

## Characterization of Ligand Exchange in 2D Hybrid Molecule-nanoparticle Superlattices

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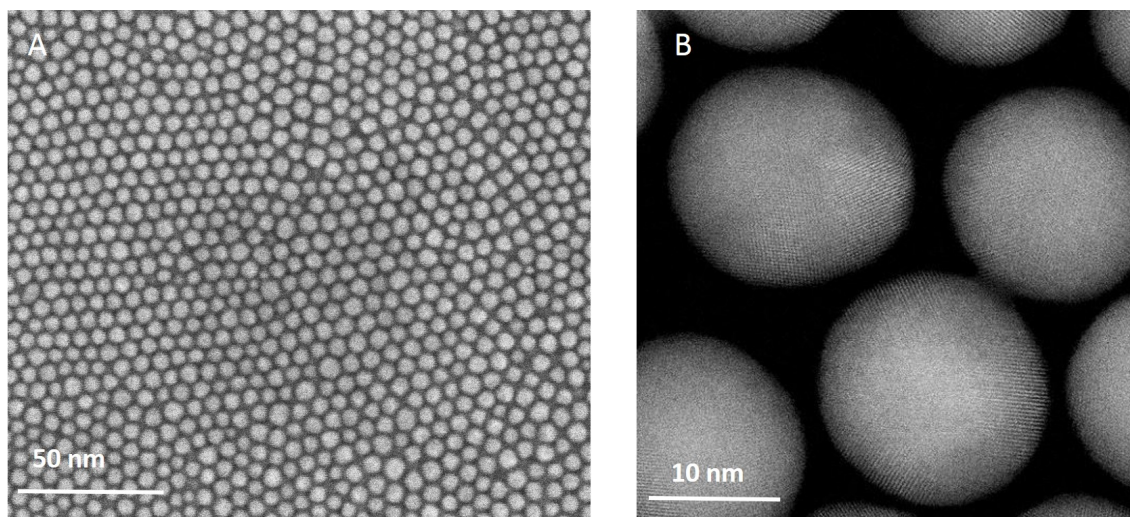
Hybrid molecule-nanoparticle composites have gained tremendous attention recently due to various applications ranging from electronics, plasmonics, and optoelectronics to biological systems and sensors [1,2]. Additionally, molecule-nanoparticle arrays with an improved conductance can have thermoelectric properties with potential applications for heat dissipation in electronic devices [3]. Often, the electrical behavior of these arrays is modified by replacing the original, saturated ligands with short molecules, this process decreases the interparticle distance and improves the coupling. However, it also reduces the volume of the array resulting in fractures and dislocations, which can negatively impact the electronic properties [4]. Alternatively, it is possible to replace the saturated ligands with conjugated species that are more conductive [5]. This approach can maintain the distance between nanoparticles, reducing the strain, while still improving the coupling between particles and the overall transport properties [6]. Here we study this ligand exchange process by using Scanning/Transmission Electron Microscope (S/TEM) imaging and Electron Energy Loss Spectroscopy (EELS) analysis to study the structure and the elemental composition distribution of a molecule-nanoparticle superlattice.

Following self-assembly of the nanoparticle array on top of a wafer surface, the 2D monolayer is transferred to silicon nitride TEM support films utilizing a microcontact printing method. Then, the ligand-exchange process, which replaces the initial nanoparticle ligands (oleylamine) with dithiolated ligands (terphenyl-dithiol), is performed by immersing the whole system into a 1 mM solution of terphenyl-dithiol overnight. More details on the ligand exchange process has been reported previously. [5] Scanning electron microscope (SEM) imaging was done with FEI Nova NanoSEM430 operated at 20kV. TEM imaging and EELS were performed with JEOL ARM-200F operated at 200kV.

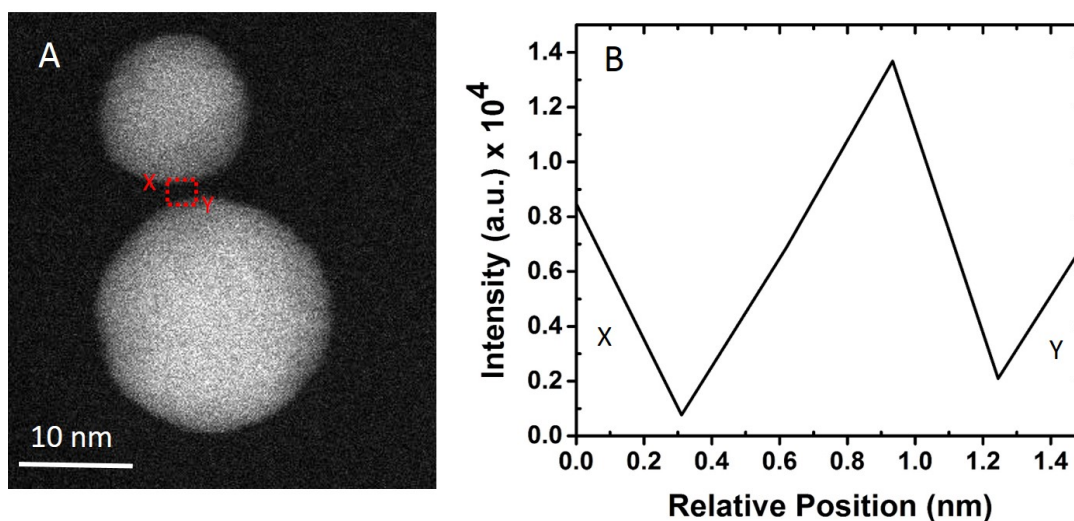
An SEM image of the hybrid array is shown in Figure 1A, which demonstrates that the nanoparticle array forms a well-ordered, hexagonal closed-pack array, and that the nanoparticles have an average size of  $13 \pm 0.5$  nm. Figure 1B is a high angle annular dark field (HAADF) image of the molecule-nanoparticle array, which reveals the crystallinity of each nanoparticle. To obtain a better understanding of the ligand exchange process, and its impact upon the transport properties, EELS spectrum images (SI) of the area between nanoparticles was acquired to show the elemental distribution across the interparticle region. Figure 2A represents the high angle annular dark field (HAADF) STEM image of the Au nanoparticles, which served as a survey image during EELS acquisition. Figure 2B shows the sulfur integrated EELS profile from the marked area with the dotted line in the survey image. EELS integrated profile reveals the presence and intensity of sulfur between the nanoparticles, which confirms the success of the ligand exchange process and provides insights into interdigitation and bonding. It is important to characterize the ligand exchange process as it influences the transport properties of the system and can impact the efficiency of the system when used as a thermoelectric material [7].

References:

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**Figure 1.** A) SEM image of Au nanoparticles demonstrating hexagonal closed pack array. B) HAADF STEM image of Au nanoparticles depicting the crystallinity nature of each nanoparticle.



**Figure 2.** A) HAADF STEM image of Au nanoparticles with a marked dotted line box as a survey image for EELS SI acquisition. B) Sulfur integrated EELS profile taken from the marked area in the HAADF image where the origin of the plot corresponds to the upper nanoparticle or the area marked as X in the ADF image.