Molecularly Guided Assembly of Colloidal Nanoparticles in Solution and on Substrates

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Plasmonic nanoparticles are increasingly important tools in sensing, drug delivery and catalysis, but an increasing number of synthetic and assembly techniques are required to design the desired nanostructures. Synthesis of nanoparticles and the assembly of these particles into larger combinations typically fall into two categories: top-down methods, typically using lithographic or nanoimprinting techniques, and bottom-up synthesis, typically using molecularly guided self-assembly of colloidal particles. There are advantages for each method, primarily associated with the control of assembly in the top-down methods versus the versatility and variety of colloidal particles available for the bottom-up synthesis.

In this presentation, we review two applications of molecularly guided assembly of nanoparticles. The first application utilizes an entirely colloidal self-assembly method to systematically combine gold nanoparticles into dimers with very short separations [1]. The separation range can be controlled through varying the concentrations of the molecular linker, DNA, on the surface of the particles. Additionally, changing the DNA concentration reveals that at separations below 3 nm, the charge transfer through the DNA molecules in the gap reduces the plasmon coupling. This results in a decrease in the observed plasmon shift as well as a decrease in the electric field enhancement. Further reduction in the observed plasmon shift occurs when the charge transfer capabilities of DNA linker are enhanced through the DNA-directed deposition of small palladium nanocrystals in the gap, which allows for more charge

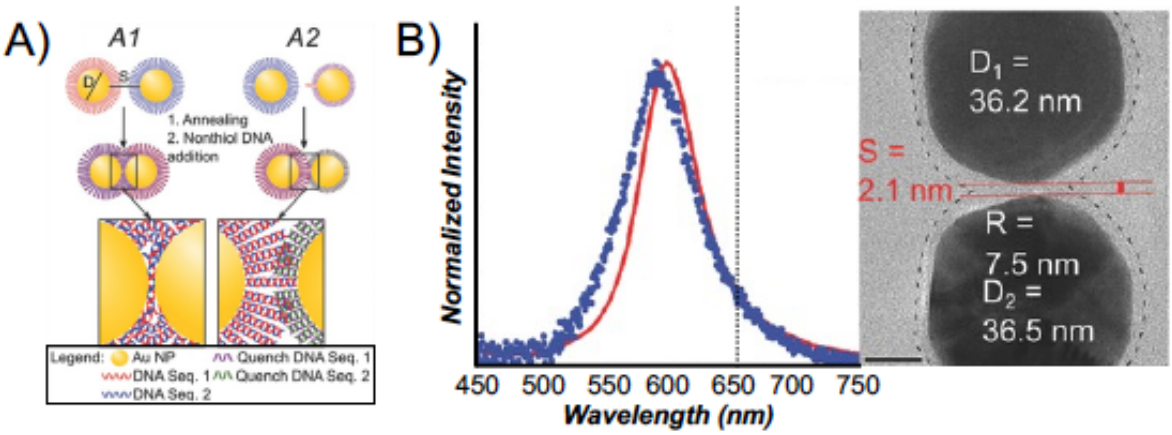

Figure 1 A) DNA-directed self-assembly of nanoparticle dimers with different concentrations of linker molecule. B) Sample spectrum (blue), simulated spectrum (red) and expected wavelength (black dashed line) of imaged nanoparticle dimer. Scale bar = 5 nm.

movement through the gap [2]. This increases the observed depolarizing of the plasmon coupling to a separation of over 4 nm.

The second application of molecularly guided assembly demonstrates the use of molecular components to create an electrostatic differential on lithographically patterned surfaces in order to attract colloidal nanoparticles with an opposite surface charge. This technique has been utilized to attach negatively charged palladium nanocubes to patterned gold nanodisks that are modified with molecular components to create a positive surface charge. The palladium nanocubes are subsequently used as a hydrogen sensor, where the gold plasmon resonance serves as a monitor for the change in the permittivity and volume expansion of the palladium as is absorbs hydrogen [3]. Additional uses for the molecular assembly on lithographically designed substrate are being explored in nanofluidics, other sensing applications and catalytic routes.

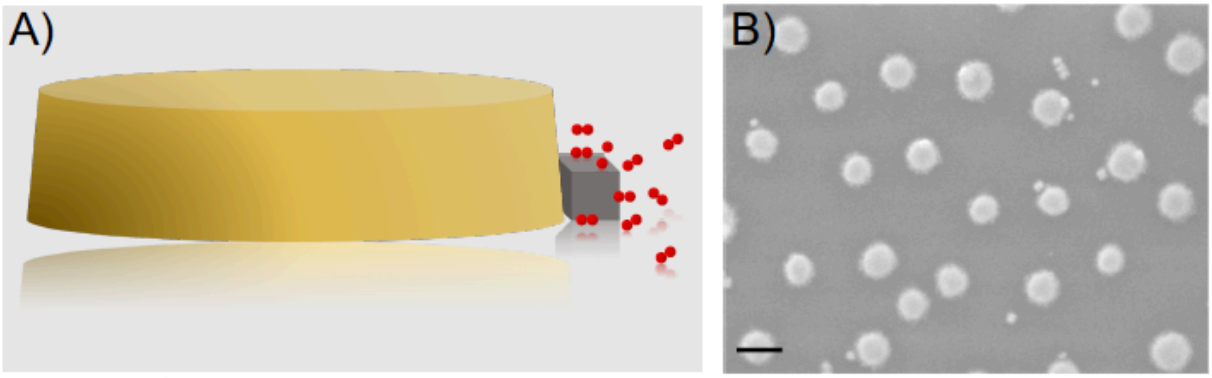

Figure 2 A) Schematic of gold nanodisks with palladium nanocubes absorbing hydrogen. B) Palladium nanocubes binding to gold nanodisks. Scale bar = 100 nm.

References.

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