Nanoporous aluminum oxide micropatterns prepared by hydrogel templating

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Abstract
Micropatterned nanoporous aluminum oxide arrays are prepared on silicon wafer substrates by using photopolymerized poly(dimethylacrylamide) hydrogels as porogenic matrices. Hydrogel micropatterns are fabricated by spreading the prepolymer mixture on the substrate, followed by UV photopolymerization through a micropatterned mask. The hydrogel is covalently bonded to the substrate surface. Al\textsubscript{2}O\textsubscript{3} is produced by swelling the hydrogel in a saturated aluminum nitrate solution and subsequent thermal conversion/calcination. As a result, micropatterned porous Al\textsubscript{2}O\textsubscript{3} microdots with heights in \(\mu\)m range and large specific surface areas up to 274 \(m^2 \, g^{-1}\) are obtained. Hence, the hydrogel fulfills a dual templating function, namely micropatterning and nanoporosity generation. The impact of varying the photopolymerization time on the properties of the products is studied. Samples are characterized by light and confocal laser scanning microscopy, scanning electron microscopy, energy-dispersive x-ray spectrometry, and Kr physisorption analysis.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction
The utilization of porogenic structure matrices as ‘templates’ for nanoporous inorganic materials has become one of the standard methods of chemical bottom-up nanostructuring. In most cases, a rigid porous matrix is used, such as nanoporous silica or carbon. The desired product is synthesized inside the pores of the matrix, and the matrix is later removed by chemical etching or thermal combustion. This process is frequently referred to as ‘nanocasting’ [1–4]. Instead of rigid matrices, flexible organic polymer-based hydrogels [5, 6] offer an alternative as porogenic templates [7]. They can be easily immobilized at surfaces and therefore offer an opportunity to prepare thin porous layers, coatings, and micropatterns. Results have recently been highlighted [6]. Patterning techniques by light are of particular interest since large areas can be patterned at the same time [8–11]. We have recently used poly(acrylamide)-based hydrogels as porogenic templates for nanoporous Al\textsubscript{2}O\textsubscript{3} [12–15] and MgO [12, 13], including nanoporous films [13].

However, the term ‘template’ may also be used in a slightly different, extended sense. Instead of referring to a porogenic structure matrix at nanoscopic level, a ‘template’ may also be a mold for a defined morphology and for a certain structure at the
micrometer (or larger) length scale in the templated product. The template may control both the size and the outer shape of the product and, at the same time, its inner nanostructure, such as nanoporosity. Here we present some first results and a proof of concept for a synthesis in which the template, a micropatterned array of hydrogel microdots, fulfills both roles. The microstructure is replicated to the structure of the templated product, aluminum oxide ($\text{Al}_2\text{O}_3$), and, simultaneously, the hydrogel acts as a porogen, i.e. it creates nanopores in the $\text{Al}_2\text{O}_3$. This procedure allows the fabrication of miniaturized structures with large surface-to-volume ratios, with potential future use in microfluidic systems for application in such fields as catalysis [16, 17], biotechnology [18], healthcare [19] or sensing [20, 21].

2. Results and discussion

Micropatterned arrays of nanoporous aluminum oxide were fabricated in a two-step procedure. The first step comprises of creating an array of poly($N,N$-dimethylacrylamide) (PDMAAm)-based hydrogel microdots at the surface of a silicon wafer. Other polymers were used for pore formation as well. However, variation of the polymer has little impact on the structural properties of the products. Hence, the method is quite robust against variations in polymer structure [14]. In the second step, the hydrogel serves as a template for the preparation of aluminum oxide microdots. These microdots are intrinsically nanoporous and exhibit large surface-to-volume ratios due to the porogenic impact of the hydrogel (figure 1).

In a typical synthesis process (figure 2; detailed information is provided as supplementary material (available online at stacks.iop.org/NANO/31/445601/mmedia)), the silicon wafer surface was first activated by treatment with a $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution, followed by anchoring 3-(trichlorosilyl)propyl methacrylate (figure 2(a)) to the wafer surface. This compound will serve as an adhesion promoter for the hydrogel. Successful decoration of the wafer surface with the adhesion promoter was verified by an increase in hydrophobicity, measured by contact-angle analysis (supplementary material, figure S1, table S1). PDMAAm hydrogel microdots were then fabricated at the wafer surface by a UV-induced photopolymerization procedure (figure 2(b)). An aqueous prepolymer solution of $N,N$-dimethylacrylamide (DMAAm) monomer, $N,N'$-methylenebis(acrylamide) (NMBA) co-monomer (for cross-linking), and 2,2-dimethoxy-2-phenylacetophenone (DMPA, as photo-initiator [22]; figure 2(c)) was spread at the pre-treated silicon wafer surface. Non-attached hydrogel dots show a degree of swelling of approx. 8. However, fluid uptake of surface-attached hydrogels is more complex since they cannot swell isotropically. The wafer was placed in a sealable incubation chamber and covered with a photomask that exhibits a regular arrangement of holes with a diameter of 250 $\mu$m. Illumination of the chamber with UV light led to selective polymerization and polymer cross-linking in the unmasked areas (i.e. through the holes). Subsequent flushing with water removed the unreacted prepolymer mixture.

Figure 3 shows an optical microscopic image as well as scanning electron microscopic (SEM) images of thus-obtained, water-free hydrogel microdots, prepared with a UV exposure time of 12.5 s. The gel consists of cross-linked PDMAAm strands that are covalently bonded to the wafer surface through the adhesion promoter. The microdot array pattern (figures 3(a) and (b)) corresponds to the photomask.
The hydrogel microdots were then used as templates for nanoporous aluminum oxide (Al$_2$O$_3$) microdots. The wafer with the hydrogel dots was immersed in a saturated aqueous solution of aluminum nitrate (Al(NO$_3$)$_3$) overnight. By this procedure the hydrogel swells, i.e. it takes up large quantities of the solution. The material was then dried and exposed to ammonia vapor at room temperature to convert Al(NO$_3$)$_3$ to Al(OH)$_3$/AlO(OH) [23, 24]. The resultant material is a composite of the aluminum hydroxide phase with interwoven PDMAAm strands. Former studies have shown that the polymer strands form bundles in this kind of composite [6, 13]. Finally, the composite was calcined at 500 °C, which leads to the combustion of the polymer strands and, simultaneously, to the formation of Al$_2$O$_3$, as previously studied by TGA [12, 13]. (The entire process is described in detail in the supplementary material.) X-ray spectrometry (EDX) studies confirmed the composition of the products (O/Al ~ 1.5; see supplementary material, figure S5 and table S3). Characterization by x-ray diffraction (XRD) was not possible due to the low amounts of material, but former studies have shown that materials prepared under very similar conditions can be identified as γ-Al$_2$O$_3$ with low crystallinity [12, 13]. α-Al$_2$O$_3$, on the other hand, is expected only when higher calcination temperatures are applied under otherwise similar conditions [25].

Al$_2$O$_3$ microdots templated from the above-mentioned hydrogel dots are displayed in figure 4. The pattern of the array is preserved (figures 4(a) and (b)), confirming that the dots are still attached to the silicon wafer substrate quite firmly. We propose that, in addition to weak interactions, the formation of Si–O–Al bonds under the employed synthetic conditions. The microdot shape of the Al$_2$O$_3$ dots is less uniform (figures 4(c) and (d)) than that of the hydrogel template. Several cracks are observed, and flake-like fragments have been partly detached or peeled off entirely. Still, the truncated cone-like shape of the microdots is conserved to some degree, confirming that the hydrogel has served as a template for both the Al$_2$O$_3$ microstructure (periodic array of the dots) and its morphology (truncated cone). The dimensions of the microdots are significantly larger than those of the hydrogel dots. Their average diameters are 383 µm at the bottom and 235 µm at the top; their height is ca. 132 µm. The resulting volume of 10.1 · 10$^6$ µm$^3$ is almost five times larger than for the dry hydrogel dots, which is attributable to substantial swelling of the hydrogel upon impregnation with the aqueous Al(NO$_3$)$_3$ solution. The deterioration of the microdot morphology, on the other hand, is explained by shrinking of the Al$_2$O$_3$ upon calcination. High-magnification SEM images of the Al$_2$O$_3$ microdots (figures 4(e) and (f)) reveals a somewhat rougher surface than in case of the hydrogel dots. Future work will be dedicated to improving the morphological fidelity; the results presented here provide a proof of concept.

As mentioned in the introduction, the rationale behind using an organic polymer hydrogel as the matrix for Al$_2$O$_3$ is to achieve a dual templating effect. In addition to the replication of the morphology (array of microdots with conical shape), the hydrogel also serves as a porogenic template, i.e. it creates porosity in the Al$_2$O$_3$ microdots. This is because the polymer strands in the hydrogel form

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**Figure 3.** Optical microscopic image (a) and SEM images (b)–(f) of Poly(N,N-dimethylacrylamide) hydrogel microdots anchored to a silicon wafer surface (prepared by illuminating for 12.5 s).
Figure 4. Optical microscopic image (a) and SEM images (b)–(f) of Al₂O₃ microdots (templated by hydrogel microdots prepared by illuminating for 12.5 s).

bundles of a few nanometers thickness. When removed from the Al₂O₃-hydrogel composite by combustion, these bundles leave behind nanopores in the Al₂O₃ microdots. This has been shown in former studies of Al₂O₃ prepared by using PDMAAm-based hydrogels under similar conditions, although with longer illumination times for cross-linking. Those Al₂O₃ materials exhibited nanopores with widths of ca. 4 nm and specific pore volumes of 0.4–0.5 cm³ g⁻¹; the specific surface areas were 250–370 m² g⁻¹ [12–14]. In the present case, characterization of the porosity by N₂ or Ar physisorption analysis is not possible, because the sample amounts are far too small. However, Kr physisorption still allows the assessment of the specific surface area by the BET method, as shown in figure 5. The samples used for these measurements were prepared without the photomask, under otherwise identical conditions as for the Al₂O₃ microdot arrays. The products are continuous layers of Al₂O₃ that yield sufficient amounts of material for five-point BET analysis. The data reveal specific surface areas of 200–274 m² g⁻¹ (depending on the illumination time), a little less than in the materials mentioned above, which is likely due to the overall shorter illumination time. Still, the surface areas are altogether high, which is a strong indication for nanoporosity. Based on the comparison with our above-mentioned previous results, we propose that the average pore diameters and specific pore volumes in the materials presented here will likely be slightly smaller, approx. 3 nm (pore size) and 0.3 cm³ g⁻¹ (pore volume).

3. Conclusions

In summary, we have prepared regular arrays of poly(N,N-dimethylacrylamide) hydrogel microdots at a silicon wafer surface and used them as a template for the preparation of nanoporous Al₂O₃ microdots. The hydrogel templates define the morphology of the Al₂O₃ dots and simultaneously serve as porogenic matrices for the generation of nanoporosity. The products possess specific surface areas above 200 m² g⁻¹.

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