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Evaporation induced self-assembly of zeolite A micropatterns due to the stick–slip dynamics of contact line

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Abstract

In this study, a new surfactant–solvent system was described for the preparation of periodic stripe patterns of zeolite A on solid substrates. The evaporation induced self-assembly of zeolite A particles was due to the stick–slip dynamics of the three-phase contact line of the colloid solutions in acetone containing 10% (v/v) poly(dimethylsiloxane) (PDMS) fluid (2 cst.). In order to investigate the possible effects of particle size and the particle concentration on the stick–slip dynamics, three types of zeolite A samples with different particle sizes (zeolite A-I: 250–500 nm, zeolite A-II: 100–250 nm and zeolite A-III: 0–100 nm) were utilized to prepare 0.007–0.06% (w/v) colloidal dispersions. Zeolite A micropatterns were self-assembled on the surface of glass, high density polyethylene (HDPE) and poly(tetrafluoroethylene) (PTFE) substrates, which were placed vertically inside the colloid solutions and held against the wall of the cylindrical vial during the evaporation of acetone. The stripe patterns of zeolite A particles were analyzed with field emission scanning electron microscope (FE-SEM) and optical microscope. The widths of microstripes and the distance between the stripes were found as 2–20 μm and 40–60 μm respectively depending on the particle concentration. By using the stick–slip dynamics of colloids, the linear micropatterns of zeolite A nanocrystals were prepared with low cost and low energy.

Keywords: Self-assembly; Stick–slip dynamics; Zeolite A; Micropattern; Nanoparticle

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1. Introduction

Over the last decade, considerable efforts have been directed toward the preparation of functional zeolite nanoparticles because of their potential applications in membranes, catalytic coating reactors, chemical sensors and biomedical materials. Furthermore, the use of zeolite micropatterns for biological applications [1], the incorporation of zeolites in microchemical systems [2] and the fabrication of zeolite-based microreactors [3] found growing interest. Micropatterning of oriented zeolite monolayers on glass by covalent linkage [4] and patterning of continuous zeolite films on glass by direct dipping in synthesis gel [5] have been studied.

Extensive studies are being conducted on micropatterning of colloidal nanoparticles. Micropatterns made of ceramic powders have been prepared from colloidal suspensions using self-assembled monolayers (SAM) on gold and silicon wafer substrates [6]. It was reported that the aqueous colloidal dispersions of aluminum oxide and tin oxide adhered only to the hydrophilic micropatterns whereas they repelled from the hydrophobic areas in a simple dip coating process. The maximum resolution of ceramic micropatterns was in the order of 5 μm. In another study, photolithographed self-assembled monolayers of (3-mercaptopropyl)-trimethoxysilane were utilized in the fabrication of colloidal gold micropatterns on SiO_2-coated Si substrates [7]. It was pointed out that this approach could be applicable to the assembly of microelectronic circuits and microbiosensors.

To demonstrate the potential application areas, some examples of other micropatterning techniques are also reviewed below. For instance, the fabrication of TiO_2 micro-patterns on Si wafers was demonstrated using laser direct writing and post-annealing [8]. A nickel micropattern with a 9 μm line width and 12 μm line intervals was obtained on an insulating board via anodizing aluminum, laser irradiation, nickel electroplating, insulating board attachment and aluminum substrate dissolution [9]. Chemical etching was used to pattern tin oxide film on silicon substrate up to 5 μm width for the fabrication of two-

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dimensional micro-gas sensor array [10]. Micropatterns with sizes of 10–100 μm were created in poly(dimethylsiloxane) using laminar flows of liquids in capillaries [11]. Application of micropatterning techniques to the fabrication of scaffolds specifically designed to support chondrogenesis was studied [12]. It was demonstrated that the surface-patterned scaffolds promote adhesion, restrict spreading and maintain key aspects of the chondrogenic phenotype.

Although the importance of zeolites in micro- and nanoscale systems has been demonstrated in the literature, a limited number of studies have been performed about the formation of zeolite micropatterns directly from the solution phase. Here, in our study, in the light of recent developments in colloid science, the spontaneous deposition of zeolite A micropatterns from the colloidal dispersions of nanoparticles in 10% (v/v) PDMS–acetone system was demonstrated without using any pretreatment of substrate surface. Micropatterning of zeolite nanocrystals on the surface of substrate was due to the stick–slip dynamics of contact line of PDMS–acetone system during the evaporation process. In a similar procedure, the formation of ZSM-5 zeolite films from nanosuspensions has been investigated by using high polarity solvents, such as water and formaldehyde [13]. However, the direct micropattern formation and the stick–slip dynamics have not been reported previously for any other colloidal zeolite–solvent system.

2. Experimental

2.1. Preparation of nanosized zeolite A samples

Zeolite A-I (250–500 nm) was prepared from commercial zeolite A powder (Ege Kimya) by means of grinding in poly (dimethylsiloxane) (PDMS, 2 cst) (ABCR Inc.). The other zeolite A nanopowders, zeolite A-II (100–250 nm) and zeolite A-III (0–100 nm), were prepared by using the hydrothermal crystallization method. Sodium aluminate solution was prepared by using Al foil (1.2753 g), anhydrous NaOH (Aldrich) (4.1497 g) and deionized water (35.1768 g). Sodium silicate solution was prepared from Na_2SiO_3 ($d=1.37$ kg/L, $Na_2O=7.5–8.5\%$, $SiO_2=25.5–26.5\%$) (Merck) (7.0593 g), anhydrous NaOH (1.5034 g) and deionized water (66.7350 g). Filtered clear solutions were used immediately after preparation.

The hydrothermal crystallization experiments were carried out in a polypropylene vessel (250 mL), which was placed in a temperature controlled oven kept at 75 °C. Sodium aluminate solution was heated up to 75 °C under stirring and then the sodium silicate solution was added gradually within 10 min. About 3 mL 0.26% (w/v) seed solution of commercial zeolite A was added after 30 min of mixing. Zeolite crystals were allowed to grow for 5 h. In order to terminate the growth process, a part of reaction mixture (50 mL) was removed from the reaction vessel and filtered. Produced zeolite A-III (0–100 nm) powder was washed with excess amount of water and dried at 110 °C for 4 h. Another part of synthesis mixture (10 mL) were removed from the crystallization vessel and placed in a tightly closed polypropylene bottle and kept at 75 °C for 14 h. At the end of crystallization, prepared zeolite A-II (100–250 nm) powder was also washed with excess amount of deionized water and dried at 110 °C for 4 h. The purity of zeolite A nanopowders, zeolite A-I (250–500 nm), zeolite A-II (100–250 nm) and zeolite A-III (0–100 nm) were analyzed by x-ray diffraction technique.

2.2. Preparation of zeolite A colloids

Zeolite A nanopowders (about 0.02 g) were dispersed in liquid PDMS (2 mL) and stirred for 10 min before the addition of acetone (Merck) (10 mL). Grinding of powder samples in PDMS was also performed for better dispersion. Colloid solutions were decanted with the aim of separating possibly agglomerated and large particles, which were settled to the bottom of the beaker. In order to prepare different concentrations of colloids, some part of colloid solution (5 mL) was taken in each step and diluted to the half concentration by adding proper amount of acetone (5 mL). The particle concentrations of zeolite A colloid solutions were also determined from the measurement of turbidity at 420 nm. The calibration graph of turbidity for each zeolite sample was generated using the turbidity measurements of the colloids of known particle concentrations.

2.3. Preparation of zeolite A micropatterns

The preparation of periodic stripe micropatterns of zeolite A was carried out as shown in Fig. 1 by using the evaporation-induced self-assembly process. Glass micro slides (26×76 mm^2) (Iso Lab.) were used as the substrates and they were placed in polyethylene vials ($R=30$ mm, $h=50$ mm) containing the colloid solutions of zeolite A powders (5 mL) and hold against to the wall of the container. The linear micropatterns of zeolite A nanocrystals were allowed to self-assemble on glass substrates for 1 h during the evaporation of acetone at 20 °C (the rate of acetone evaporation: 6.9 mg/min). The self-assembly of zeolite A-III (0–100 nm) nanoparticles on the surface of glass (Iso Lab), HDPE and PTFE (Penn Fibre, Ft-Washington, PA, U.S.) substrates was also performed at 25 °C for 1 h (the rate of acetone evaporation: 9.2 mg/min) and at 50 °C for 15 min (the rate of acetone evaporation: 31.6 mg/min). The substrates were dipped into 3 mL colloid solution of zeolite A-III in a glass vial ($R=20$ mm, $h=28$ mm, 5 mL) and the formation of micropatterns was observed.

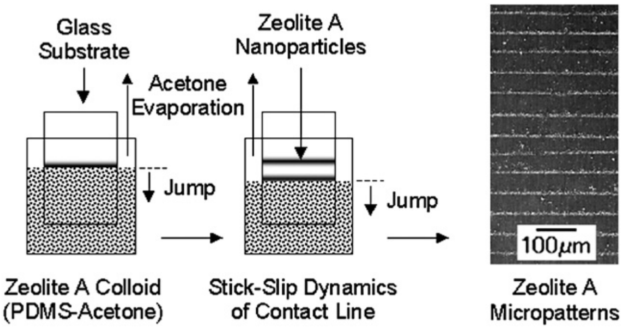

Fig. 1. Evaporation induced self-assembly of zeolite A stripe patterns from colloids.