Processing of Nanoparticle Structure and Composites

Edited by
Tom Hinklin
Kathy Lu

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Introduction

This volume contains a collection of papers from the Controlled Processing of Nanoparticle Structures and Composites symposia held during the 2008 Materials Science and Technology conference (MS&T08)—a joint meeting between ACerS, AIST, ASM International, and TMS at the David L. Lawrence Convention Center, Pittsburgh, Pennsylvania, USA, October 5–9, 2008.

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NANOPARTICLE-BASED BULK MATERIAL TEMPLATING

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ABSTRACT

Nanoparticle size decrease has opened a whole new field for unique particle-based materials forming. This study is focused on making molds with micron-size feature arrays and freeze casting of surface templated materials. Polydimethylsiloxane (PDMS) and silicone molds with micron-size feature arrays are made using a mold core templated by a focused ion beam. Templated surface feature transfer ability is compared for the PDMS and silicone molds. The process can make complex, near-net shape, and fine feature arrays. This work provides a new approach for surface templating of nanoparticle based materials.

INTRODUCTION

Templating is a key enabler for fulfilling the promise of nanotechnology.[1-3] It capitalizes on the special material properties and processing capabilities at the nanoscale, and promotes the integration of nanostructures to multifunctional micro-devices and meso-/macro-scale architectures and systems, as well as the interfaces across multi-length scales. Nanoparticle-based processing has been an active research area in this regard because of the potential to create large surface area materials and integrate heterogeneous structures. However, most current efforts are either focused on nanoparticle suspensions or nanoparticle-based thin film structures. The barriers for developing bulk nanostructured materials are agglomeration, inhomogeneous microstructures, and lack of structural control across multi-length scales.

More recently, templated materials containing intricate, nanometer-scale structures have been developed. They frequently exhibit novel, highly anisotropic, or enhanced properties, directly related to the dimensionality and the extra degrees of freedom of the nanostructure.[4-6] In our prior work, substantial efforts have been devoted to developing high solids loading nanoparticle suspensions.[7-11] This development opens up numerous opportunities for templating nanoparticle-based bulk materials. In addition, the small size of the nanoparticles offers the potential to engineer nanostructured materials to produce unique features in large surface areas.

Based on our knowledge in making high solids loading nanoparticle suspensions, a templating approach is used to make nanoparticle-based materials. A focused ion beam (FIB) based process is pursued to produce the designed features on silicon wafer first. Then polymeric molds are made using the FIB templated silicon wafer. High solids loading Al_2O_3 nanoparticle suspension is cast into the polymeric molds and converted into solid state by freeze casting. The work shows a new approach of producing micron-size feature arrays on the surface of Al_2O_3 nanoparticle materials.

EXPERIMENTAL PROCEDURE

Template Making

The starting template for making the molds was obtained using a dual beam FIB instrument (FEI Helios 600 NanoLab, Hillsboro, OR). The instrument is composed of a sub-

nanometer resolution field emission scanning electron microscope (SEM) and a field emission scanning Ga^+ beam column. The specimen used in templating can be moved by 150 mm distance along X and Y axes and tilted from -5 to 60° by a high precision specimen goniometer. The Ga^+ source has a continuously adjustable energy range from 0.5 kV to 30 kV, and an ion current between 1.5 pA and 21 nA. The patterning beam spot size and resolution vary with the ion beam current and voltage and can be tuned to as small as 5 nm. The FIB instrument also has a high resolution, 24 bit digital patterning engine capable of simultaneous patterning and imaging. Si wafer (p type, (100) orientation) was used as the starting template material for making the polymeric molds.

Mold Making

PDMS ($(H_3C)_3Si[Si(CH_3)_2O]_nSi(CH_3)_3$, Dow Corning Corporation Midland, MI) and silicone (RTV 664, General Electric Company, Waterford, NY) were used as the polymeric mold making materials with the templated silicon wafer as the mold core. Silicone molds without the templated features have been produced before.[7-11] In this study, silicone base compounds and the corresponding curing agent were homogeneously mixed at 10:1 ratio before being poured over the silicon wafer. After that the silicon wafer and the silicone mixture were placed under 40 Pa pressure for air removal. Since the silicone mixture had high viscosity, the vacuuming process was repeated three to five times before being kept at 40 Pa for 15 minutes. Then the molds were cured for 24 hrs in air. The PDMS molds were made using a similar process. PDMS base compounds and the corresponding curing agent were mixed at 10:1 ratio. The mixture proved much less viscous than the silicone system. It was poured over the silicon wafer and allowed to sit for a few minutes. The silicon wafer and the PDMS were then placed in a vacuum chamber and subjected to a pressure of approximately 27 Pa. This effectively removed all porosity resulting from the air bubbles inherent in the PDMS mixture. Once all air had been removed the silicon wafer and PDMS were placed into a drying oven at 100°C. After 45 minutes the solidified PDMS mold was separated from the silicon wafer.

Al_2O_3 Suspension Making

Al_2O_3 nanoparticles with specific surface area of 45 m^2/g were used in this study (Nanophase Technologies, Romeoville, IL). Average Al_2O_3 particle size was around 38 nm with a normal size distribution from 10 to 50 nm.[7] For the Al_2O_3 nanoparticle suspension preparation, poly(acrylic acid) (PAA, M_W 1,800, Aldrich, St Louis, MO) was used as a dispersant with the segment as $[-CH_2CH(CO_2H)-]$; glycerol ($C_3H_8O_3$, Fisher Chemicals, Fairlawn, NJ) was used as part of the dispersing medium with the molecular formula as $CH_2OH\text{-}CHOH\text{-}CH_2OH$. Water-glycerol mixture at a ratio of 9:1 (water: glycerol) was used as the dispersing medium. The mixture was homogenized for 5 minutes using a ball mill before use. Al_2O_3 nanoparticles were added into the dispersing medium in 10 g increments along with 2.0 wt% of PAA dispersant (on Al_2O_3 basis). Since low pH promotes PAA dispersant adsorption onto Al_2O_3 nanoparticles,[12] HCl solution was added to lower the pH to 1.5. The suspension was ball milled for 12 hrs with periodic adjustment of pH to 1.5. Suspensions of approximately 20 vol% Al_2O_3 solids loading were made by this procedure. After this step, Al_2O_3 nanoparticles were again added in 10 g increments, along with 2.0 wt% of PAA dispersant (on Al_2O_3 basis) to make 35 vol% solids loading suspension. NH_4OH was used to adjust the suspension to pH 9.5. The suspension was then mixed for 24 hrs for complete homogenization.

Templating

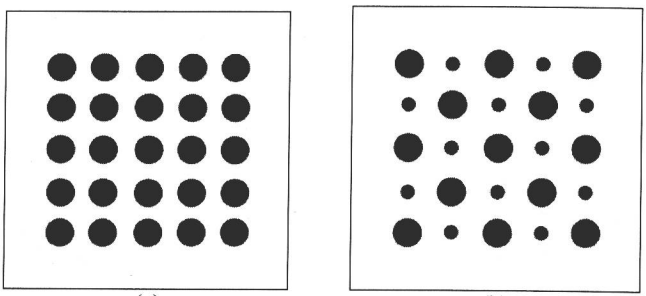
Al_2O_3 nanoparticle suspension was filled into the silicone and PDMS molds immediately after the suspension preparation using a disposable pipette. Care was taken to completely fill the molds and avoid air bubbles. The filled molds were kept under ambient conditions for 1 hr. After this pre-rest, the samples were frozen in a freeze dryer (AdVantage El-53, SP Industries Inc., Warminster, PA) immediately. The freezing rate used was 0.25°C/min. The freezing temperature was -35°C. At the freezing temperature, the samples were kept for 2 hrs before the chamber pressure was decreased to 1 Pa. The filled molds were kept at -35°C and 1 Pa pressure for 10 hrs and then heated to room temperature in stages (-20°C for 8 hrs, -10°C for 4 hrs, -5°C for 5 hrs, and 5°C for 5 hrs). During the entire process, a pressure of 1 Pa was maintained.

The templated surfaces of the freeze dried Al_2O_3 nanoparticle samples were analyzed using a LEO550 field emission SEM (Carl Zeiss MicroImaging, Inc, Thornwood, NY). To illustrate the three dimensional nature of the templated features, all the SEM images were taken at 45° tilt angle.

RESULTS AND DISCUSSION

Templated Silicon Mold Core

To template micron size features of different shape and size from the Al_2O_3 nanoparticle suspension by freeze casting, two steps are needed in making the freeze casting molds. The first step is to make the mold core with a designed pattern. The second step is to make the molds that can confine the Al_2O_3 nanoparticle suspension and produce solid state Al_2O_3 samples with fine features. As mentioned, a silicon wafer is used as the mold core and the designs to be produced on the silicon wafer are shown in Figure 1. There are three different patterns: homogenous circle arrays, heterogeneous circle arrays, and homogenous square arrays. Each array size is 100x100 μm. The larger size circles are 10 μm in diameter, the small size circles are 5 μm in diameter, and the squares are 10 μm in edge length. The feature-to-feature distance is 15 μm. The features at the array edge are 20 μm from the designed pattern boundary. During the FIB patterning, the white area material is removed. The black area material is left intact.



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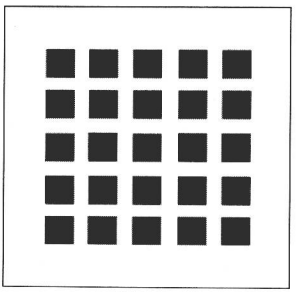

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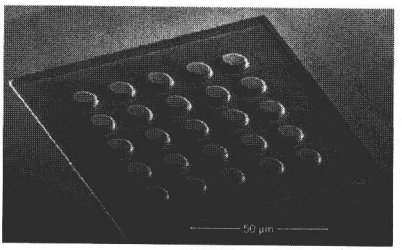
Figure 1. Feature array designs for FIB patterning: (a) homogenous circle arrays, (b) heterogeneous circle arrays, and (c) homogenous square arrays.

Under 30 kV voltage and 21 nA beam current patterning condition, the patterns created are shown in Figure 2. As shown, the arrays have well-defined size, shape, and feature arrangement, as well as smooth surfaces. The patterning time is approximately 70 min for the homogenous round and square island arrays and 30 min for the heterogeneous round island arrays. The feature height is controlled by the patterning time. The homogenous round and square island array height is approximately 4.8-5.0 μm, and the heterogeneous round island array height is approximately 2.0-2.5 μm. One observation is that it is important to obtain well focused ion beam for patterning. Good beam focus produces smoother feature surfaces and the same pattern in a faster rate.[13]



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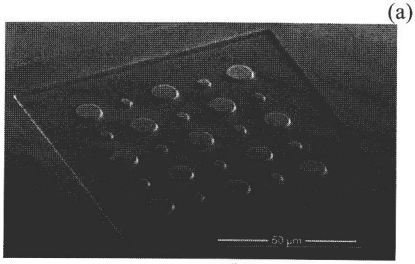

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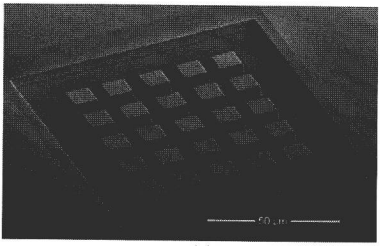


(c)

Figure 2. Feature arrays produced from FIB patterning: (a) homogenous round island arrays, (b) heterogeneous round island arrays, and (c) homogenous square island arrays.

PDMS and Silicone Molds

The PDMS and silicone molds are made from the silicon mold core with the feature arrays shown in Figure 2. Figure 3 shows the SEM images of the surface of the PDMS mold with the features present. Figure 4 shows the SEM images of the surface of the silicone mold with the features present. For both polymeric molds, the feature arrays are accurately produced in an inverse manner. The new cavity features are well defined and free of porosity. The depth of the heterogeneous round cavity features is roughly half of those of the homogeneous round and square cavity features. The large flaw in one of the square features in Figures 3(c) and 4(c) is a result of a chip-off on the silicon wafer, demonstrating the feature array's reproducibility.

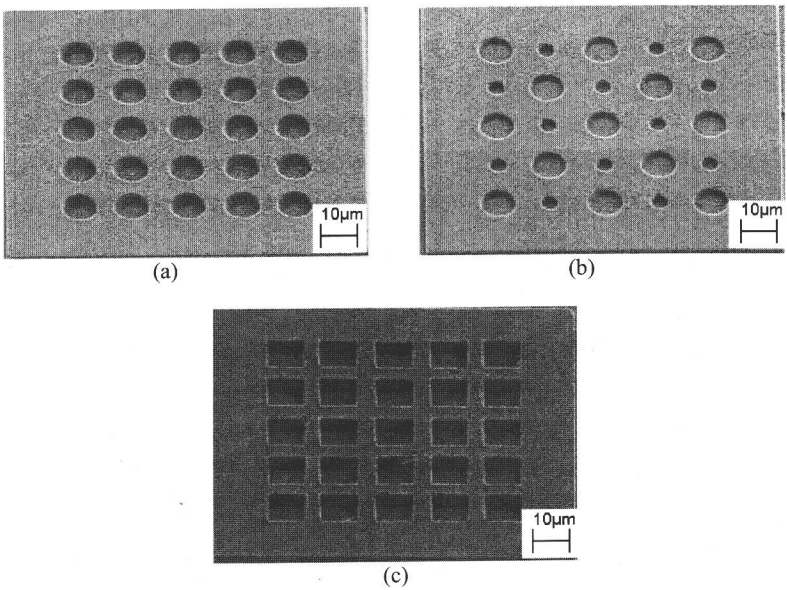


Figure 3. Cavity feature arrays produced on PDMS mold using FIB patterned silicon wafer core: (a) homogenous round cavity array, (b) heterogeneous round cavity array, and (c) homogenous square cavity array.

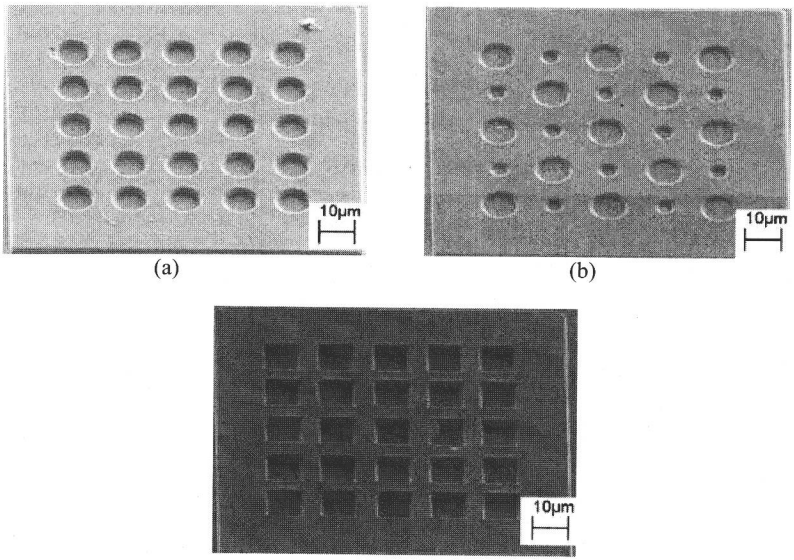


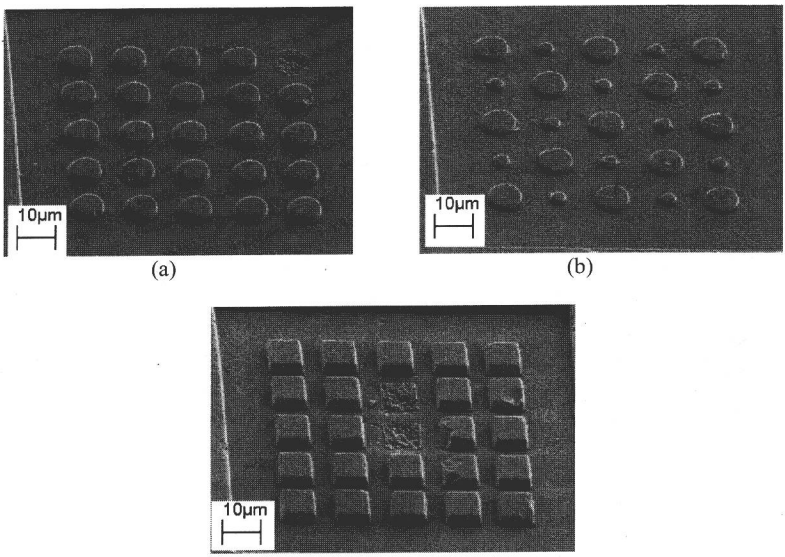
Figure 4. Cavity feature arrays produced on silicone mold using FIB patterned silicon wafer core: (a) homogenous round cavity array, (b) heterogeneous round cavity array, and (c) homogenous square cavity array.

Even though both PDMS and silicone mold materials produce equally desirable and defined feature shapes and arrangement, the molds made from the two materials have different characteristics. The silicone mold is more rigid than the PDMS mold at room temperature. Also, the silicone mold has opaque blue color while the PDMS mold is transparent. The different mold rigidity and transparency are products of the inherent chemical composition differences between the two materials.

Templated Al_2O_3 Nanoparticle Samples

Figure 5 shows the SEM images of freeze dried Al_2O_3 nanoparticle feature arrays produced with the PDMS mold. Figure 6 shows the SEM images of freeze dried Al_2O_3 nanoparticle feature arrays produced with the silicone mold. As it shows, the feature arrays are reproduced on the surface of the freeze-dried Al_2O_3 nanoparticle bulk samples. However, there is a clear feature reproducibility difference. The PDMS mold results in better defined features than the silicone mold for the Al_2O_3 nanoparticle samples. The freeze cast samples from the PDMS mold have sharper corners and edges, precise arrangement, and uniform height. There are some cracks and fracture for individual features, but the arrays are generally well controlled. This means the compliant PDMS mold becomes more rigid under the freeze casting condition, which is conducive for feature shape retention. In contrast, the feature arrays from the silicone mold, through, are severely deformed; there is substantial feature-to-feature difference. As to be shown in Figure 7, the silicone molds with gold-platinum coating can reproduce the designed feature

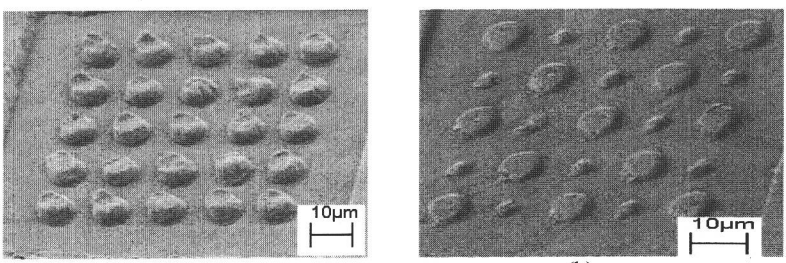
arrays under freezing casting conditions. This means the silicone mold can maintain its rigidity and templated mold shapes at the freezing condition. The main cause for the poor feature reproducibility results from the mold surface affinity with the Al_2O_3 nanoparticle suspension. The sticking of the Al_2O_3 nanoparticle features to the silicone mold surface leads to the severe distortion of the features. This aspect will be further quantified in future studies.



(a) (b)

(c)

Figure 5. Al_2O_3 nanoparticle arrays produced from PDMS mold: (a) homogenous round island array, (b) heterogenous round island array, and (c) homogenous square island array.



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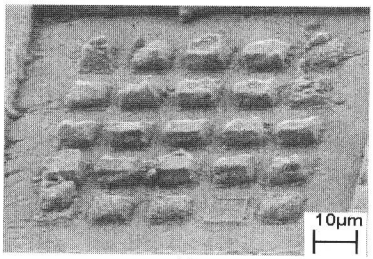

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Figure 6. Al_2O_3 nanoparticle arrays produced from silicone mold: (a) homogenous round island array, (b) heterogeneous round island array, and (c) homogenous square island array.

The formation of bulk, solid state Al_2O_3 nanoparticle samples is sensitive to the freeze casting conditions.[14] A pre-rest of an hour has to be used in accordance with previous work in order to effectively remove the air bubbles trapped inside the Al_2O_3 nanoparticle suspension.[7-11] Freezing rates, drying rates, and drying temperatures need to be carefully controlled. Freezing rate is the most significant parameter affecting the density and integrity of the freeze cast samples. Fast freezing rates result in an increase in the porosity of the templated Al_2O_3 nanoparticle samples and substantially lower the sample strength. Slow freezing rates can reduce the porosity and improve the strength of the Al_2O_3 nanoparticle sample. The freezing rate for the 35 vol% solids loading Al_2O_3 suspension needs to be 0.25°C/min or less. The time and temperature of the drying steps have a smaller effect on the templated Al_2O_3 nanoparticle samples, but still affect the final results. The current drying time and temperature seem to be too elaborate and can be further simplified.

The fundamental cause for the cracking and fracture of the features seen in Figures 5 and 6 is the higher than desired interfacial energy, or affinity, between the molds and the Al_2O_3 nanoparticle samples. Coating the molds with a gold-platinum layer shows to be an effective approach to reducing the feature cracking and damage. For example, some silicone molds have been coated with a 10 nm gold-platinum layer. Figure 7 shows the corresponding freeze cast feature arrays. There are almost no cracks or fractures on the features, most noticeably for the square features. Again the defect due to the chip-off from the silicon wafer is reproduced. The gold-platinum nanolayer appears to decrease the adherence between the molds and the Al_2O_3 nanoparticle samples and result in less feature fractures and cleaner mold. However, the gold-platinum layer should not be rubbed or scratched in order to avoid nanolayer damage. Wettability of the Al_2O_3 nanoparticle suspension vs. different mold surfaces is being investigated in our studies.

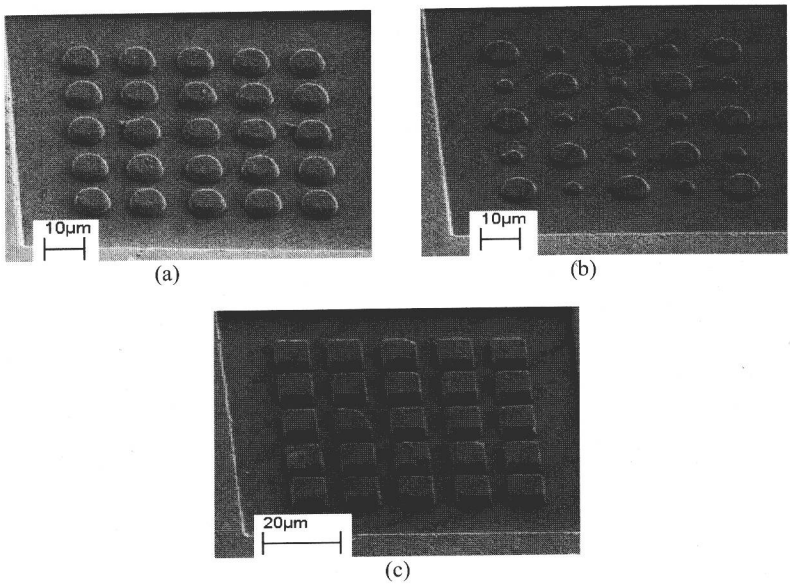

Figure 7. Al_2O_3 nanoparticle patterns produced from silicone mold coated with 10 nm thickness gold-platinum layer: (a) homogenous round island array, (b) heterogeneous round island array, and (c) homogenous square island array.

Throughout the templating process, the cleanliness of the mold is crucial for producing well defined features. Many of the defects seen in the samples can be traced back to what is present in the dirty mold. Mold cleaning with distilled water and ethanol tends to leave residue behind. A concrete cleaning procedure would improve the templating process. Coating the mold with a fresh gold-platinum nanolayer seems to simultaneously address this issue.

CONCLUSION

A nanoparticle-based templating process has been studied using Al_2O_3 nanoparticle suspension. With templated silicon core to make PDMS and silicone molds and high solids loading Al_2O_3 nanoparticle suspensions of good flowability to fill the molds, micron-size arrays of different size and shape islands have been created on Al_2O_3 nanoparticle material surfaces. The PDMS molds produce more desirable features under the reported freeze casting condition. Coating a 10 nm thickness gold-platinum layer on the silicone mold surface enables creation of well defined Al_2O_3 nanoparticle feature arrays. This templating process can be applied to large surface area nanoparticle-based materials and poses great potentials for direct device fabrication.

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FOOTNOTE

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