



Design of hybrid gradient porous surfaces with magnetic nanoparticles



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ARTICLE INFO

Article history:

Received 27 March 2015

Received in revised form

26 May 2015

Accepted 10 June 2015

Available online 14 June 2015

Keywords:

Breath figures

Gradient porous surfaces

Hybrid films

ABSTRACT

This article describes the preparation of hybrid gradient porous surfaces by using the breath figures approach. In a first step gradient porous surfaces were created from polymeric blends consisting of a linear polystyrene as major component and amphiphilic copolymers of poly(styrene-co-acrylic acid) as minor component. THF was used as solvent conducting to porous surfaces with a gradual variation of the pore size in a radial manner due to the long evaporation time. A detailed investigation of the influence of chemical composition of the copolymer (i.e. ratio styrene/acrylic acid) on the porous films was carried out. These films were successfully employed to prepare hybrid gradient surfaces by incorporating of magnetic nanoparticles inside the cavities. For this purpose two different strategies were explored. On one hand a magnetic nanoparticles aqueous suspension was placed on the porous surface with a magnet below the film, and subsequently the colloidal suspension was removed. Alternatively, the magnetic suspension was placed onto the surface and left until complete evaporation. A further step of peeling off the top layer also conducts to the decoration of the nanoparticles exclusively in the interior of the holes. Both strategies allow the preparation of hybrid surfaces with a variation of the content of magnetic nanoparticles magnetic inside the holes as a function of the radial position.

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1. Introduction

The preparation of well-ordered microporous polymeric films has attracted a great interest in recent years due to their potential in a variety of applications [1]. Although there are many methods to prepare porous films with different pore sizes, shapes and morphologies, the breath figure method is probably one of the most explored to obtain honeycomb-patterned films in a very simple manner [2–7]. Basically this approach makes use of the condensed water droplets as dynamic templates to produce pores at the polymer/air interface. In the breath figures approach, a polymer solution (prepared in volatile solvents) is cast onto a substrate under humid atmosphere. The rapid solvent evaporation decreases the interfacial temperature resulting in the condensation of water vapour and formation of droplets on the solution surface. Moreover, by using the appropriate conditions (temperature, polymer

concentration, relative humidity ...) the water droplets can self-assemble into hexagonal arrays. Finally, after the complete solvent and water evaporation porous structures are formed on the surface of the polymer film. The key advantages of this method that make it very attractive are its simplicity and particularly its versatility. Aspects such as the dimension of the pore (nanometre to micrometre scale), shape (round, elliptical, rectangular) and chemical functionalities can be easily tuned by controlling experimental parameters like relative humidity, temperature, solvent or polymer concentration [8–11]. Indeed recent investigations demonstrated that the use of non very volatile solvents such as THF favours the formation of gradient porous surfaces, in which the diameter varies gradually from the edge of the sample to the centre in a radial manner [12]. Since the evaporation during the film formation occurs from the edge to the centre, the water vapour condensation takes place to a larger extent toward the centre of the droplet thus leading to an increase of the pore diameter compared to the pores formed at the periphery. It was also demonstrated that the incorporation of amphiphilic copolymers in a polymeric blend enhances the formation of a more homogeneous gradient

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preventing coagulation. The breath figures mechanism implies precipitation of the polymer around the condensed water droplets and the orientation of the hydrophilic part of the polymers preferably toward the water, therefore amphiphilic structures can stabilize the condensed water. Hence, when the films are obtained from amphiphilic polymers as unique component [13–16] or the amphiphilic structures are used as additive [17–19], the cavities formed at the surface ended enriched in the polar groups or segments. Relative to this, a systematic investigation has been previously done related to the relationship between the amphiphilic copolymer composition and the final film morphology using block copolymers as unique component based on polystyrene and poly(*N,N*-dimethylaminoethyl methacrylate) [20].

Herein, a series of statistical amphiphilic of poly(styrene-*co*-acrylic acid) with variable styrene to acrylic acid ratio have been synthesized and used as a component of a blend mixed with polystyrene in THF as solvent. In particular, the influence of the copolymer composition on the formation of gradient porous surfaces has been studied, analysing how the hydrophilic/hydrophobic balance affects both the regularity of the pattern and the gradient pore size. Besides, hybrid gradient porous surfaces were successfully prepared from the films by incorporating of magnetic nanoparticles inside the cavities. Only few examples have been reported dealing with the decoration of breath figures film with magnetic materials, and all of these strategies implies the *in-situ* decoration of the pores during the film formation [21–23]. Regarding the post-modification approaches, examples found in literature concern the incorporation of other inorganic nanoparticles on the surface of previously prepared breath figures films, i.e. decoration with CdTe nanocrystals by dipping [24] or the synthesis of silver nanoparticles on the entire surface of the porous structures [25], rather than the exclusively decoration of the pores. Herein we have addressed two approaches both based on the post-incorporation of the magnetic nanoparticles after the porous surface formation. More interesting, due to the special characteristic of these films wherein the pore size progressively decreases from the centre to the edge of the film, magnetic patterned surfaces with a gradual variation of the magnetic domain sizes along the films have been obtained. Considering that the preparation of magnetic pattern is currently an area of great demand, the assembly of magnetic nanoparticles into the holes of gradient porous surface can find a variety of potential applications in sensors systems and magnetic separation and purification, among others. The magnetic separation techniques are of great interest in molecular biology as the increasing use of magnetic labelling. For instance, target biomolecules, drugs or cell immobilized on magnetic nanoparticles can be separated from a sample solution and easily detected or transferred to a desired localization. Nowadays micro total analysis systems (μ TAS) offer several improvements in all those processes as reduced reagent usages and decreased operation time, gaining importance in the basic-science research and clinical area [26]. In this sense micro-structure surfaces with a magnetic gradient could be useful in the fabrication of μ TAS suitable for the separation of magnetic labelled compounds. The gradient in pore size will provide a pattern in which the concentration of such as compounds could be varied throughout the surface, thus this surface could be used, for example, to study processes as function of concentration such as the detection limit in sensor systems, or drug delivery processes.

2. Experimental section

2.1. Materials

Styrene (Sty, Aldrich, 99%), *tert*-butyl acrylate (tBA, Aldrich, 98%), *N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%)

were all purified by distillation. Ethyl 2-bromoisobutyrate (EBriB, Aldrich, 98%), copper (I) bromide (CuBr, Aldrich, 99.999%), trifluoroacetic acid (TFA, Aldrich, 99%) were used as received. High molecular weight polystyrene (Aldrich, $M_w = 2.50 \cdot 10^5 \text{ g mol}^{-1}$) was used as polymeric matrix and used as received. Tetrabutylammonium bromide (Bu_4NBr , 99%) was purchased from Acros organic whereas iron (99.5%) and cobalt foils (99.9%) were obtained from Goodfellow. Ammonia (30%, Panreac) and tetraethyl orthosilicate (TEOS, Aldrich, 98%) were used as received. The AR solvents 2-propanol, dichloromethane (DCM), tetrahydrofuran (THF) were purchased from Scharlau and utilized without further purification. Round glass coverslips of 12 mm diameter were obtained from Ted Pella Inc.

2.2. Synthesis of statistical copolymers of P(Sty-*co*-AA)

Several statistical copolymers of styrene and *tert*-butyl acrylate were first synthesized by atom transfer radical polymerization (ATRP) varying the styrene initial feed molar fractions from 0.1 to 0.9 and using in all the reactions a [monomer]/[initiator]/[ligand]/[CuBr] = 50/1/1/1. For instance, in the preparation of P(Sty-*co*-tBA) ($f_{\text{Sty}} = 0.5$), CuBr (0.086 g, 0.6 mmol), PMDETA (0.104 g, 0.6 mmol) and both monomers, styrene (1.562 g, 15.0 mmol) and *tert*-butyl acrylate (1.923 g, 15.0 mmol) were accurately weighted and transferred into a Schlenk tube. The mixture was purged with argon for 30 min and subsequently the EBriB initiator (0.117 g, 0.6 mmol) was injected. The reaction was heated at 85 °C under argon atmosphere. At the desired time, the viscous solution was diluted with chloroform and purified by passing it over an alumina column. The P(Sty-*co*-tBA) copolymers were isolated by precipitation in methanol (for initial feed tBA composition < 0.4) or by drying in vacuum (for initial feed tBA composition ≥ 0.5). In the last step, the *tert*-butyl groups of the copolymers were hydrolyzed in the presence of TFA (5 equivalent of TFA to 1 equivalent of tBA) to obtain the P(Sty-*co*-AA) amphiphilic copolymers. In a typical procedure, 3.618 g of the copolymer P(Sty₃₀-*co*-tBA₃₅) (prepared with an initial feed tBA composition of 0.5) were dissolved in dichloromethane (36 mL) and subsequently TFA (9.462 g, 83 mmol) was added to the solution. The reaction was left at room temperature during 24 h. The solvent was removed by rota-evaporation, and the copolymer, P(Sty₃₀-*co*-AA₃₅), was dissolved in THF before being purified by dialysis against distilled water (3500 MWCO).

2.3. Synthesis of silica coated CoFe₂O₄ magnetic nanoparticles

Cobalt ferrite nanoparticles were synthesized electrochemically according to a previous described protocol [27]. Briefly iron (2 cm²) and cobalt (2 cm²) were used as anodes and placed parallel to each other whereas a cylindrical iron counter-electrode (120 cm²) was placed around them. The reaction was carried out in aqueous solution using Bu_4NBr as electrolyte and applying a current density

Table 1

Molecular characteristic of the P(Sty-*co*-tBA) copolymers synthesized by ATRP. Feed molar fractions, *f*, and copolymer molar fractions, *F*; theoretical and determined by SEC average number molecular weight M_n^{th} and M_n^{SEC} , respectively; and dispersity (\bar{D}).

Copolymer	f_{Sty}	F_{Sty}	F_{tBA} (F_{AA})	M_n^{th} (g mol ⁻¹)	M_n^{SEC} (g mol ⁻¹)	\bar{D}
C1	0.10	0.10	0.90	6300	7800	1.38
C2	0.20	0.17	0.83	6200	9000	1.45
C3	0.30	0.28	0.72	6100	8200	1.30
C4	0.40	0.39	0.61	5900	8000	1.31
C5	0.50	0.46	0.54	5800	7700	1.28
C6	0.60	0.60	0.40	5700	7000	1.19
C7	0.70	0.69	0.31	5600	8300	1.29
C8	0.80	0.77	0.23	5500	7800	1.20
C9	0.90	0.87	0.13	5400	7300	1.17

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