SCALABLE FABRICATION OF ACTIVE NANOGAPS WITH SUB-NANOMETER TUNABILITY FOR NANOSCALE SENSORS AND ACTUATORS

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ABSTRACT

We present a platform for scalable fabrication of mechanically-active nanogaps with sub-nanometer tunability for extreme miniaturization of microelectromechanical systems with applications in sensors and actuators. In our approach, molecular layers serve as nanoscale springs to overcome stiction due to surface adhesive forces and enable dynamic and reversible reconfiguration at the few-nanometer regime. Our additive manufacturing approach is based on dry and high-yield contact printing of bottom-up assembled nanoparticles. Using this technique, we fabricated arrays of active plasmonic resonators with a nanoparticle-on-mirror design and a molecular spacer. Under temperature cycling, this platform allows for the optical detection of sub-nanometer thermal expansion of the resonator nanogap, demonstrating the extreme sensitivity of these nano-actuators.

KEYWORDS

Additive manufacturing, Bottom-up fabrication, Plasmonic resonators, Contact printing, Molecular springs

INTRODUCTION

Miniaturized microelectromechanical devices with critical dimensions few-nanometers in size have long been desired for their improved sensitivity, energy-efficiency and speed, enabling new applications. However, building devices reliably at this scale has been a long-standing challenge as the dominating surface adhesive forces at the nanoscale can lead to stiction, inducing structural instability and collapse during fabrication or operation. Here, we present a platform for scalable fabrication of mechanically-active nanogaps with sub-nanometer tunability using molecular springs. Our approach presents two unique features to balance the surface forces. First, the molecular layer provides structural support for miniaturization to sub-5 nm dimensions. Second, its tailorable mechanical properties yield controlled and reversible tuning. Scalable and deterministic fabrication of such mechanically-active hybrid organic-inorganic constructs is beyond the capabilities of conventional techniques. To this end, we present an additive manufacturing strategy based on dry and high-yield contact printing of bottom-up assembled nanoparticles.

We demonstrate our platform in form of an active gold nanoparticle-on-mirror plasmonic resonator composed of a metallic nanostructure separated from an underlying metallic thin-film by a nanometer-thin dielectric molecular spacer, as shown in Figure 1. In this structure, the optical response is sensitive towards minute changes in the gap size [1, 2]. This provides a powerful probe of the mechanical tunability at the sub-nm regime, while also serving as building blocks for engineering of emerging nanoscale sensors, actuators, reconfigurable optical devices and tunable metasurfaces.

FABRICATION APPROACH

Our fabrication technique relies on a two-step additive manufacturing process, shown in Figure 2a. First, synthesized gold (Au) nanoparticles with a molecular coating are deterministically positioned through capillary assembly onto a lithographically-defined topographical template made out of polydimethylsiloxane (PDMS). Then, the assembled particles are transfer-printed onto a template-stripped gold receiving substrate with sub-nm surface uniformity. Unlike existing techniques which require solvents, surface modifications or sacrificial release layers to promote the transfer [3, 4], we achieve > 95% transfer yield and < 50 nm positional accuracy in a single dry contact-and-release step without any mediations. This is achieved by engineering the van der Waals forces during transfer through template design. As a result, surfaces remain pristine and well-defined molecular gaps can be realized. An example 50 × 50 array of nanoparticle-on-mirror resonators based on ~ 54 nm gold nanocubes with ~ 1.5 nm molecular spacer is shown in Figure 2b.

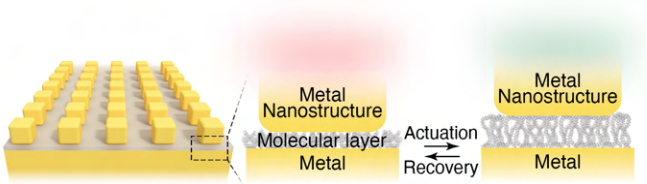

Figure 1: Mechanically-tunable nanogaps with molecular springs in the form of particle-on-mirror plasmonic resonators with a reversibly tunable optical response.

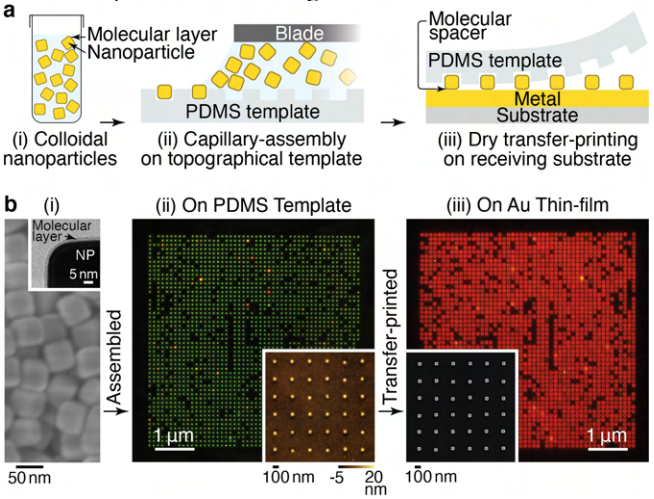

Figure 2: Scalable fabrication of tunable molecular nanogaps with nanoparticle contact printing. (a) Fabrication process: (i) Au nanocubes are synthesized with a molecular surface coating. (ii) Individual nanocubes are assembled using capillary assembly onto a lithographically-defined PDMS template. (iii) Assembled nanocubes are dry-transferred onto a template-stripped Au substrate. (b) Example particle-on-mirror resonators formed using the process in (a). (i) Scanning electron microscope (SEM) image of colloidal Au nanocubes with the inset showing a transmission electron microscope (TEM) image of the molecular layer formed on a nanocube surface. (ii) Dark-field image of assembled 50 × 50 array of ~ 54 nm Au nanocubes, with the inset atomic force microscope (AFM) image showing the surface topography. (iii) Dark-field image of the 50 × 50 array dry-transferred onto a template-stripped Au film forming plasmonic resonators with ~ 1.5 nm active molecular nanogaps. The inset shows a representative SEM image of the transferred nanocubes.

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Figure 3 highlights the dependence of the plasmonic response of the resonators to the gap between the nanoparticle and the underlying metal thin-film. We fabricated arrays of resonators with different Al_2O_3 thicknesses deposited through atomic layer deposition. The dark-field scattering spectra show a blue shift in the plasmonic resonance wavelength as the gap size increases, which matches closely with the expected resonance modeled using a finite-difference time-domain simulation.

To demonstrate the dynamic and reversible tunability afforded by a molecular spacer, we tested the resonators in Figure 2b under thermal cycling. In this design, the molecular layer is composed of ~ 1.5 nm-thick mixture of Triton X-45 and sodium dodecyl sulfate. Shown in Figure 4, as the sample is heated to 50°C, the molecular layer undergoes thermal expansion, resulting in an increase in the gap size and accordingly, a blue shift in the resonance wavelength. Once cooled, the molecular layer relaxes and reduces the gap, leading to a red shift in resonance. Due to the extreme sensitivity of the optical resonance to gap dimensions [1, 2], highlighted in Figure 3c, the observed ~ 1.2 nm resonance shift upon heating corresponds to a mere ~ 26 pm-displacement in the gap region. This highlights the potential of molecular springs as a platform to realize controlled and reversible mechanical tuning at the sub-nm scale.

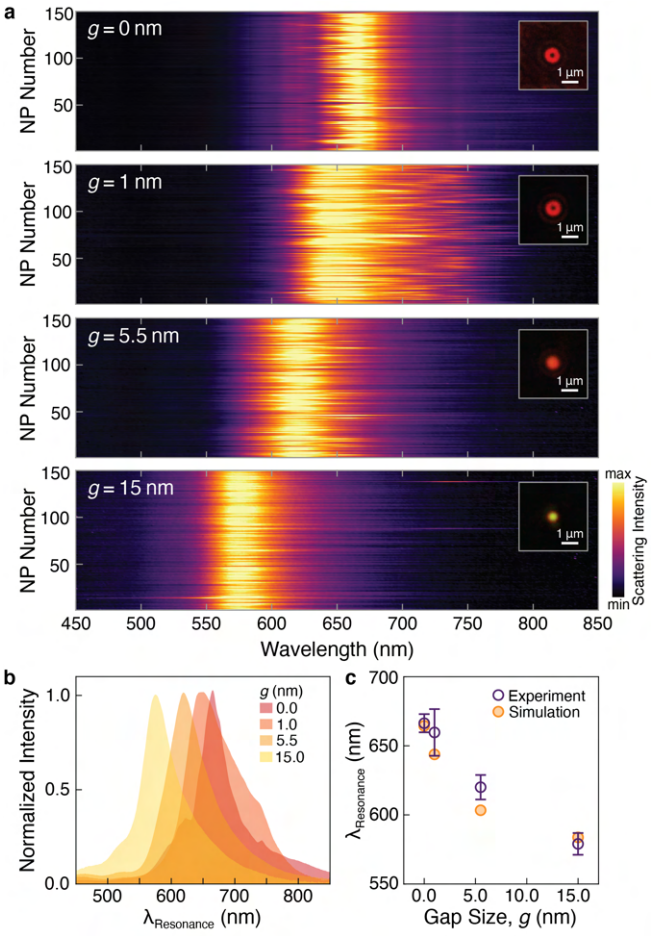

Figure 3: Strong dependence of plasmonic response to the nanogap size, g. (a) Scattering spectra of nanoparticle (NP)-on-mirror resonators with different thickness Al_2O_3 spacers showing a blue shift in the plasmonic resonance wavelength ($\lambda_{Resonance}$). The inset to each plot shows a dark-field image of a resonator. The change in the plasmonic response with the gap size is further displayed in (b) the scattering spectra ensemble average of resonators at different nanogap size, and (c) experimental and simulated resonance wavelength at each nanogap size.

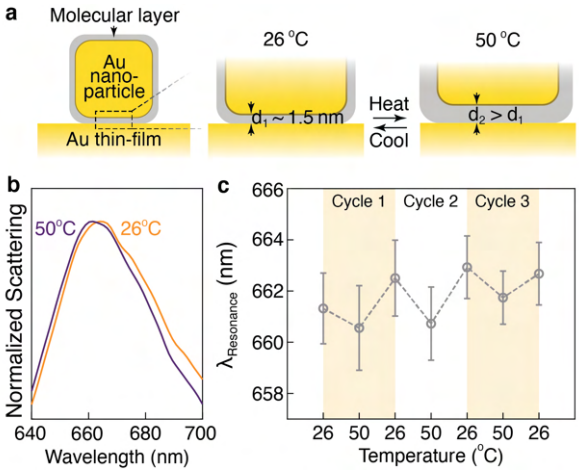

Figure 4: Molecular gap with controlled and reversible sub-nanometer tunability. (a) Schematic of the plasmonic resonators undergoing temperature cycles which induce changes in the gap due to thermal expansion of the molecular spacer. (b) A blue shift in the resonance wavelength is observed as the sample is heated and molecular gap expands. (c) Changes in the resonance wavelength shown through several heating and cooling cycles display a reversible tunability.

CONCLUSION

In summary, we have demonstrated an approach for scalable fabrication of precisely-defined mechanically-active nanogaps with sub-nanometer tunability using molecular springs. This platform provides a unique opportunity for dramatic miniaturization of mechanically-active devices to the extreme nanoscale, a process that is not feasible through conventional approaches. This opens up diverse opportunities for new applications in sensors, actuators and reconfigurable optical devices and systems.

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