Multicomponent Nanoscale Systems Fabricated with a Macromolecular Toolbox

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Research Achievement: Incorporation of biomolecules into nano-object design provides a unique opportunity to establish highly selective interactions between the components of nanosystems. The encoding and structural plasticity, provided by biomolecules, can allow for self-assembly of various nanoscale objects into well defined architectures. We are developing a range of strategies to use biomolecules as site-specific scaffolds, smart assembly guides and selective binding agents. These approaches are appealing as new effective ways for material fabrication and may produce new classes of engineered nanomaterials with potential use in novel optical and electrical devices as well as biomedical applications.

In my talk, I will describe our current progress in the fabrication of well-defined hybrid structures containing biomolecules and inorganic particles. Recently, we demonstrated that certain DNA motifs when attached to nanoparticles provide interaction that favors the formation of ordered superlattices. This opens a route to 3D fabrication of materials from a wide variety of nanoscale components - a task which is difficult to achieve using conventional lithographic techniques. We have also explored applications of DNA-based assembly approaches for fabrication 2D arrays, quasi-0D clusters, and on-demand reconfigurable systems.

Many unique phenomena emerge after arranging a few nanoscale objects into clusters, or so-called artificial molecules. The strategy of using biomolecules as linkers between nanoparticles has proven especially useful for construction of such nano-clusters. However, conventional solution-based reactions typically yield a broad population of multimers and require extensive purification, thus limiting the fabrication yields. We have developed a novel high-throughput method for producing clusters of DNA-encoded nanoparticles using stepwise assembly on a solid support (Fig. 1). This method efficiently bestows particles with anisotropy and generates remarkably high yields of well-defined dimer clusters and Janus (two-faced) nanoparticles. Using this approach we successfully fabricated, with yields exceeding 75%, dimer clusters that have well defined separation between cluster components determined by a designed linker. A similar approach was used for fabrication of anisotropic clusters using Janus particles with different, DNA-controlled binding properties on each Janus face. For example, we formed clusters containing about 5 small particles located on one hemisphere of a larger particle. The developed method was employed for assembly of homogenous (gold-gold) and heterogeneous (gold-silver) nanoparticle dimers. Using light and x-ray scattering methods and electron

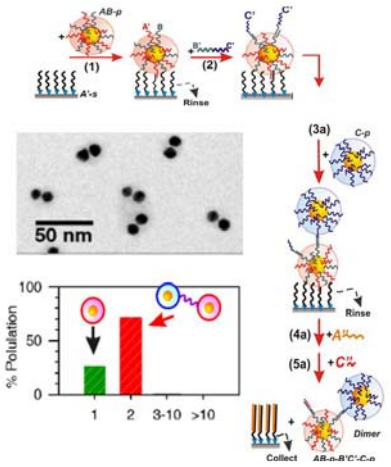

Fig. 1. Schematics of stepwise encoded assembly of dimer nanoclusters. TEM image of assembled structures. Histogram reveals ~75% assembly yield without additional purification.

microscopy, the details of cluster morphology were investigated. Additionally, optical studies showed that wavelength shift due to plasmonic coupling within gold-gold dimers depends exponentially on intra-dimer spacing. Recent work on the use of these clusters for real-time label-free sensing of nucleic acids will be also discussed.

Bio-inspired approaches for self-assembly of nanoscale components into static structures furnish a basis for the emerging paradigm in non-lithographical fabrication of designed nanomaterials. At the same time, the structural plasticity of biomolecules is auspicious for the creation of nanosystems that are dynamic, reconfigurable, and responsive. We have created and studied nanosystems that were assembled incorporating a reconfigurable DNA device into 3D superlattices or into clusters of two particles. The device allows for the post-assembly re-organization of the superlattices and clusters upon addition of molecular stimuli, simple DNA strands, while preserving the structural integrity of the systems. We investigated, using in-situ structural methods, the reconfiguration processes and observed two well defined and on-demand switchable states in the systems of superlattices and cluster assemblies.

Branched DNA nanostructures (scaffolds) offer design flexibility for precise placement of nanoparticles in 2D arrays. However, typically utilized methods rely on a single flexible chain to anchor a particle at a specific site. This results in some uncertainty in a particle position, and minimal control of nano-object orientation. We have designed scaffold motifs (Fig. 2) with spaced clusters of binding sites that allow multiple linkages to nanoparticles without introducing substantial disorder into the assembly. Additionally, we have developed a surface modification for DNA encoded particles that resolves a known problem of particle aggregation in the Mg-rich environment that is required for scaffold stabilization.

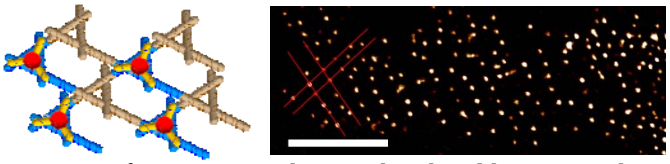

Fig. 2. Left: DNA array decorated with gold nanoparticles (red spheres). Right: A scanning electron micrograph of this system. Red lines mark a unit cell, scale bar is 200nm.

Future Work: We will use self-assembly fabrication methods as described above to create binary systems based on various types of nanoparticles and chromophores, in which DNA motifs and arrays control the inter-component distances and global system structure. Combining group expertise in assembly, structural characterization and single optical methods we will study distance-dependent light-driven interactions between different constituents of the system. In particular, we will construct systems composed of metallic and semiconductor particles to study energy harvesting and transfer, fluorescence quenching and enhancement processes arising from pair-wise and collective interactions in the designed nanosystems.

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