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Direct nanoscopic imaging of the hydrated nanoparticle–ligand interface

Taylor J. Woehl¹ & Damien Alloyeau²

1. Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, College Park, MD, USA

2. Laboratoire Matériaux et Phénomènes Quantiques, UMR 7162 CNRS/Université Paris Cité, Paris, France

e-mail: tjwoehl@umd.edu; damien.alloyeau@univ-paris-diderot.fr

Abstract.

The ligand–nanoparticle interface helps to control nanoparticle synthesis and functional properties, but determining its structure and dynamics is challenging owing to the lack of high-resolution direct imaging methods. Now, liquid-phase transmission electron microscopy has uncovered the micellar packing and surface adsorption dynamics of a surfactant ligand on gold nanorods.

The structure and dynamics of the interfaces between soft and hard materials are key to understanding the formation and properties of functionalized nanomaterials. Indeed, surface functionalization is a well-established strategy to control the size, shape, stability and self-assembly of colloidal nanoparticles. Surface ligands can also enable the reactivity of electrocatalysts to be tuned or the life cycle of nanomaterials to be modulated in biological environments to improve theragnostic (combining treatment with diagnostics) performance and to reduce toxicity^{1,2}. However, the study of the structure and spatial distribution of ligands at the nanoparticle surface in a liquid has been limited to ensemble measurements or atomistic calculations. Indeed, gaining experimental evidence of the atomic-scale mechanisms that rule the accessibility and physicochemical properties of nanoparticle surfaces remains challenging. Direct imaging of soft–hard material interfaces in liquids would enable scientists to take a fresh look at the growth mechanisms, chemical reactivity, degradability and interactions of nanoparticles in complex liquid environments.

Now, writing in *Nature Chemistry*, Bals and colleagues use high-resolution transmission electron microscopy (TEM) imaging in liquids to reveal that the widely used ligand cetyltrimethylammonium bromide (CTAB) adopts heterogeneous, shape anisotropic, and dynamic ligand layers on gold nanorods³. The research team used ultraclean graphene liquid cells to enable direct imaging of the structure of CTAB on gold nanorods in liquid pockets of water that were less than 100 nm in thickness (Fig. 1a). Besides minimizing surface contamination, the ultraclean graphene enables high spatial resolution and mitigates radiation damage to the organic ligands.

Direct imaging of the gold–ligand interface supports a micellar ligand conformation stabilized by CTAB–Ag complexes, which challenges our current understanding of the interfacial structure.

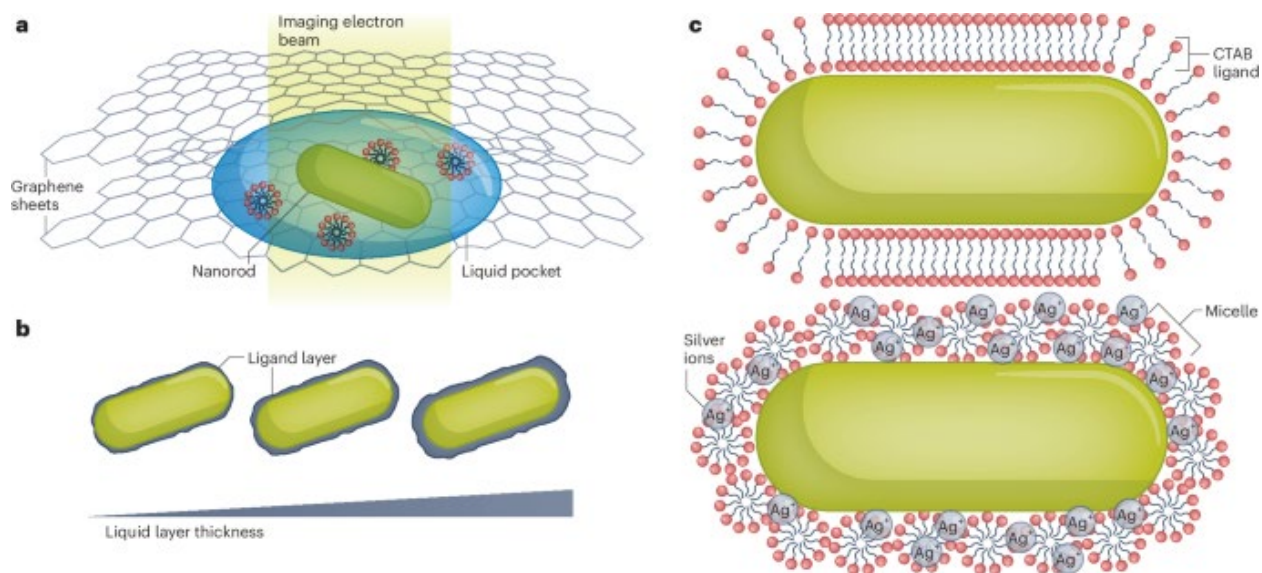


Fig. 1: Liquid-phase transmission electron microscopy imaging and graphene liquid cells reveal the structure and dynamics of the hydrated ligand–nanorod interface. **a**, Gold nanorods were encapsulated in liquid pockets (of water) less than 100 nm thick between two ultraclean graphene sheets and imaged with high-resolution transmission electron microscopy. **b**, Increasing the hydration by increasing the liquid thickness increased the thickness of the ligand layer (the ligand is cetyltrimethylammonium bromide, CTAB). **c**, The top schematic shows the widely reported bilayer model for the ligand layer structure and the bottom schematic shows the micellar model for the ligand layer, supported by the work of Bals and colleagues.

Previous work has used TEM to image ligands on dried nanoparticles, but it is well known that drying causes changes to ligand arrangement⁴. Critically, the present work reveals that the ligand layer structure and thickness changes as a function of the thickness of the liquid pocket (Fig. 1b), indicating that sufficient hydration is required to observe the native ligand conformation with direct imaging. The TEM imaging revealed that the thickness of the ligand layer is facet-dependent and that the ligand layers are patchy with nanometre-scale roughness. This roughness is consistent with prior molecular dynamics simulations and strongly suggests that CTAB is arranged in packed micellar structures at the gold surface as opposed to forming an interdigitated bilayer structure (Fig. 1c)⁵. Bals and colleagues analysed the hydrated ligand using energy-dispersive X-ray spectroscopy, which revealed the presence of silver ions, suggesting that CTAB–Ag complexes have an important role in stabilizing the ligand layer and mediating facet-dependent growth rates. Together, these observations contribute to a holistic understanding of the ligand–layer structure

and suggest potential mechanisms for how reactants are transported to the nanorod surface during synthesis.

Using liquid-phase TEM, Bals and colleagues also imaged the dynamics of the motion of CTAB micelles in the liquid and their interactions with the ligand layer on the gold nanorods. Previous work has shown that soluble macromolecules, such as polymers and vesicles^{6,7}, can be directly imaged in a solvent using liquid-phase TEM. Here the team observed the motion of a single CTAB micelle — discerned by its characteristic ellipsoid shape — and its deformation and fusion with the ligand layer on a gold nanorod. This observation emphasizes the dynamic nature of the water–ligand–gold interface, with important implications for understanding the mechanism of ligand-mediated facet growth during nanoparticle synthesis. Density functional theory simulations have suggested that the facet-selective nanoparticle growth is mediated by the surface mobility of ligands rather than by the facet–ligand binding affinity⁸. Future work using this approach has the potential to test this hypothesis directly and to settle major unsolved questions about how ligands mediate faceting during colloidal nanoparticle growth.

A key enabling technical advance in this study is the use of ultraclean graphene obtained by an improved polymer transfer method. The ultraclean graphene forms nearly contaminant-free liquid cells as indicated by electron and X-ray spectroscopic analysis. The high-energy TEM beam can impart substantial radiation damage to hydrated organic ligands and polymers⁹, but the graphene-encapsulated nanorods prepared by Bals and colleagues demonstrate unusual resistance to electron radiolysis, with ligand layers displaying no damage after receiving a total dose of hundreds to thousands of electrons per square ångström. Their resistance to radiation damage might be due to the ability of graphene to scavenge oxidizing radicals and its low secondary electron yield¹⁰.

One limitation of the study is the spatial resolution, which is restricted by the requirement for a relatively thick liquid layer of about 100 nm needed to fully hydrate the ligand layer. Direct imaging reveals the thickness and roughness of the ligand layer, but the internal structure of the potentially micellar ligand layer remains below the achievable spatial resolution. It therefore remains unclear how the micelles pack onto different nanoparticle facets and whether the micelles adopt the same conformation as in solution. The researchers hypothesize that water channels between micelles facilitate the transport of gold ions during nanorod growth, but the resolution required to confirm this remains unattainable with liquid-phase TEM at present.

The spatial resolution is further limited by radiation damage, image drift and thermal molecular motion. A distributed and correlative imaging method, including complementary cryogenic electron microscopy imaging, will probably be required to uncover the molecular structure of the ligand layer¹¹. Further improvements to liquid-phase TEM imaging resolution will require advances in hardware and software, such as low-dose imaging, more sensitive detectors, chromatic-aberration correction or diffractive imaging techniques like ptychography. Deep-learning-based image denoising could also help to improve the trade-off between resolution and beam damage. TEM images are two-dimensional projections of a three-dimensional structure, which makes it challenging to resolve the internal structure of the ligand layer; however, high-resolution electron tomography is expected to reveal additional molecular details.

There remains room to improve the spatial resolution, but this study of hydrated organic–inorganic interfaces by liquid-phase TEM opens up broad prospects for determining the role of ligands in crucial dynamical processes in materials science, such as nanoparticle growth and etching, catalytic reactions, nanoparticle–nanoparticle interactions, and the formation of protein coronas, to name but a few.

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