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Coupling of breath figure method with interfacial polymerization: Bottom-surface functionalized honeycomb-patterned porous films

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ABSTRACT

A new and facile method was designed for the fabrication of asymmetrically polyaniline (PANI) functionalized polystyrene (PS) honeycomb-patterned porous films in a single step. The method involves the coupling of breath figure process with an interfacial polymerization, wherein the PS solution containing benzoyl peroxide in an organic solvent was cast under humid conditions over an aqueous solvent containing aniline and methane sulfonic acid. PANI was coated on the bottom surface at the organic/aqueous interface by an interfacial polymerization method, whereas a porous patterned PS was fabricated on the top surface by the breath figure method. The films revealed a translucent insulating PS top surface and a conducting green PANI bottom surface. The obtained films represented asymmetrical composition, color, morphology, conductivity, and contact angle on either surface.

1. Introduction

Patterned porous films with micro- or nano-sized pores mimicking natural honeycomb like structure have attracted great interest because of their specific characteristics such as large specific surface area, good structural and mechanical strength, and low density [1–3]. Functional patterned porous films have been widely utilized in various applications, such as super hydrophobic surfaces, size and shape selective separation, sensing materials, biomaterials, and photo-electronic materials [1,4–6]. These films can be obtained by adopting various techniques, such as photolithography, soft lithography, anodized lithography, nano-imprint lithography, self-assembly, and template methods [1,2,5]. However, among these methods the self-assembly of water droplets with the breath figure (BF) technique is a simple, rapid, template-free and economical approach that has enticed utmost research interest [1,3].

Widawski et al. was the first to report on the use of the BF technique for the fabrication of honeycomb-patterned (HCP) porous films [7]. They obtained polystyrene (PS) HCP films by casting polystyrene-block-polyparaphenylene solutions (2–100 g/L) in CS_2 under humid atmosphere. Since then, the BF technique has been extensively used and continuously modified into methods such as static BF, dynamic BF, use of non-aqueous vapors, use of different substrates, and combination of BF with other methods, including spin coating and dip coating [4,6,8]. BF technique is also adopted in tandem with other methods to obtain functionalized organic/inorganic HCP films [6,9–13]. Thus, BF technique provides an immense potential to use for advanced functionalization of materials by adopting it along with other methods.

PS is a widely used synthetic aromatic polymer. It is generally transparent and mostly used as a plastic-ware. PS has been successfully utilized for the fabrication of HCP films and moreover polystyrene-block-polyparaphenylene is the first polymer to be used for BF method [7]. Functionalization of PS with conducting polymers was proven to extend its applications [14–17]. Polyaniline (PANI) has been one of the most intensively investigated intrinsically conducting polymers because of its interesting properties, such as tunable conductivity, facile production, mechanical and environmental stability, biocompatibility, light weight, and low cost [10]. PANI is extensively applied in electro-chromic devices, energy storage devices, corrosion protection, anti-static coatings, sensors, biomedical applications, tissue engineering, and hydrogen storage [18–22]. Utilization of PANI in the form of HCP films will be

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more efficient because it combines the advantages of both PANI and HCP films. Few reports are available on PANI HCP films, where they have used composites [23,24], templates [25–28] or surfactant assisted techniques [29]. However, most of these reports for the fabrication of PANI HCP films are laborious, multi-step and time consuming.

Recently, we have obtained symmetrically PANI functionalized poly(ε-caprolactone) (PCL) HCP films for the first time by using reactive template rather than structure directed templates used in previous methods [10]. Polymer solutions containing PCL and benzoyl peroxide (BPO) in chloroform were fabricated under high humid conditions to obtain PCL-BPO honeycomb patterned films. The films were treated with aqueous aniline hydrochloride solution to polymerize aniline at the interface of the PCL film and aniline hydrochloride solution. PCL-BPO films served dual role of a template as well as an oxidant.

Compared to symmetrically functionalized films, asymmetrically functionalized films can be designed to own unique features such as anisotropic electrical, magnetic, optical, adhesion or wetting properties due to their asymmetric structure and composition. Guo T et al. has fabricated hydrophobic polyimide HCP films by BF method over hydrophilic anodic aluminum oxide which showed unidirectional water penetration from hydrophobic surface but not from hydrophilic surface [30]. Therefore, the asymmetrically functionalized films could find tremendous interest in various research aspects of physics, chemistry and biological applications.

In this study, we introduce a new and facile method for the fabrication of asymmetrically functionalized HCP porous films. To fabricate asymmetrically functionalized HCP films, we have coupled the interfacial polymerization with BF process. Accordingly, we propose a new strategy for the fabrication of asymmetrically PANI-*functionalized*-PS (PANI-*f*-PS) HCP films through the interfacial polymerization of aniline coupled with the BF technique in a single step. Wherein, PS solution in volatile organic solvent containing oxidant was fabricated over acidic aqueous solution containing monomer, aniline under humid conditions. The interfacial polymerization will occur at the aqueous/organic interface, along with BF process, the resulting film has HCP morphology, with PS on one surface and PANI on other surface. The HCP films express asymmetry in composition, morphology, electrical conductivity, and water contact angle. The films were characterized by color, SEM, EDX, UV-Vis, conductivity, and contact angle measurements.

2. Experimental

2.1. Materials

Polystyrene (PS) (M_n, 170,000), aniline, benzoyl peroxide (BPO), methane sulfonic acid (MSA), and other reagents were procured from Sigma–Aldrich (USA) and used as received without any further purification.

2.2. Fabrication of asymmetrical PANI-f-PS HCP films

HCP films were cast from the polymer solutions containing BPO in a similar procedure reported in our previous report [10]. The most significant modification was the coupling of interfacial polymerization along with BF process.

In a typical procedure, 0.25 g of PS and a calculated amount of BPO were added with 5 mL of tetrahydrofuran (THF) and then sonicated for 20 min to obtain a uniform PS–BPO solution. Subsequently, 1 M aq. MSA solution containing aniline was poured into a glass Petri dish (5 cm diameter). To this aqueous solution, 2 mL of ethyl acetate was added as a protective layer to avoid the immediate contact of reactants and prevent the mixing of THF and water. The PS–BPO solution was slowly added over the ethyl acetate layer without disturbing the interface. The reaction solution was allowed to evaporate under humid conditions (70% relative humidity) until a translucent film was obtained. The resulting film exhibited a translucent (white/colorless) top surface and a green bottom surface; green is the characteristic color of PANI.

In the present work, the amount of aniline was varied as 20, 40, 60, and 80 μL and the amount of BPO was taken in double amount w.r.t. aniline mole. The films thus obtained will be abbreviated as PANI-*f*-PS-2, PANI-*f*-PS-4, PANI-*f*-PS-6, and PANI-*f*-PS-8, respectively. The schematic representation for the fabrication of PANI-*f*-PS films is presented in Scheme 1. For comparison, pristine PS HCP film was also prepared without adding reactants.

2.3. Characterization

The optical images of PANI-*f*-PS patterned film were obtained by using optical microscope fitted with a digital system; the images were captured using i-solution software. The morphologies of the PANI-*f*-PS films were characterized via SEM (CX-100, COXEM, Daejeon, South Korea). The elemental composition distribution of the samples was determined using a SEM (FEI Inspect F50, Hillsboro, USA) equipped with EDX and energy backscattering electron instrument (Pegasus with Hikari). The analysis was performed by covering a relatively large sample area and a high-voltage (20 keV) maximized resolution. The UV–Vis spectra of the films were obtained with an Evolution 201 spectrophotometer (Thermo Scientific, MA, USA) using a sample concentration of 2 mg mL^{-1} in NMP. DC electrical measurements were obtained with a four-point probe technique using a 6220 constant current source and a 2182A digital electrometer (Keithley, Cleveland, Ohio, USA). Water contact angles on the films were measured with a contact angle analyzer (CAM 100, KSV Co., Connecticut, USA).

3. Results and discussion

For asymmetrically functionalized PANI-*f*-PS HCP films, polymer solution comprising BPO is used for the fabrication of HCP films by following a similar procedure reported in our recent report [10]. In the previous study, symmetrically PANI functionalized PCL HCP films were fabricated by following a two-step procedure. Wherein the PCL solution containing various amounts of BPO in chloroform were fabricated into HCP films by BF method. HCP films were then used as a reactive oxidation template for the polymerization of aniline at the PCL film–solution interface by immersing the film in an aqueous aniline hydrochloride solution. By meeting the PCL-BPO film with aniline hydrochloride solution, an interfacial polymerization is taken place at film/solution interface and resulted in symmetrically functionalized PCL-PANI HCP films. As it is a two-step process the choice of commonly used organic solvent, chloroform did not affect the overall method.

But in the present work, we have focused on the asymmetrical functionalization in a single step by coupling BF process with interfacial polymerization. As a result we have outlined a scheme to fabricate the polymer solution containing BPO over aqueous layer containing aniline which will result in an interfacial polymerization at liquid/liquid (polymer solution/aqueous substrate) bottom surface while BF process will occur on top surface. Therefore the use of chloroform ($\rho = 1483$ kg m^{-3}) was not feasible in the present case as the density of solvent is higher than water ($\rho = 997$ kg m^{-3}) which will sink into the water and BF process is not possible. An immediate precipitation of polymer was observed by casting the polymer solutions (PS-BPO) in chloroform directly over water surface resulting in the lump of polymer mass.

Solvents were chosen by careful consideration of the solubility