

Synthesis of Janus Nanorods for Assemblies of Thermo-responsive Rod Pairs

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ABSTRACT

Janus particles offer unique functionality; for example micron-scale Janus spheres are used for electronic paper. At the nanoscale, reproducible, scalable fabrication of Janus particles is one of the key enabling technologies for “bottom-up” assembly processes. For example, self-assembly of Au nanorod pairs created from Au Janus rods would provide a bottom-up, self-limiting assembly pathway alternative to current e-beam lithography methods. Commonly, Janus particles are synthesized using one of two masking concepts, either self masking resulting from directional vapor deposition or substrate masking to block non-directional modification chemistry. Using surface masks and non-directional chemistry, the ligand size was found to provide a limited range of tunability of the extent of asymmetric functionalization. This was found to agree well with geometrical-based theoretical predictions. The extent of asymmetry in the nanoparticle coverage was found to affect the protoassemblies of rods, where the greater the attractive coverage the larger the protoassemblies formed. This approach can potentially enable affordable fabrication of tangible quantities of thermo-responsive nanorods pairs for fundamental and application studies of gold nanorods pair spacing parameters and the effect on optical properties such as surface plasmon resonances.

Keywords: Janus, gold nanorods, self-limiting assembly, nanorod pairs

1 INTRODUCTION

The need for precisely engineered nanostructures is universal (electronics, medicine, materials, etc). Protoassemblies of smaller component engineered nanoparticles provides a key step to achieving a wider range of material properties for these applications[1-6]. For example, paired metal nanorods structures can be used to create magnetically inductive loops for novel optical properties[7-9]. To date, most paired structures have been formed using top-down approaches in a 2D fashion, such as those used to make gold rod pairs for negative index of refraction applications. Oil-water interfaces[10, 11] and surface masking are other approaches to perform an asymmetric ligand exchange[12] or asymmetric metal deposition[13] onto a microparticle or nanoparticle. Attempts to scale-up the reaction throughput using parallel

fluid flows have successfully created micron-sized Janus particles[14-16]. Ideally, a surface-masking approach is desired that can utilize a smaller 3D substrate such as colloids to increase the surface area to volume ratio available for surface masking reactions[17] while maintaining a nanoscale size of the particles being functionalized.

This work selects gold nanorods as the target Janus particle, with the goal of creating self-limiting self-assembling rod-pair structures that may potentially have optical properties, such as surface plasmon resonances, that depend on the spacing parameter between the rods. Previous work into nanorods assemblies[18-26] has shown the self-limiting rod-pair assembly to be elusive. The current challenge is to create a bottom-up assembly approach that enables self-limiting assembly of nanorod-pairs. By controlling the “sticky” surface areas of the nanorods, we propose to drive reactions towards increased rod pair yield and decreased random, amorphous aggregation. Creating Janus particles will require several key components to be combined successfully. The first will be the controlled and reversible attachment of the nanorods to a surface-masking substrate. The second will be addressing chemistry specifically to the unmasked nanorod surfaces. Additionally, high throughput reactions, and scalability of the reaction are important factors that should be desired.

2 RESULTS AND DISCUSSION

The reversible deposition and release of the nanorods is accomplished primarily through electrostatic interactions. The CTAB surfactant inherently on the nanorods has a native positive charge in aqueous solutions. Using metal oxide surfaces that have a slight negative charge, or polymer cation exchange resins, the rods are able to bind to the masking surface. The energy for the subsequent release of the nanorods will be provided by sonication.

It must be demonstrated that this process by itself will not damage the particles in any significant fashion. In Figure 1, rods are attached to a masking surface and imaged by SEM. XPS data shows the relative gold content on the masking substrate as increasing quantities of gold nanorods are incubated with the masking substrate.

The surface-masked nanorods can now have chemistry selectively performed only on the exposed surface of the nanorods. The grafting density of the ligand being exchanged onto the unmasked surfaces depends on the ratio of the nanorod diameter to the ligand’s van der Waals

diameter. For small organic molecules (< 16 carbons), and a 10nm diameter rod, approximately 78 to 89% of the nanorod surface is available for ligand exchange, based on simple geometric and trigonometric calculations.

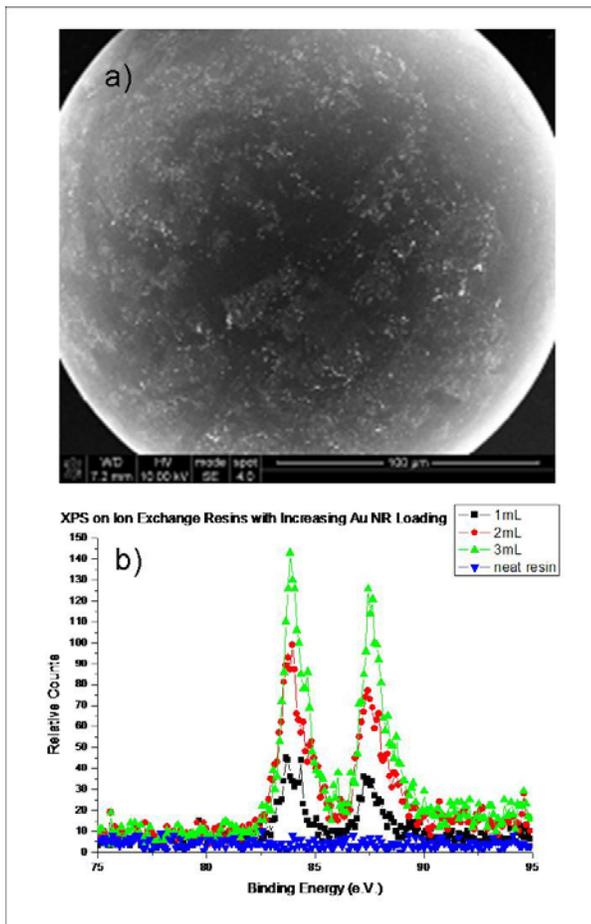


Figure 1: a) SEM of gold nanorods deposited onto a surface-masking colloid; b) XPS showing increasing Au absorption on surface as quantity of Au nanorods is increased.

Recent work by Ionita, et. al. using EPR experiments demonstrated that thiol molecules are not able to “walk” around laterally on the surface of a gold nanoparticle[27]. This suggests that once the thiol molecules are attached in a Janus fashion to the nanorods by the surface-masking technique, the nanorods will retain their asymmetric character of their new chemical coating.

A series of thiols with different chain lengths were examined for their grafting density on the surface-masked nanorods to explore this concept. Samples of the rods were then deposited onto fresh silicon wafers for XPS analysis. The atomic compositions were observed as well as the ratios of atoms in various bonding states such as C-C vs. C-S. Comparing these observations with predictions by the molecular formulae of the surfactants and the ligands exchanged, the relative stoichiometries of each on the surface of the nanorod could be estimated.

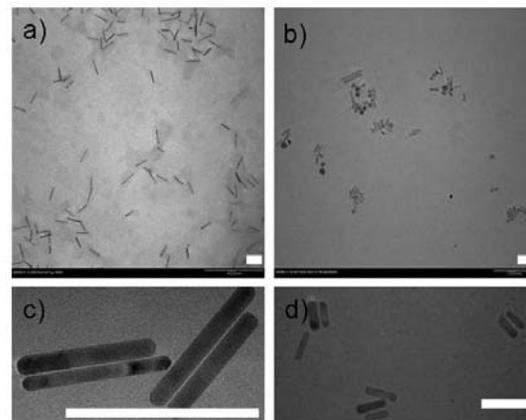


Figure 2. Equimolar rod concentrations of a) single nanorods and b) nanorod pairs, self-assembled from Janus nanorods made by surface masking methods; rod pairs from c) 3C and d) 16C linkers; scale bars=100nm.

The series of Janus nanorod samples was then allowed to self-assemble into rod pairs based on either hydrophobic-hydrophilic interactions between the rods and solvent, or chemical cross-linking between terminal functional groups on the ligands. The resulting structures were imaged by TEM. Examples of chemical cross-linked nanorod pairs are shown in Fig 2b, and are in equimolar concentration to single nanorods shown in Fig 2a. Rod pairs were typically found to be at least 30% of the structures observed.

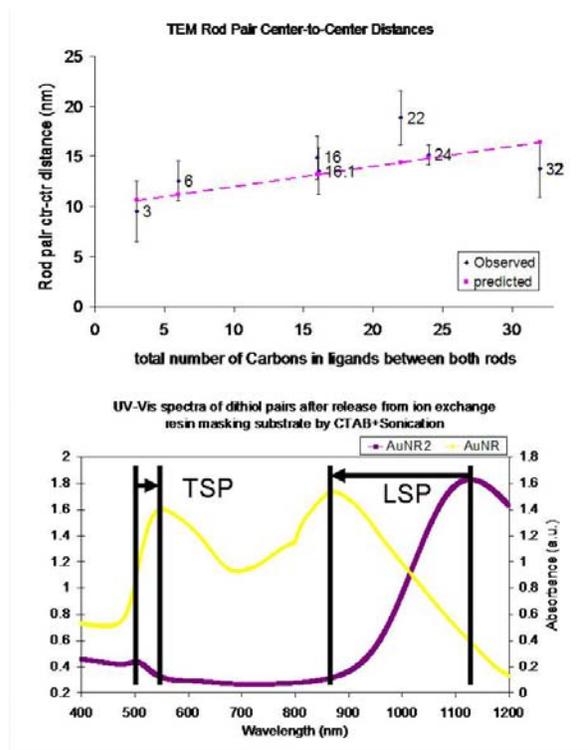


Figure 3. Spacing parameters between nanorods as a function of linker size.

The space between the nanorod pairs was then measured and plotted as a function of the size of the linkers in Figure 3. A prediction line is overlaid in Figure 3 representing the approximate length of the short-chain organic molecules in a purely trans conformation. The observed spacing results agreed well with the predicted values, demonstrating that a static series of various spacings between nanorods is achievable.

Also in Figure 3, the UV-Vis spectra of single rods is compared to the rod-pairs. The yield of rod-pairs released from the surface-masking substrate was found here to be about ten percent compared to the stock single nanorod solution. The peak around 520nm is from the transverse surface plasmon resonance (TSP), and is a function of the diameter of the gold in the structure. One would expect a red-shift in the TSP when the amount of gold in the structure doubles with the formation of rod pairs. The peak around 1100nm is from the longitudinal surface plasmon resonance (LSP), and is a function of the aspect ratio of the gold structure. Since higher aspect ratios lead to red-shifts in the LSP, one would expect a blue-shift in the LSP when a rod pair structure is formed, as the aspect ratio is now cut in half by the doubling of the width of the gold structure.

To expand the series of spacing parameters available, larger ligands were attached using the same EDC coupling chemistry. Amine-terminated molecules such as the coiled-coil peptides shown in Figure 4 were attached to a carboxyl-terminated thiol 90% Janus grafted nanorod. The 3-MPA had been attached to the nanorods in a Janus fashion with approximately 90% grafting density. The predicted size of the coiled-coil peptide is 2.45nm, and the observed coating thickness was 2.36nm. This experiment is a proof-of-concept that larger amine-containing molecules, such as biomolecules or polymers, can be successfully attached to gold nanorods in a Janus fashion for later use in self-limiting self-assembly of rod-pair structures. The use of amine-terminated thermo-responsive polymers could then be employed to create a dynamic array of rod pair spacing parameters.

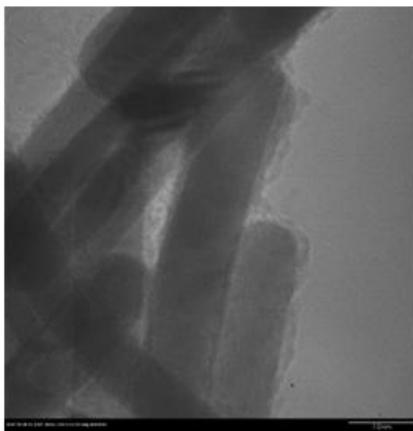


Figure 4. Coiled-coil peptide coating gold nanorods with a 90% Janus grafting density.

3 CONCLUSIONS

In conclusion, using surface masks and non-directional chemistry, Janus nanorod functionalization was achieved. The ligand size was found to provide a limited range of tunability of the extent of asymmetric functionalization. A limited range of static tunability of rod-spacings was also provided by varying the ligand size. Finally, using a model system of a coiled-coil peptide attached to gold nanorods in a Janus fashion, proof of concept was provided that large linkers, such as thermoresponsive polymers containing amine groups, could be attached to gold nanorods in a Janus fashion, enabling future work into dynamic rod-pair spacing parameters.

MATERIALS AND METHODS

3.1 Au NR synthesis:

Au nanorods were grown by a seed-mediated, bi-surfactant method[28]. All chemicals were ordered from Sigma Aldrich and used as received.

3.2 Janus Rods by Ion Exchange Resin Negative Masking:

Au NR were absorbed onto DOWEX 50W-X8 resin for 24 hrs. The clear supernate was removed, and the resin was washed 3X with milliQ water. Next, the thiol ligand was reacted with the exposed nanorods surface for 24 hrs, at a stoichiometry of 2:1 thiol:surface gold atoms. The resin was washed 2X, then 0.1M CTAB solution was added. The resulting suspension was sonicated for 10 minutes to release the rods from the resin.

3.3 Amine Coupling to Janus Nanorods:

3-mercaptopropionic acid (MPA) was added by negative masking to gold nanorods. Before the Janus MPA rods were released, typically, 267uL of 2.5nM rod solution was added to 0.100g of resin. After removing the supernate and washing with milliQ water, a 1:250 dilution of MPA in water was added to the resin and reacted for 24 hrs. After another wash, 300uL of a 50ng/uL peptide solution was added to the resin with a fresh solution of 100uL of 10mM N-hydroxysuccinimide and 100uL of 75mM N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC). After another milliQ water wash, the rods were released using CTAB and sonication.

3.4 Instrumentation:

A Phillips 200CM Lab6 TEM was used at 200kV acceleration voltage and 400 mesh carbon-coated copper grids (Ted Pella). A Cary 500 UV-Vis spectrophotometer was used with a 1mm path length quartz cuvette. SEM images were obtained using a Quanta SEM. A Surface Science XPS was used; detector angle was 45 degrees, and samples were observed in multiple locations and rotated on

the stage such that discrepancies arising from observation geometry could be averaged out. For image analysis, NIH Image J was used.

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