Unraveling the True 3D Structure of Colloidal Assemblies by Liquid Cell Electron Tomography

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The colloidal bottom-up approach of nanoparticles self-assembling into ordered structures with tailored properties has recently attracted significant interest in various scientific fields. Therefore, their comprehensive structural and morphological characterization is essential, as the properties of these nanostructures are strongly correlated with their three-dimensional (3D) arrangement. Electron tomography is a common technique used for such nanoparticle characterization [1,2]. However, external forces that can affect the structure, such as the capillary forces caused by the common vacuum environment inside the microscope, are often neglected, resulting in misconnections between the obtained structure and the properties of the assemblies. As these materials are intended to be used in dispersion, our goal is to analyze the 3D arrangement of the assemblies in their native liquid environment. This innovative approach will allow us to establish a connection between the structure and properties of the assemblies under real working conditions.

In this contribution, we compare 3D reconstructions obtained in dry and liquid environments. We focus on two types of self-assemblies: gold NPs encapsulated in a polymeric shell and CTAB-coated gold nanorod bilayers. A commercial K-kit (Bio MA-TEK) liquid cell and a modified version with an increased angular tilt range (Tomochip [3]) were used depending on the assembly size. For larger assemblies, as the encapsulated gold NPs it is necessary to use larger window gap cells. However, this results in a larger background signal and limited tilt angles. On the other hand, smaller assemblies, such as the nanorods bilayers studied in this work, that can fit

into the Tomochips, can benefit from a larger tilt range and lower background signal due to their reduced window gap.

The challenges of liquid-phase electron tomography have been addressed. Firstly, we adapted a fast acquisition approach to minimize the time and, therefore, the beam exposure of the sample, reducing possible beam damage. Secondly, we performed an interative denoise and rigid registration methodology to overcome challenges including increased background signal, low signal-to-noise ratios (SNR) resulting from scattering effects, and lengthy acquisition times required for two-dimensional (2D) projection images. Finally, we incorporate a compressed shape sensing method during 3D reconstruction to mitigate missing wedge artifacts from the limited tilt range and improve the SNR in the tilt series [4].

A comparison between similar 3D investigations performed in the native liquid environment and in dry state revealed a general decrease in interparticle distances in the latter. This effect can be assigned to the compression effect of the capillary forces generated by the vacuum environment of the electron microscope during dry characterization. These observations emphasize the importance of conducting measurements under liquid-state conditions to accurately characterize NP self-assemblies and provide essential insights into the underlying physical and chemical mechanisms that govern these structures.

Graphic:

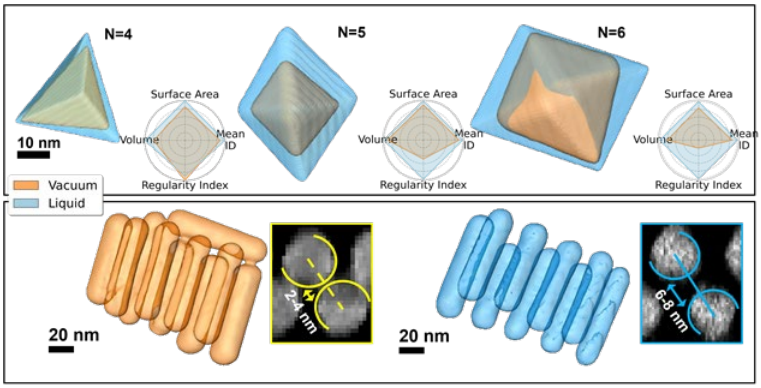

Figure 1. (top) Quantification analysis of the polyhedron formed by N=4, 5, and 6 on the gold NPs assemblies characterized in dry (orange) and liquid (blue) environments. (bottom) Interparticle measurements performed on the nanorod bilayers in dry (orange) and liquid (blue) environments.

Keywords:

Colloidal assembly, Tomography, Liquid TEM

Reference:

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