

Fabrication of pore-selective carboxyl group functionalized polyimide honeycomb-patterned porous films using KOH humidity

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HIGHLIGHTS

- A new strategy was developed for the pore selective carboxyl functionalization.
- Polyimide reacts with KOH humidity to form carboxyl functionalized porous films.
- Pore functionalization was enhanced by delayed introduction of KOH humidity.
- Reactive carboxyl pores can be used as a template for further functionalization.
- Silver functionalized porous polyimide films by ion-exchange self-metallization.

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ABSTRACT

Carboxyl group functionalization in honeycomb-patterned porous (HCP) films was obtained by breath figure process using polyimide (PI) which can react with KOH humidity at the polymer solution/aqueous alkali droplet interface to form carboxyl groups. PI containing CO-NR₂ imide ring group reacts with KOH for imide ring-cleavage reaction by interfacial reaction. In order to obtain pore-selective carboxyl group functionalized PI HCP films, we have suggested a new strategy introducing KOH humidity with time interval after using initial water humidity during breath figuring process. The carboxyl group functionalized pores can be applied to obtain ordered microarray of biological and inorganic materials, which have potential applications in biosensors, separations, medical biology, etc.

1. Introduction

Highly ordered porous polymer films have attracted considerable attention because of their potential applications in various fields, such as tissue engineering, surface enhanced Raman scattering, optoelectronic devices, sensors, etc. [1–4]. Thus, various techniques have been developed for the fabrication of porous materials, such as phase separation [5,6], emulsion templating [7,8], direct foaming [9,10], polymer foam replication [11,12], freeze drying [13,14] and breath figure (BF) method [15–18]. Among them, the BF method is a simple and convenient technique to fabricate honeycomb-patterned porous (HCP) films [18]. In BF method, polymers soluble in volatile organic solvents are subsequently cast under high humid conditions [19,20].

In addition to the highly ordered porous films, pore-selective functionalized HCP films have attracted a great amount of interest because of their specific applications such as tissue engineering, cell culture

substrates, and catalysis [21–26]. Recently, HCP films with carboxyl group functionalized pores have demonstrated as the reactive substrates for micro-patterning of biological ligands such as carbohydrates, antibodies, or proteins which can find applications in many fields such as biology, biosensor technology, biomedical devices, and tissue engineering [27–32]. Min et al. have reported carboxyl group pore-decorated HCP films fabricated from polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) block copolymer for attaching biotin which reacts with streptavidin leading to an organized array of proteins [27]. León et al. have prepared the switchable and pH responsive porous films with carboxyl group enriched pores, using blends of polystyrene (PS) and an amphiphilic block copolymer of poly(L-glutamic acid), which have negative charge to immobilize cationic molecules at pH above the pK_a of the poly(L-glutamic acid) [28]. In another report of León et al., carboxyl group pore decorated HCP films from PS-*b*-PAA have been used to immobilize alkaline phosphatase enzyme [29]. All above studies rely on

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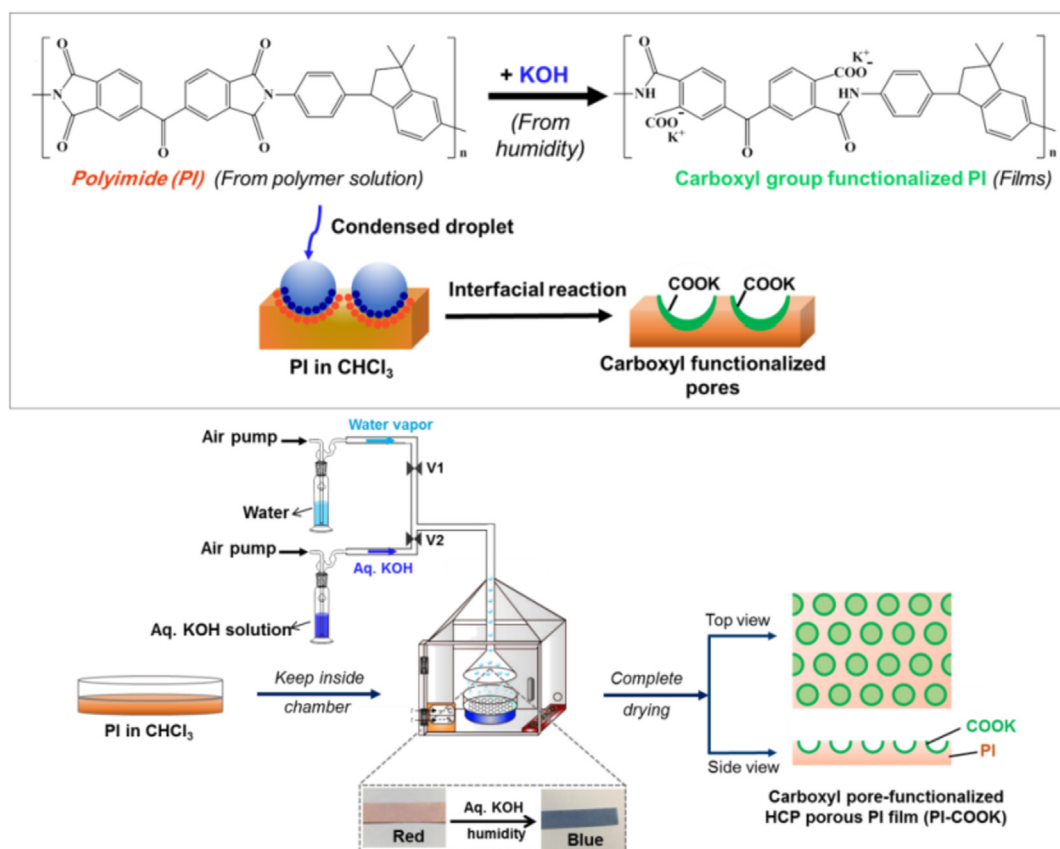
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Scheme 1. Schematic representation showing the fabrication of the pore-selective carboxyl functionalized PI HCP films (PI-COOK) via BF method under aq. KOH humidity with a time interval after using initial water humidity. The color change of litmus paper in the chamber under KOH humidity indicates that alkaline KOH is included in the humidity.

self-assembly of amphiphilic material around water droplets during BF method, further the preparation of amphiphilic material with specific structure, molecular weight and complete self-assembly is difficult, making the process complicated and laborious. Hence there is a necessary to search for new methods to simplify the process to obtain carboxyl group functionalized films. Recently, we have reported a simple method for the functionalization of PS HCP films with polyaniline functionalized pores by interfacial polymerization during BF process. Wherein a PS solution containing benzoyl peroxide (BPO) acting as a polymerization initiator was cast under a humid condition containing aniline hydrochloride humidity. Aqueous aniline hydrochloride was condensed onto polymer solution surface and then reacted with BPO at the condensed droplet/polymer solution interface resulting in the polyaniline functionalized PS HCP films [33].

Polyimide (PI) contains a ring of CO-NR₂ groups called imide linkage, can be hydrolyzed in the presence of alkali to form carboxyl group through imide ring-cleavage reactions. Based on this property, PI films functionalized with carboxyl group have been reported by immersing the PI films to the potassium hydroxide solution [34–38].

In the present study, carboxyl group functionalization in HCP polymer films was fabricated by BF process using PI which can react with KOH humidity at the polymer solution/aqueous droplet interface to form carboxyl groups. PI containing CO-NR₂ imide group reacts with alkali through imide ring-cleavage reactions by interfacial reaction. In order to obtain pore-selective carboxyl group functionalized PI HCP films, we suggest a new strategy introducing KOH humidity with time interval after using initial water humidity during breath figuring process for the delaying of the interfacial reaction. The distribution of carboxyl groups is proved through silver particles distribution by sequential reactions of potassium carboxylate group with Tollens's reagent followed by the reduction of silver ions to silver with hydrogen

peroxide. The obtained films were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TGA), and elemental mapping analysis.

2. Experimental section

2.1. Materials

Polyimide resin powder (PI) was purchased from Alfa Aesar (USA). Silver nitrate (AgNO₃, 99.0 wt %), ammonium hydroxide solution (28.0–30.0 wt % NH₃ basis), hydrogen peroxide solution (H₂O₂, 30 wt %), potassium hydroxide (KOH basis, ≥85 wt %), and other reagents were purchased from Sigma-Aldrich (USA). All reagents were used as received and without any further purification. 0.1 M silver ammonia complex solution (Tollens's reagent, [Ag(NH₃)₂]OH) was prepared in laboratory by drop-wise addition of 0.1 M aq. ammonia solution into 0.1 M silver nitrate solution until a clear and transparent solution was obtained.

2.2. Fabrication of carboxyl group functionalized PI HCP films

In a typical procedure, carboxyl group functionalized PI HCP films were cast under aq. KOH humidity: 0.3 g of PI was dissolved in 5 mL of chloroform under stirring for 30 min to obtain a uniform PI solution. The solution was poured into a glass Petri dish (5 cm dia.) and placed in a closed chamber. KOH humidity was introduced by blowing ambient air through the 5 M aq. KOH solution using an air pump with a flow rate of 0.7 L min⁻¹. The presence of alkali humidity inside the chamber was tested by red litmus paper which shows the color change to blue. The film was obtained after complete drying followed by washing with

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