FABRICATION OF 3-D HYBRID POLYMER-MAGNETITE NANOSTRUCTURES WITH GEOMETRIC SHAPE ANISOTROPY

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ABSTRACT

This paper reports fabrication of three-dimensional (3-D) hybrid polymer-magnetite nanoparticles with designed asymmetric shapes. The fabrication strategy exploited in this work is to fabricate nanotemplates for positional assembly of target water soluble polystyrene (PS) and iron-oxide (Fe_3O_4) nanoparticles, producing 3-D hybrid nanostructures as designed. This work has demonstrated 3-D asymmetric PS-Fe_3O_4 composite nanostructures (e.g. "nano-broccoli-flowers") with a feature size of sub-20 nm exhibiting ferromagnetic properties. Such magnetic 3-D asymmetric nanostructures may have specific advantages over 0-D symmetric spherical counterparts due to their geometric anisotropy, for example offering additional design freedom for nanoparticle functionality in biomedical and clinical applications.

KEYWORDS

3-D, Nanoparticles, Nanofabrication, Polymer composite, Magnetite

INTRODUCTION

Fabrication and investigation of nanometer-sized structures, devices and complex systems is attracting increasing attention in applications where scale confers functionality, such as biomimetics, stereochemistry, and nanoelectromechanical systems (NEMS). For example, polymer-based 3-D asymmetric nanostructures such as magnetic 3-D composite nanostructures with designed geometries can have specific advantages over 0-D symmetric nanoparticles in applications where such anisotropy can lead to performance and functionality enhancement, such as improved therapeutic agents [1]. However, advanced synthesis techniques to produce 3-D hybrid functional nanostructures in a designated way have met with limited success.

Although conventional "bottom-up" chemical synthesis and self-assembly strategies such as emulsion polymerization [2] and solvent evaporation-induced self-assembly [3] are able to produce polymer-based nanoparticles, one major problem of using such methods remains the lack of capability to produce various arbitrary desirable 3-D nanostructures at specific positions. This is mainly due to limited knowledge of how to perform molecular manipulation with precise control. In addition, compared to the fabrication of pure polymer 3-D nanoparticles, it is more difficult and complex to process composite materials.

Recently we have demonstrated a fabrication strategy, Nanolithography-based Molecular Manipulation (NMM), which has shown significant potential for design and fabrication of 3-D polymer nanostructures in a precise manner [4]. It allows the combination of "top-down" nanolithography (e.g. electron-beam lithography (EBL)) with "bottom-up" chemical modification (e.g. surface initiated polymerization (SIP)), producing nanotemplates with specific surface functionalities for molecular manipulation and synthesis of 3-D nanoparticles. In this work, we have further exploited the NMM approach and studied the feasibility of fabrication of 3-D organic-inorganic hybrid nanostructures, e.g. polystyrene-iron (III) oxide (PS-Fe_3O_4) magnetic nanoparticles. Such products have advantages of geometric anisotropy and hybrid material functionalities, combining the biocompatibility of PS with the magnetic properties of Fe_3O_4, with potential biomedical and clinical applications. Although surface fabrication techniques produce lower quantities of material compared to volumetric conventional chemical synthesis, increased potency and specificity may compensate in specific applications that require high precision with selective functionality in the small scale.

EXPERIMENTAL

Materials and Reagents

Water soluble paramagnetic Fe_3O_4 nanocrystals (5 ± 2 nm in diameter, surface functionalized by poly(acrylic acid) (PAA), Fig. 1(a)) were prepared using a high temperature hydrolysis approach [5]. They present negative charge in aqueous solution. Amine functionalized polystyrene (PS) latex (20 ± 5 nm in diameter, Fig. 1(b)) was purchased from Molecular Probes Inc., USA. They present positive charge in aqueous solution. All other chemicals are purchased in A.C.S. grade from Sigma-Aldrich Chemical Company, USA.
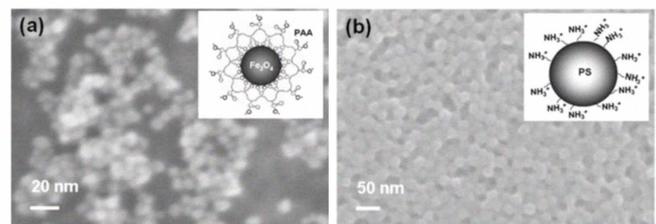
Figure 1: SEM images of (a) surface functionalized Fe_3O_4 NPs (5 ± 2 nm in diameter, surface functionalized by poly(acrylic acid) (PAA)) and (b) polystyrene (PS) nanoparticles (20 ± 5 nm in diameter, surface terminated by amine groups). Inserts are schematic illustrations of the nanoparticles respectively.

Fabrication of Nanotemplates

Figure 2 schematically illustrates the fabrication process of the nanotemplate as reported in [4]. Typically, the fabrication begins with "top-down" e-beam lithography (EBL) (Fig. 2(a)). A silicon substrate bearing a thin Si_3N_4 film (60 nm, deposited by low-pressure chemical vapor deposition (LPCVD)) is patterned by EBL (JEOL JBX-9300FS EBL system, 100 kV) followed by two subsequent steps of reactive ion etching (RIE) to create a series of nanoholes (100 nm and 200 nm in diameter respectively) with an aspect ratio of approximately 1:1 (Fig. 2(b)). A thermal oxidation (1100 °C, dry oxidation) is then carried out to reduce the pattern feature size, simultaneously creating 3-D SiO_2/Si_3N_4 nanostructures (Fig. 2(c)). "Bottom-up" surface initiated polymerization (SIP) [6] is subsequently used to functionalize 3-D nanostructures, selectively grafting a polyelectrolyte layer of poly(vinyl pyridine) (PVP) (positive charge in aqueous solution) onto the SiO_2 surface in order to further reduce the feature size and functionalize the template surface (Fig. 2(d)). The resulting nanotemplates possess 3-D recessed nanopatterns and anisotropic surface functionalities through the grafted PVP brushes (Fig. 2(d)).

Synthesis of Hybrid 3-D Nanoparticles

Figure 3 schematically illustrates the synthesis process of 3-D composite nanoparticles using the fabricated nanotemplates. Water soluble paramagnetic Fe_3O_4 nanocrystals (5±2 nm in diameter) present negative charge in aqueous solution due to the surface functionalized poly(acrylic acid) (PAA) (Fig. 1(a) and the insert in Fig. 3(a)), while the surface NH_2-terminated PS latex (20±5 nm in diameter) presents positive charge (Fig. 1(b) and the insert in Fig. 3(a)). Both materials are suspended in de-ionized (DI) water with a number ratio of 10:1(Fe_3O_4:PS), and it is highly likely that they form a composite complex with surface negative charge (Fig. 3(a) insert). The synthesis process begins with immersion
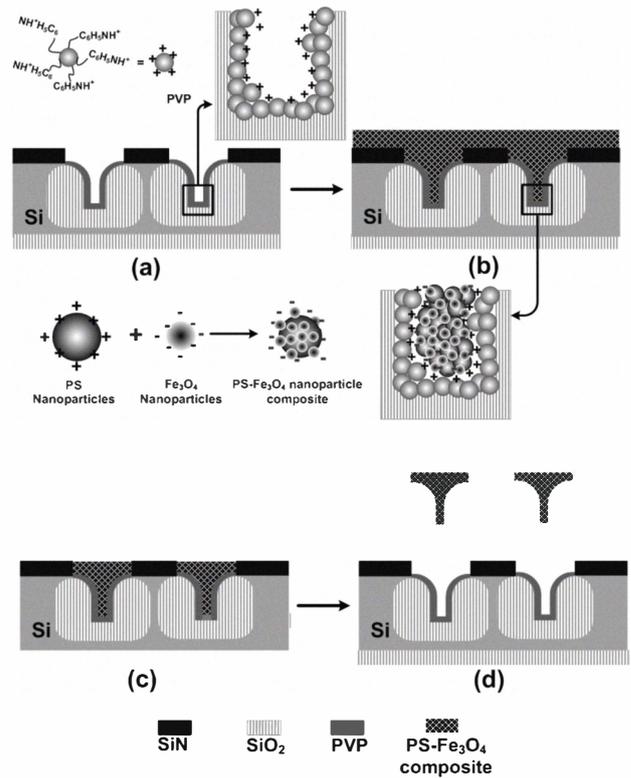
Figure 3: Schematic illustration of nanofabrication of 3-D polymer-magnetite composite nanostructures. (a) Immersion of the nanotemplate in aqueous PS-Fe₃O₄ nanoparticle suspension followed by degassing, (b) the dip-coating process followed by annealing, (c) removal of physically adsorbed PS-Fe₃O₄ material by soaking the template in an alkaline bath accompanied with ultrasound, (d) solution extraction to release the resulting molded 3-D PS-Fe₃O₄ composite nanostructures.

of the nanotemplate in nanoparticle aqueous suspension under ultrasonication for degassing (30 min). A dip-coating technique [7] using a lab-made setup (Fig. 4) uniformly introduces the composite onto the template surface (50 μm/min) followed by annealing (120 °C, 2
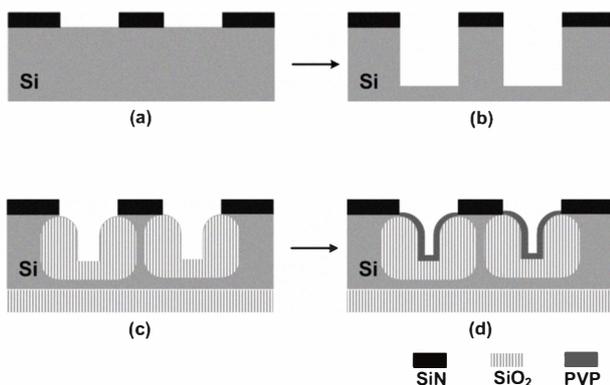
Figure 2: Schematic illustration of fabrication of nanotemplates. (a) EBL followed by RIE to pattern Si₃N₄ layer, (b) RIE to transfer the nanopattern into Si substrate, (c) thermal oxidation to reduce the feature size creating 3-D SiO₂/Si₃N₄ nanostructures, (d) SIP to selectively functionalize the SiO₂ surface.
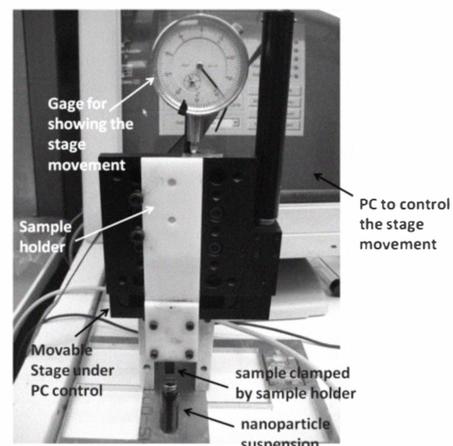
Figure 4: Apparatus for dip-coating process. The chip is clamped and held by a sample holder. The sample holder is fixed on a movable stage which is programmed and controlled by the computer.

hours) (Fig. 3(b)). During annealing the polymer component melts and tends to wet the Fe_3O_4, forming the composite. Further, the composite replicates the nanotemplate. A cleaning step (Fig. 3(c)) then is carried out to release the PS-Fe_3O_4 composite layer that is simply physically adsorbed on the template surface (Si_3N_4) by soaking the template in an alkaline bath ($NH_3 \cdot H_2O$, pH=13~14) under ultrasonication (5 min). Replicated 3-D nanoparticles are eventually released in the same alkaline bath (24 hours) followed by ultrasonication (5 min) (Fig. 3(d)). Then the emptied nanotemplate is ready for another synthesis.

RESULTS AND DISCUSSION
Nanotemplates

Figure 5 shows top and lateral views of two series of fabricated nanotemplates: 200 nm 3-D nanoholes with sub-50 nm feature size and 100 nm 3-D nanoholes with sub-20 nm feature sizes respectively. They possess 3-D nanosites and specific surface functionalities through the grafted poly(vinyl pyridine) (PVP) brushes (characterized by XPS (X-ray photoelectron spectroscopy)). The morphology evolution of the patterned nanoholes after thermal oxidation is due to anisotropic growth of SiO_2 in the x, y and z directions, as well as the use of Si_3N_4 (60 nm) as a mask layer to suppress oxidation in the z direction. More characterization and discussion about NMM fabrication of nanotemplates can be found in [4, 5].

3-D PS-Fe_3O_4 Nanoparticles

Figure 6 shows two series of resulting 3-D composite nanoparticles, namely "nano-broccoli-flowers". The first series (Figs. 6(a)-(d)) have flower "corolla" and "stamen" of 200 nm and sub-50 nm in diameter respectively produced by using the 200 nm nanohole template (Fig. 5(a)). The second series (Figs. 6(e)-(f)) have flower "corolla" and "gynoecium" of 100 nm and sub-20 nm in diameter respectively fabricated by using the 100 nm nanohole template (Fig. 5(b)).

From the first series of produced "nano-broccoli-flowers" (Figs. 6(a)-(d)), it can be observed that nanopatterns from the template have been successfully molded and transferred into PS-Fe_3O_4 composites. Moreover, the sub-50 nm feature size from the nanotemplate (Fig. 5(a)) has also been properly preserved. Therefore the feasibility of NMM-based
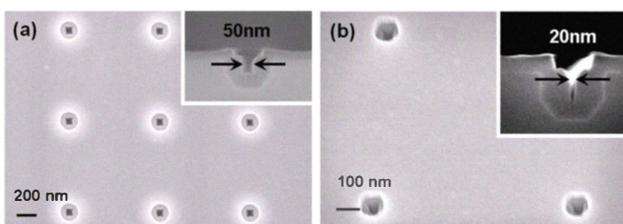
synthesis of 3-D PS-Fe_3O_4 hybrid nanostructures is demonstrated. Further, it is noticed that the resulting composite nanostructures have lost some structural details of the template, such as the total pattern height and the precise square shape of the centric feature that results in the flower "gynoecium". However, this issue was not present in fabrication of pure polymer (e.g. PS) nanostructures using similar nanotemplates. It is attributed to the implementation of the inorganic Fe_3O_4 component into the polymer PS for 3-D synthesis. Fe_3O_4 is a metallic oxide with much higher melting point than the organic polymer of PS (105 °C). During annealing (120 °C) Fe_3O_4 nanocrystals remain as solid particles, while PS melts, and tends to wet and carry Fe_3O_4 nanocrystals replicating the nanotemplate. This issue can be solved by careful selection of materials and proper modification of the polymer and the inorganic nanoparticle surface to improve their wetting properties and adherence to each other. Strategies can include functionalization of the core Fe_3O_4 particle surface with a shell polymer that is more compatible and miscible with PS material, or replacement of PS by another polymer candidate that is more compatible with and easy to wet PAA-functionalized Fe_3O_4 particles.

Figures 6(e)-(f) show the primary results of resulting 3-D "nano-broccoli-flowers" produced by using a template with smaller shape and feature size (100 nm hole opening and sub-20 nm feature size) (Fig. 5(b)). It can be observed that the produced 3-D nanostructures have many similarities to the template's 3-D nanopatterns, so the concept and the feasibility of molding sub-20 nm recessed
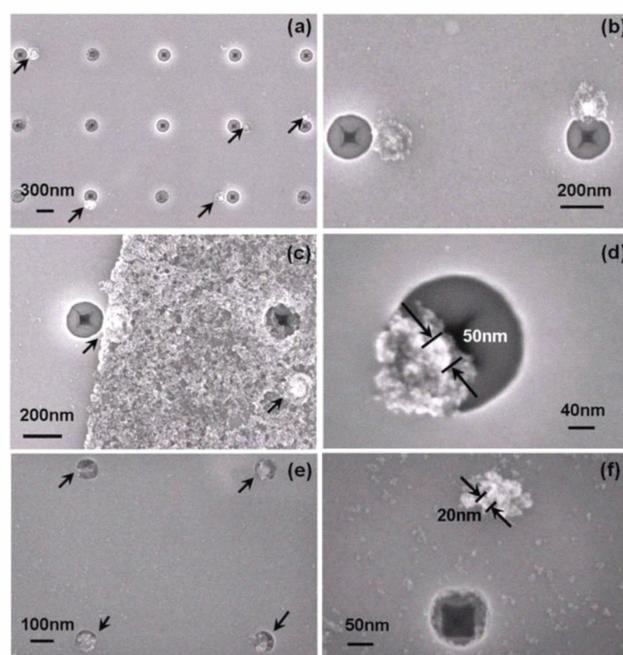
Figure 6: SEM images of 3-D PS-Fe_3O_4 "nano-broccoli-flowers" (a-d) with "corolla" and "gynoecium" of 200 nm and sub-50 nm in diameter, and (e-f) with "corolla" and "gynoecium" of 100 nm and sub-20 nm in diameter respectively.

Figure 5: SEM images of (a) 200 nm nanoholes with sub-50 nm feature size and (b) 100 nm nanoholes with sub-20 nm feature size after thermal oxidation.

nanosites using PS-Fe$_3$O$_4$ composites is demonstrated. On the other hand, it is also noticed that these resulting 3-D nanostructures have lost more feature details than the sub-50 nm ones (Figs. 6(a)-(d)). This reveals that the issue of material compatibility and miscibility becomes significant and potentially limits the fabrication capability when the feature size of template is less than 20 nm. One possible way to address this is to modify and optimize the material property and surface functionality as mentioned previously.

In addition, it is found that the implementation of the Fe$_3$O$_4$ component in the polymer material leads to some difficulty during the cleaning step (Fig. 3(c)). The cleaning step is used to release the PS-Fe$_3$O$_4$ composite layer that is physically adsorbed on the Si$_3$N$_4$ template surface. Figure 6(c) presents resulting 3-D nanostructures as well as the template which was not able to be properly cleaned and thus has a layer of composite residue on the surface. This issue was not present when the manipulated material was pure polymer such as PS. It is primarily attributed to complex affinities and static interactions between the PS-Fe$_3$O$_4$ composites and the template surface. The composite residue terminates a number of nanosites on the template and thus leads to a reduced synthesis yield in the next template-assisted fabrication. The residue can be removed by using a series of solvent etchants including acetone to dissolve PS and phosphoric acid to etch Fe$_3$O$_4$.

The synthetic PS-Fe$_3$O$_4$ nanoparticles and their aggregations show proper ferromagnetic properties in a gradient magnetic field. Figure 7 shows a preliminary result indicating that the nanostructures can be manipulated by magnets due to the embedded Fe$_3$O$_4$ component. Future study will include the characterization of the synthetic 3-D nanostructures in a given external field to exploit the interrelationship between 3-D nanostructure morphology and their performance for biomedical and clinic applications including nanomedicines and therapeutic agent. Precise tools can be utilized to perform this characterization, such as Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Nuclear Magnetic Resonance (NMR). Careful experimental design and setup would be needed to properly translate and transfer the existent molecular-level information and their associations.
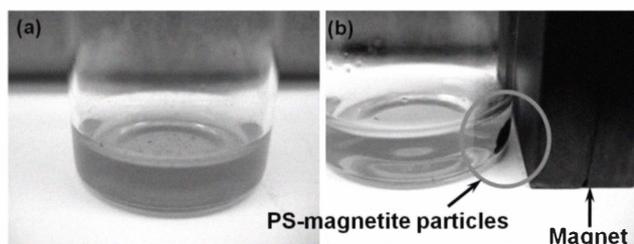
Figure 7: Photos of the response of released PS-Fe$_3$O$_4$ composite particles (a) without and (b) with magnetic field.

CONCLUSION

In this paper, proof-of-concept 3-D hybrid polymer-magnetite nanoparticles with sub-20 nm feature size ("nano-broccoli-flowers") have been demonstrated by exploiting the nanolithography-based molecular manipulation (NMM) strategy. The feasibility of integrating hybrid materials' functionalities (e.g. biocompatibility and magnetic property) and arbitrary structural anisotropy (e.g. 3-D) into synthetic nano-sized particles (e.g. sub-20 nm) in a designated way is proved. Potential applications of such 3-D nanoparticles can be in drug delivery system (DDS), magnetic resonance imaging (MRI) and cancer therapy. In addition, such 3-D nanoparticles can serve as models to help us experimentally understand more about molecular-level interactions and their self-assembly to validate the theoretical high-performance-computing study. Although surface template synthesis techniques produce lower quantities of material compared to volumetric particle synthesis (e.g. emulsion polymerization), increased potency and specificity may compensate in many specific applications.

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