Microporous and Mesoporous Materials 191 (2014) 59–66

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Fabrication of nano- to micron-sized patterns using zeolites: Its application in BSA adsorption

Salih Kaan Kirdeciler [a,b], Can Ozen [b,c,d], Burcu Akata [a,b,e,*]

[a] Department of Micro and Nanotechnology, Middle East Technical University, 06800 Ankara, Turkey
[b] Central Laboratory, Middle East Technical University, 06800 Ankara, Turkey
[c] Department of Biotechnology, Middle East Technical University, 06800 Ankara, Turkey
[d] Center of Excellence in Biomaterials and Tissue Engineering (BIOMATEN), Middle East Technical University, 06800 Ankara, Turkey
[e] The Center for Solar Energy Research and Applications (GÜNAM), Middle East Technical University, 06800 Ankara, Turkey

ARTICLE INFO

Article history:
Received 14 September 2013
Received in revised form 25 December 2013
Accepted 26 February 2014
Available online 6 March 2014

Keywords:
Zeolite patterning
Protein adsorption
Photolithography
Electron beam lithography

ABSTRACT

Nano to micron-sized zeolite A (Z-A) and silicalite (Z-SIL) patterns were generated using the combinations of electron beam lithography (EBL) or photolithography (PL) with direct attachment method to be able to generate differentiated areas on a single surface in a cheap and facile way. The possibility to generate minimum sized zeolite patterns on top of zeolite monolayers was investigated by using EBL to understand the capability of the system for the first time. Also generation of large scale zeolite patterns on top of a different zeolite monolayer was investigated by using PL allowing the generation of differentiated surfaces for various potential applications such as selective adsorption studies. With this combination, it was shown that creating 3D zeolite architectures of different types with a perfect control in all dimensions was possible without the using any chemical linker. In order to test the potential different behaviors that zeolites of different properties are offering in the adsorption of biomolecules, zeolite patterned surfaces developed by PL were subjected to adsorption studies with bovine serum albumin (BSA). Irrespective of zeolite type, BSA always preferred the patterned regions rather than the underlying zeolite monolayers. It can be speculated that the obtained difference in roughness values facilitates the protein to be selectively adsorbed onto surfaces with increased roughness, i.e., the patterned regions. Moreover, we observed ~2-fold fluorescence intensity difference between Z-SIL and Z-A patterns, which were subjected to FITC-BSA solution. Hydrophobic interactions and charge repulsion are considered as two critical forces responsible for the observed adsorption differences.

1. Introduction

The design of selective coatings for advanced applications, such as selective adsorption, sensor arrays, patterning of biomolecules and nanoparticles, miniaturized electronics and magnetic devices as well as development of microfluidic channels and lab-on-a-chip systems have attracted growing attention. The spatial control of hydrophilic/hydrophobic properties of surfaces is another parameter that is demanded on such surfaces [1,2]. Arrays of patterns of nanoporous thin films are also known to be very useful as substrates for biological applications [3]. Several approaches are currently available for preparing such surfaces of different length scales with varying properties that are fabricated considering the intended usage area. The overall purpose of these studies is to change the features on such surfaces from nanometer to micrometer resolution with complete control in the size of the pattern features and the chemical/physical properties of the patterned and unpatterned surfaces. More challenging approach would be to create different chemical/physical properties on the same surface with the same control on fabrication. In general, this can be realized through the combination of hydrophilic/hydrophobic materials by lithographic means on the same surfaces [1].

Fabrication of thin films with nanopores has been of great interest and a difficult challenge to accomplish [3]. Attachment of different zeolites onto surfaces in a desired way is an alternative and promising method for production of hydrophilic/hydrophobic nanoporous regions on substrates and in that way, it is also possible to benefit from the other unique properties of zeolites. Thin films fabricated using zeolites can bring additional advantage of increased surface area allowing reduction in the overall size of an

* Corresponding author at: Department of Micro and Nanotechnology, Middle East Technical University, 06800 Ankara, Turkey. Tel./fax: +90 312 2106459.
E-mail address: akata@metu.edu.tr (B. Akata).

http://dx.doi.org/10.1016/j.micromeso.2014.02.041
1387-1811/

array by maximizing the total number of reaction sites enabling rapid evaluation of different bioactivities. Furthermore, it is possible to tailor the type of these surface groups by controlled chemical or thermal modification of these active sites leading to varying bioactivities [4]. Furthermore, the nanochannels of zeolites can be used as hosts for the supramolecular organization of molecules and complexes, which allows the use of these materials in many different applications [5,6]. Combining different types of zeolites possessing different morphologies, acidities and thus selectivity to different compounds on the same substrate would be another challenge to achieve the above mentioned combination of physical/chemical properties on a single substrate. Such substrates would also benefit from having versatile active sites with thermal and mechanical stabilities. Zeolite nanoparticles have been widely studied in the last decade and have drawn much interest due to their large external surface area compared with conventional zeolite crystals, high dispersibility in both aqueous and organic solutions, high thermal and hydrothermal stabilities, and tunable surface properties such as adjustable surface charge and hydrophilicity/hydrophobicity. The unique properties make nanozeolites promising candidates for microfluidic surface modification and protein immobilization.

In spite of all the benefits that zeolites and zeo-type materials could bring into such applications, one of the main drawbacks is their powder form upon synthesis and the need to form well organized zeolite mono-multilayers on different substrates. General approach for attaching zeolite microcrystals on different substrates is to use chemical linkers [5–8] and an excellent review was reported by Yoon et al. [9]. This route usually adds an extra step to the fabrication process leading to difficulties to adapt the developed methodology to large scale areas. A relatively easier approach would be to eliminate the chemical linker [10–13]. There are also several studies performed by Yoon et al. where zeolite micropatterned zeolite mono-multilayers were produced on glass substrates by microcontact printing [14] and photolithography [15]. In addition to this, the combination of electron-beam lithography (EBL) and direct attachment methodology was shown to allow full control in zeolite film thickness generating zeolite micropatterns with lines as small as a single zeolite nanoparticle [16].

In this paper, the aim is to generate different 3D architectures of varying chemical/physical properties on the same substrate using no chemical linkers. This aim was investigated through the use of two completely different zeolite types possessing totally different morphologies, pore structures, chemical and surface properties. The created zeolite nano-micro scale patterns will be a novel alternative to selectively adsorb proteins as a function of changing hydrophilic/hydrophobic properties, the surface roughness and chemistry of zeolites in addition to the leading increased surface area and number of reaction sites. For that purpose, both electron beam lithography (EBL) and photolithography techniques were combined with direct attachment technique to produce a variety of different line patterns of well controlled nano to micron sizes. Furthermore, FITC conjugated BSA was adsorbed on the prepared patterns to be able to investigate the selectivity of these molecules on differentiated areas on a single surface using two different types of zeolites.

2. Experimental

2.1. Materials and substrates

Zeolite A nanoparticles were synthesized from a mixture having the following chemical composition: 11.25 SiO_2:1.8 Al_2O_3:13.4 $(TMA)_2O$:0.6 Na_2O:700 H_2O Tetraethylorthosilicate (TEOS, 95% Acros) was used as the silica source and aluminum isopropoxide (98%, Acros) was used as alumina source.

Silicalite particles were synthesized from a mixture having the following composition: TPAOH:4 TEOS:350 H_2O, where the silica source was again Tetraethylorthosilicate (TEOS, 95% Acros). The resulting solid nanoparticles were centrifuged at 13,000 rpm, washed with deionized water and dried at 80 °C. NANO950 poly(-methyl methacrylate) (PMMA) C7 (average MW = 950,000, 7% in chlorobenzene) was purchased from MicroChem (Newton, MA, USA) and used as electron beam (EB) resists. Methyl isobutyl ketone (MIBK)/Isopropanol (IPA) (1:2 (v/v)) was used as a developer for EBL. Ultrapure water (>18 MΩ), obtained using a MES UltraPure water system, was used for all substrate cleaning steps.

P-type Si (0 0 1) wafers were subjected to thorough cleaning without removing the native oxide layer prior to use. After each step, the wafers were blow dried with dry N_2 gas.

Albumin–fluorescein isothiocyanate conjugate and Fluorescein 5(6)-isothiocyanate was purchased from Sigma–Aldrich.

2.2. Direct attachment of zeolites on Si wafer

The direct attachment method was used to attach zeolites on Si wafer surfaces based on the literature report [13]. Si wafers were cut into 1 cm × 1 cm pieces and placed on a piece of clean paper. About 2 mg of zeolite powder was put onto the substrates. Then they were pressed and rubbed onto the surface with the help of a finger. Finally, the zeolite assembled Si wafer substrates were heat treated at 100 °C in a conventional oven for 30 min forming the final zeolite assembled substrates (i.e., silicalite substrates; SIL or zeolite A substrates; ZA).

2.3. Formation of zeolite patterns on monolayer of zeolites

2.3.1. Formation of zeolite patterns with EBL on monolayer of zeolites

3 wt% of PMMA was obtained by diluting PMMA C7 with proper amount of chlorobenzene. In order to form zeolite patterns of one type on another type of zeolite assembled Si wafer substrate (i.e., zeolite A on silicalite substrate; ZA-SIL or vice versa; SIL-ZA), 3 wt% of PMMA in chlorobenzene was spun on Si wafers coated with any type of zeolite monolayer (ZA or SIL) using the above mentioned procedure with 6000 rpm forming approximately 400 nm thick resist films (Scheme 1). After coating the resist, substrates were pre-baked for 30 min at 160 °C. Patterns were defined by utilizing EBL system (Xenos XeDraw2 Pattern generator attached CamScan CS3000 SEM). Patterned substrates were developed in MIBK/IPA solution for 60 s, rinsed in IPA, washed in flowing deionized water, and finally dried with N_2 gas. Zeolite direct attachment method was applied second time onto the PMMA coated surfaces. Prepared thin films (SIL-ZA or ZA-SIL) were put into an oven at 100 °C for 30 min. Then the substrates were rinsed and ultrasonicated in acetone and dried using N_2 gas.

2.3.2. Formation of zeolite patterns with photolithography on monolayer of zeolites

AZ 5214 photoresist (Microchemicals) was spin coated on zeolite monolayers with 6000 rpm for 40 s and the resulting resist thickness was approximately 1 μm (Scheme 2). Coated zeolite monolayers with photoresists were pre-baked at 110 °C for a minute. Masks were aligned on the photoresist coated wafers and utilized by photolithography system at GÜNAM, METU. Patterned surfaces were developed using AZ 726 (Microchemicals) metal ion free developer solution for approximately 10 s, rinsed and washed with distilled water and dried with N_2 gas flow. Direct attachment methodology was applied onto the patterned surfaces with the same manner explained in the formation of zeolite patterns with EBL on zeolite monolayers (Section 2.3.1). Prepared