass petri dish (5 cm diameter) under humid conditions (70% relative humidity). To obtain a uniform honeycomb-pattern, humid air was blown onto the polymer solution surface through an air pump at a flow rate of 0.6 L min⁻¹. After partial drying of polymer solution (60–80 min), 1 mL of titanium butoxide was added onto the surface of PS solution surface and the film was completely dried under humid conditions. Titanium butoxide reacts with condensed micro-water droplets and form TiO₂. The films thus obtained have white TiO₂ precipitate covered on the PS film. The surface TiO₂ powder was removed by gentle tapping, and the films were abbreviated as PS-*pf*-TiO₂. The TiO₂ powder removed from the surface of PS-*pf*-TiO₂ film was recovered for further analysis.

For the comparison, pristine PS films were fabricated following similar fabrication procedure without pouring titanium butoxide.

2.3. Characterization

The surface and cross-section morphologies of the PS and PS-*pf*-TiO₂ films were characterized by scanning electron microscope (SEM, Model: CX-100, COXEM, Daejeon, South Korea). For SEM analysis, the films were cut into 1 cm × 1 cm and mounted on a copper grid using a double sided adhesive carbon tape and gold-sputtered to avoid possible charging effects. Elemental

composition distribution on PS-*pf*-TiO₂ film was determined using a SEM (FEI Inspect F50) equipped with EDX and energy backscattering electron instrument (EBSD) (Pegasus with Hikari). The analysis was performed by covering a relatively large sample area and a high-voltage (20 keV) maximized resolution. X-ray diffraction (XRD) patterns of obtained TiO₂ nanoparticles in the process, and PS-*pf*-TiO₂ film samples were studied using a D8 Advance X-ray diffractometer (Bruker AXS, Germany) with CuK α radiation ($\lambda = 1.54 \text{ \AA}$) with a scan rate of 1.5° min⁻¹. The UV-Vis spectra of the films were obtained with an Evolution 201 spectrophotometer (Thermo Scientific, MA, USA) by dissolving the films in chloroform. X-ray photoelectron spectroscopy (XPS) spectra was recorded using a spectrometer with Mono Al K α (1486.71 eV) radiation at a power of 120 W (8 mA, 15 kV). Water contact angles on the films were measured with a contact angle analyzer (CAM 100, KSV Co. Connecticut, USA). For UV irradiation effects on the water contact angles, the PS and PS-*pf*-TiO₂ HCP films were irradiated using a 200 W mercury-xenon lamp (4500 mW cm⁻² intensity at 365 nm; UV Spot Light-source Lightning Cure LC8, Model - L9588-01, Hamamatsu Co. Japan).

3. Results and discussion

Fig. 1 shows the schematic representation forwarded at various reaction conditions for the time intervals of pouring titanium butoxide solution to the PS solution, and shows the obtained results by digital photographic images and with corresponding SEM images. Fig. 1(a) shows the photo image of pristine PS film without pouring titanium butoxide, which shows a good complete film with translucent white color. The typical SEM image obtained from the corresponding film shows HCP morphology with empty pores as shown in Fig. 1(a₁). Fig. 1(b–e) shows the photo images of PS films obtained by pouring the titanium butoxide solution with time interval of 0, 10, 30, and 60 min during the fabrication of PS solution, respectively. The photo images of Fig. 1(b–d) obtained by the time interval of 0, 10, and 30 min, respectively did not show good surface morphology. The films were cracked, brittle, and appear to be relatively thick white films compared to pristine PS film. The typical SEM images obtained from the corresponding films as shown in Fig. 1(b₁–d₁) also show non-patterned uneven porous morphology with empty pores. This observation might be due to the fact that the fabrication of PS solution was performed by a blend state with titanium butoxide, which resulted in an inhibiting role in the normal BF process.

Whereas Fig. 1(e) shows the films obtained by the addition of titanium butoxide after 60 min, which resulted in complete films with a layer of white precipitate covering the film surface, similar observation was observed for the films obtained by the addition of titanium butoxide more than 60 min (~80 min). This is because the PS solution is partially dried (not in liquid state) so that the mixing/blending of titanium butoxide with PS solution is inhibited. The added titanium butoxide reacts vigorously with the condensed micro-water droplets formed under humid conditions and formed into TiO₂ nanoparticles, whereas the excess titanium butoxide on the surface reacted slowly with the atmospheric humidity and formed TiO₂ microparticles which fused into flakes. Flakes can be easily removed from the surface after complete drying of the film. Fig. 1(f) shows the PS film after removal of surface excess TiO₂ of the PS film obtained by the addition of titanium butoxide after 60 min. Fig. 1(f) shows a similar appearance with a pristine PS film as shown in Fig. 1(a). The typical SEM image obtained from the corresponding film shows good HCP morphology with TiO₂ nanoparticles as shown in Fig. 1(f₁).

However, the films obtained by pouring titanium butoxide after complete drying (>150 min) of PS solution (i.e. dry PS film, Fig. 1(a))

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