MECHANOSYNTHESIS OF THREE-DIMENSIONAL REPLICATED NANOSTRUCTURES BY NANOLITHOGRAPHY-BASED MOLECULAR MANIPULATION

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ABSTRACT

This paper reports a nanoscopic mechanosynthesis of three-dimensional (3D) nanostructures by nanolithography-based molecular manipulation (NMM) of target molecules for the applications requiring both physical and chemical anisotropies. The reported molecular manipulators with nanometer-sized patterns and anisotropic surface functionalities are fabricated by exploiting the hybrid nanometer-scale NMM process. They are then utilized for positional nanoassembly of molecules followed by mechanosynthesis producing 3D nanoreplicas. This approach offers "top-down" design and fabrication of morphological features of nanoparticles (NPs). Three types of replicated sub-10nm polystyrene (PS) nanostructures have been successfully demonstrated in this work, namely, "nanomushrooms", "nanospikes", and high-aspect-ratio "nanofibers".

INTRODUCTION

Molecular nanotechnology is emerging as a key enabler for fabrication of molecular-scale functional structures, devices, biomimetics, and nanoelectro-mechanical systems (NEMS). [1-2] For a number of proposed applications, such as artificial molecular manipulators/reactors for guiding positionally-controlled mechanochemistry, it is important to realize the functionalized mechanical structures and devices at the nano scale in order to appropriately address molecular registration and manipulation in MEMS/NEMS. This strategy enables "top-down" design and nanoscopic fabrication of anisotropic 3D nanostructures, and envisages a variety of applications based on such programmed 3D NPs, including enhanced therapeutic and imaging contrast agents [3-5], as well as biomimics of hierarchical assemblies and multiple classes of enzymes widely existent in the biochemical world [6].

NPs hold significant promise as therapeutic agents in biomedical applications. By utilizing intrinsic 3D NPs, instead of simple constructs e.g. 0D spherical and 1D tubular NPs, the enhanced functionality of these therapeutic agents may be achieved. Compared to 0D and 1D NPs, the forces acting on 3D NPs are dependent on their orientation, surface property, and surrounding environment. This could result in an enhanced performance of 3D NPs, e.g. *in situ* hierarchical assemblies with adaptable scales, chemically/physically tunable properties according to *in vivo* hydrodynamic and biological environments, as well as improved margination and adhesive strength to the targets with a desirable therapeutic and imaging efficacy [3]. Oblate particles are demonstrated to adhere more effectively to the biological substrate than 0D spherical particles, showing improved medical efficiency. [5] Therefore, 3D NPs have been proposed as improved therapeutic agents in biomedical applications, although advanced synthesis techniques remain largely unexplored in this area.

Traditional "bottom-up" strategies seem a natural approach for the fabrication of NPs. However, since our knowledge of specific manipulation of "bottom-up" processes is limited, it is challenging to ideally control the fabrication process, and produce desirable nanostructures. In this work, we have demonstrated a feasible approach of "top-down" design and mechanosynthesis of 3D NPs with both chemical and physical anisotropies by exploiting the hybrid nanometer-scale NMM process [7]. Different types of 3D NPs with sub-10nm feature size have been successfully achieved utilizing the fabricated artificial molecular manipulators, including "nanomushrooms", "nanospikes", and "nanofibers". Although optimization of "top-down" design and fabrication process is necessary to possibly compensate for the lower quantities of materials produced by surface fabrication techniques compared to the volumetric sphere synthesis, increased potency and specificity may compensate for fewer total numbers of available particles.

EXPERIMENTAL

Materials and Reagents

Carboxylic acid functionalized PS spherical particles 20±10 nm in diameter are purchased from Molecular Probes Inc., USA. All other chemicals are purchased in A.C.S. grade from Sigma-Aldrich Chemical Company, USA.

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Fabrication

The fabrication process of the molecular manipulators is adopted from the hybrid NMM process [7] as outlined in Figure 1. It begins with "top-down" e-beam lithography (EBL). A silicon substrate bearing a thin Si_3N_4 film (60nm, deposited by low-pressure chemical vapor deposition) is patterned by EBL (JEOL JBX-9300FS EBL system, 100 kV) followed by two-step reactive ion etching (RIE) to create a series of nanoholes (100nm and 200nm in diameter respectively), as well as nanotrenches (100nm in width) with an aspect ratio of approximately 1:1 (Fig. 1b). A thermal oxidation (1100 ℃) is carried out to reduce the pattern feature size, simultaneously creating 3D SiO_2/Si_3N_4 nanostructures (Fig. 1c). "Bottom-up" surface initiated polymerization (SIP) is then used to functionalize 3D nanostructures, selectively grafting a basic polyelectrolyte layer (poly(vinyl pyridine), PVP) onto the SiO_2 surface in order to further reduce feature size (Fig. 1d). The resultant nanostructures are used as nanomanipulators for molecular assembly and mechanochemical synthesis (Fig. 2).

Figure 2 schematically illustrates the nanoscopic mechanosynthesis of 3D NPs utilizing fabricated nanomanipulators. The target molecules are 0D spherical PS NPs (averagely 20nm in diameter) which are surface functionalized by carboxylic acid groups (-COOH) and suspended in aqueous solution in a concentration of 5×10^{11} to 5×10^{14} ml^{-1}. The manipulator is firstly immersed in NPs suspension, and ultrasonication is performed (30min) for degassing the entire system. A dip-coating technique is then used to uniformly introduce arrayed NPs onto the manipulator surface in a large area [8] (Fig. 2b). The substrate (10mm×10mm) is first vertically immersed into the NPs suspension, and then pulled upward at a constant rate of 50µm/min. The manipulator is subsequently immersed into an alkaline bath (pH=13-14), e.g. sodium hydroxide (NaOH) or ammonium hydroxide (NH_3H_2O), followed by an ultrasonication (10-15min) to release the adsorbed
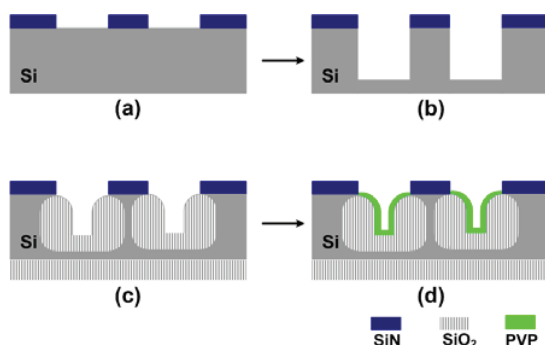

Figure 1: Schematic illustration of NMM fabrication process of molecular manipulators. (a) EBL followed by RIE, (b) RIE, (c) thermal oxidation, (d) SIP.
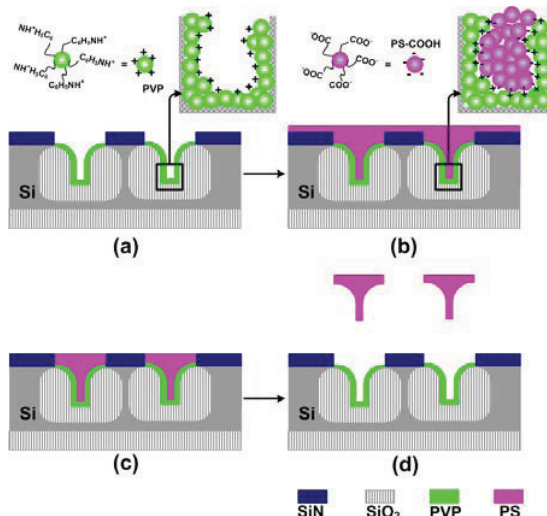

Figure 2: Schematic illustration of mechanosynthesis of 3D NPs utilizing molecular manipulators.

NPs by physical/static interaction (Fig. 2 insert). Meanwhile the ultrasonication initiates the mechanosynthesis, which mechanically rubs the remaining NPs against each other, creating friction and heat. The generated heat allows NPs to melt and replicate the manipulators' 3D nanostructures (Fig. 2c). An additional annealing step is applied (100℃, 1 hour) to facilitate the accomplishment of conformal replication. Finally, the resultant 3D replicas are released by the basic solution (NaOH or NH_3H_2O, pH=13-14, 8~10 hours) with an ultrasonication of 5min (Fig. 2d).

RESULTS AND DISCUSSION

Fabrication of Si-based Nanomanipulators

Figure 3 shows SEM (Zeiss SEM Ultra60) images of a series of resultant nanostructures in Si-based manipulators before (Fig. 1b) and after thermal oxidation (Fig. 1c). It is apparently observed (Figs. 3a and 3b) that the feature size of nanostructures patterned by EBL/RIE is reduced from 200nm to 80nm (inserts in Figs. 3a and 3b), and the structure is also simultaneously developed to 3D nanomushroom morphology. The morphology evolution is due to the anisotropic thermal oxidation in Si crystal and the usage of a Si_3N_4 layer (60nm) as a thermal oxidation mask layer. Similarly, the feature sizes of 100nm nanoholes and 100nm nanotrenches are miniaturized to sub-10nm (inserts of Fig. 3d), and their profiles are developed to 3D "nanospikes" and "nanofibers" respectively (Figs. 3c and 3d).

The resultant Si-based manipulators possess not only 3D physical nanostructures but also anisotropic surface functionalities through the grafted PVP polymers by SIP (Fig. 1d). X-ray photoelectron spectroscopy (SSX-100, Al K-α radiation, 1486.6eV)
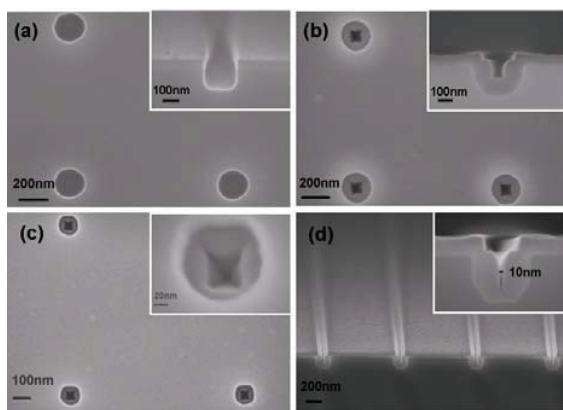
Figure 3: SEM images of 200nm nanoholes (a) before and (b) after thermal oxidation, (c) 100nm nanoholes after thermal oxidation, and (d) 100nm nanotrenches after thermal oxidation. Inserts are corresponding lateral views in a higher magnification.

Figure 4: Wide-scan XPS spectra of SiO_2 and Si_3N_4 control samples after SIP.

Table 1: Elemental Compositions

Sample	Atomic Weight %			
	C	*N*	*O*	*Si*
Si_3N_4	41.01	9.87	34.47	14.65
SiO_2	45.70	7.73	32.96	13.61

is used to characterize and compare the surface elemental composition of SiO_2 and Si_3N_4 control samples after SIP. The analysis result (Fig. 4) reveals that the nitrogen peak (N1s, 400eV) from the SiO_2 control sample after SIP corresponds to organic nitrogen from the grafted PVP polymer layer, and the nitrogen peak (N1s, 395eV) from the Si_3N_4 sample correlates to the inorganic nitride, [9] which indicates that the SiO_2 sample surface is successfully grafted by a PVP layer, while the Si_3N_4 sample surface remains the same. Composition analysis (Table 1) indicates that the molar ratio of C to N from the SiO_2 sample is 6.9 which is very close to the stoichiometric ratio of C to N in pure PVP (7), while the ratio of Si to N from the Si_3N_4 is 7.4, which is almost equal to the stoichiometric ratio of Si_3N_4 (7.5). Therefore the chemical selectivity of SIP to SiO_2 rather than Si_3N_4 surface is demonstrated (Fig. 1d).

Mechanosynthesis of 3D nanostructures

The function of the prepared artificial manipulators is to positionally nanoassemble objective molecules by a "bottom-up" approach and mechanosynthesize 3D NPs. Figure 5 shows a series of SEM images representing the mechanosynthesis procedure utilizing the manipulator with "top-down" "nanomushroom" 3D design. The obtained cap diameter of "mushroom" NPs is 200nm, and the width of their square stalks is 80 nm, indicating a conformal replication of the counter parts in the "mushroom" manipulator. Therefore the feasibility of "top-down" design and fabrication of 3D NPs is successfully demonstrated, which proves the concept of nanolithography-based molecular manipulation, and the hypothesis of utilization of artificial manipulators for molecular assembly and material synthesis.
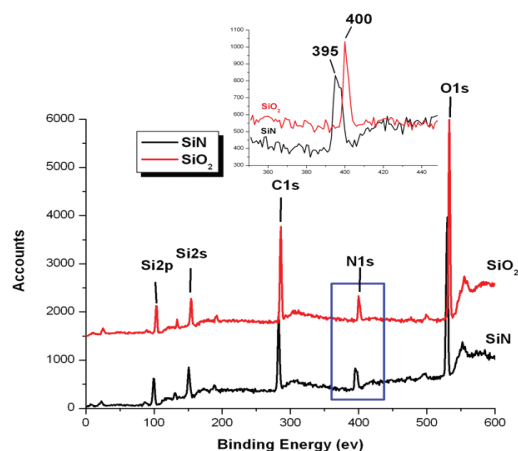
During mechanosynthesis, the anisotropic surface functionalities of artificial manipulators play an important role for molecular registration and assembly. It is observed that molecular targets deposited on a Si_3N_4 surface can be efficiently removed by the alkaline solution under ultrasonication (5 min) (Fig. 2c) due to the weak physical/static interactions between NPs and Si_3N_4 surface (Figs. 5a and 5b). In contrast, NPs that deposited on the PVP grafted SiO_2 surface present a higher resistance to the attack of the alkaline solution due to a combination of physical/static and chemical/ionic affinities (insert in Fig. 2b). As a result, NPs adsorbed on Si_3N_4 surface are easily "pulled off" the Si_3N_4 surface by the relatively strong ionic interactions between -COOH
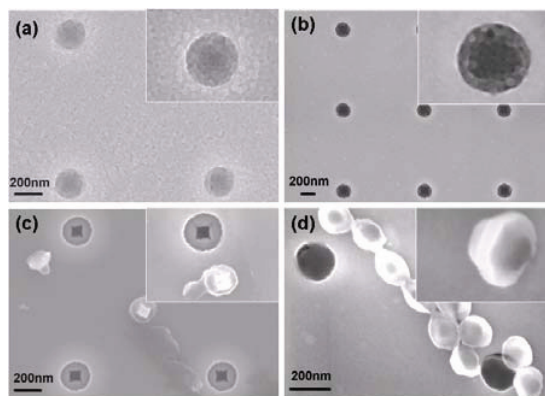

Figure 5: SEM images of nanomanipulators with 200nm hole design (a) after dip-coating in PS NPs suspension, (b) after cleaning by base solution, and released 3D "nanomushroom" particles (c) and their self-assemblies. Inserts are magnified SEM images of individual structures.
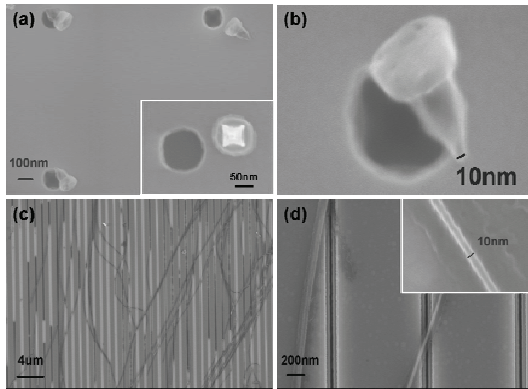
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Figure 6: SEM images of artificial "nanospikes" (a , b), and "nanofibers" (c, d). Inserts are amplified images.

groups on NPs and anions (OH⁻) from the base solution, and "dissolved" into the solution.

The ultrasonication applied during this solution cleaning step plays another important role to initiate the nanoscopic mechanosynthesis. The mechanically generated heat causes the NPs to partially melt and adhere with each other inside the nanostructures, which is the starting point of the following replication process. A subsequent annealing is performed to accomplish the conformal replication. An overload of mechanical ultrasonication can potentially shake out the attached NPs and disturb the entire mechanochemical reaction. The yield based on this fabrication process is approximately 50%-70%.

Similarly, "nanospikes" and "nanofibers" are also successfully synthesized with a feature size of sub-10nm (Fig. 6). The obtained "spike" cap is 100nm in diameter, and the "spike" tip is sub-10nm (Figs. 6a and 6b). The achieved finest parts of "nanofibers" have a feature size of sub-10 nm (Figs. 6c and 6d). The observed tips of "nanospikes" and the critical dimensions of "nanofibers" are not as sharp as their counterparts in the Si-based manipulators (approximately 1-2nm) (Fig. 3d). It can be explained by the low surface tension and the limited wettability of amorphous hydrophobic polystyrene molecules on SiO_2 surface. In fact, surface tension and the wettability of molecular targets could be further improved by decreasing the molecular weight, [10] reducing molecular size, or replacing PS by some other less hydrophobic molecules, thereby it is possible to approach 1-2nm resolution by carefully choosing molecular targets.

Subsequent study will include tuning and assembling such 3D NPs, as well as investigating the feasibility of synthesis of 3D NPs in other functional materials and compositions, e.g. polymer composites, for sensing and drug delivery applications.

CONCLUSION

In this paper, we have demonstrated a nanofabrication approach for mechanosynthesis of 3D polymeric nanostructures based on the concept of nanolithography-based molecular manipulation (NMM) for the potential applications requiring both chemical and physical anisotropies, e.g. improved medical imaging, enhanced near molecular assembly, and targeted drug delivery. Hybrid nanometer-scale NMM process is utilized to fabricate molecular manipulators with nanometer-sized patterns and anisotropic surface functionalities, which are then utilized in the nanoscopic mechanochemical reaction for positional nanoassembly of PS molecules and mechanosynthesis of 3D nanoreplicas. Three types of 3D sub-10nm NPs are demonstrated in this work including "nanomushrooms", "nanospikes", and "nanofibers". This approach allows us the capability of "top-down" design and fabrication of morphological features of NPs. Although this surface fabrication technique produces a relatively low quantity of 3D NPs compared to the "bottom-up" volumetric chemical synthesis, increased potency and specificity may compensate in selected applications.

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