

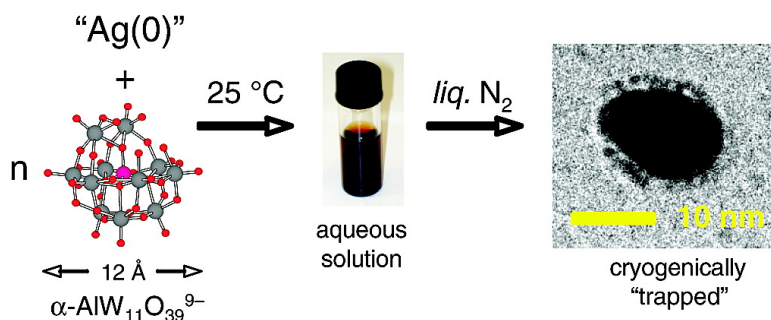
Communication

Direct Imaging of the Ligand Monolayer on an Anion-Protected Metal Nanoparticle through Cryogenic Trapping of its Solution-State Structure

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Direct Imaging of the Ligand Monolayer on an Anion-Protected Metal Nanoparticle through Cryogenic Trapping of its Solution-State Structure

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According to the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, anions stabilize metal(0) nanoparticles (NPs) in high-dielectric constant media by binding to the metal(0) surface.¹ Until now, however, anion monolayers have never been directly observed on the surfaces of metal(0) NPs in solutions of these electrostatically stabilized systems.

Our interest in this is a response to the rapidly growing list of catalytically active nanostructures obtained when polyoxometalates (POMs) are used as the protecting anion.² While the basis for their unique properties is not yet clear, it likely derives from the redox chemistry of the POMs, in combination with the ability of the metal-oxide clusters—like oxide supports in heterogeneous catalysis^{2k}—to modify the activities of metal(0) particles. To define the structure/reactivity relationships necessary for more rational design of these functional nanoassemblies, detailed structural information is needed. However, despite rapid advances in synthesis^{2a–f} and application,^{2a,c–h,l} individual POMs have yet to be directly observed on the surface of a metal(0) NP.

By contrast, organized arrays of individual POMs³ on graphite⁴ and metal surfaces⁵ have been investigated by scanning tunneling microscopy^{4,5} (STM), atomic force microscopy (AFM),^{6,5b} and X-ray specular reflectivity.^{5b} None of these techniques, however, is readily applicable to colloidal solutions.⁷ For this reason, structural studies of POM-protected metal(0) particles have relied on transmission electron microscopy (TEM) and high-resolution (HRTEM) images of carefully dried solutions.

In these images, the metal NPs are typically embedded within a poorly defined “sea”^{2a} of aggregated POM salts.⁸ We therefore speculated that as solutions are dried on coated Cu grids for TEM analysis, surface tension from the evaporating water might “shear” the highly solvated POM salts from the metal(0) particles.

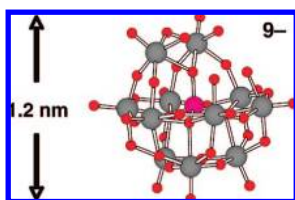


Figure 1. Ball and stick representation of $\alpha\text{-AlW}_{11}\text{O}_{39}^{9-}$ (**1**). The Al^{3+} ion at the center of the C_{3v} -symmetry cluster is in pink, W(V) atoms are in gray, and the bridging and terminal oxide ligands are in red.

To investigate this, we deployed a 1.2-nm sized POM anion as a protecting ligand, $\alpha\text{-AlW}_{11}\text{O}_{39}^{9-}$ (**1**; Figure 1). This cluster anion features 11 W atoms ($Z = 183$) for effective imaging by electron microscopy and a high negative charge for enhanced binding to a

prototypical Ag(0) NP. We then used cryogenic methods to rapidly “trap” the **1**-protected Ag(0) NPs in water “glass” at liquid- N_2 temperatures. We herein report cryoscopic-TEM (cryo-TEM) images of these samples that, for the first time, reveal the *intact solution-state structure* of an anion-protected metal(0) nanoparticle.

The POM-protected NPs were prepared⁹ by adding NaBH_4 to a 1:1 mixture of aqueous AgNO_3 and $\alpha\text{-K}_9\text{AlW}_{11}\text{O}_{39}$ (the K^+ salt of **1**),¹⁰ specifically chosen for its stability at borate-buffer pH values of 8 to 9^{10c} (for synthesis, see the Supporting Information). Samples for TEM and HRTEM (Figure 2) were prepared by placing several microliters of the solution on a carbon-coated Cu grid and allowing it to dry at room temperature. Energy dispersive spectroscopy (EDS) was used to identify $\text{K}_9\text{1}$ and Ag(0) (arrows in Figure 2B). Electron diffraction showed the Ag(0) to be polycrystalline. *No organized arrangements of 1* are observed on or near Ag(0).

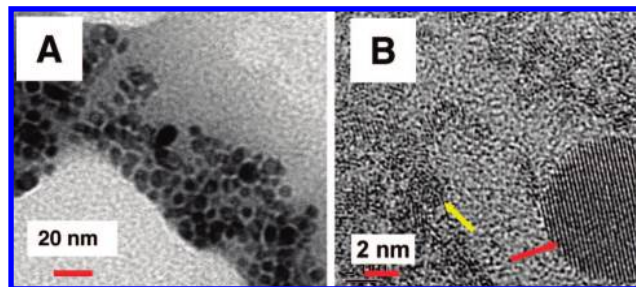


Figure 2. Effects of drying and characterization of **1**-protected Ag(0) NPs. (A) Dry-TEM image of Ag(0) (dark) embedded in a “sea” of $\text{K}_9\text{1}$ (gray), on a white grid. (B) HRTEM image of the dry sample showing **1** (yellow arrow) and a Ag(0) particle (red arrow).

Prior to obtaining cryo-TEM images, the same NP solution was placed on a lacey-carbon coated Cu grid in a controlled humidity chamber and rapidly plunged into liquid- N_2 cooled ethane. Unlike when dried (Figure 2A), the particles are now dispersed throughout the vitreous matrix (Figure 3A).

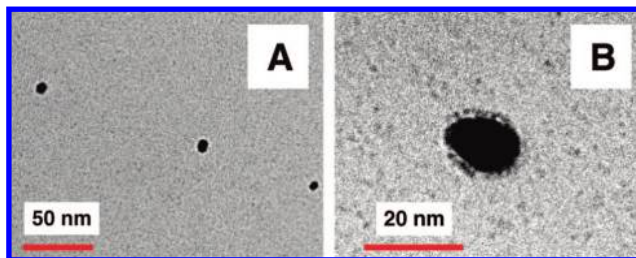


Figure 3. Cryo-TEM images of **1**-protected Ag(0) particles “trapped” in cryogenically frozen water–glass. (A) Individual **1**-protected NPs with no evidence of aggregation. (B) A single Ag(0) NP at 150 000 \times magnification, protected by a monolayer of **1**. Freely solvated POMs appear as dark “dots” in the background of panel B.

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At higher magnification (Figure 3B), an apparent self-assembled monolayer (SAM) of individual cluster anions, **1** (1.6 ± 0.2 nm in thickness in the image), is seen around the periphery of a Ag(0) particle. This does not imply that molecules of **1** form a single “ring” around the Ag(0) particle. Rather, molecules of **1** on the upper and lower surfaces of the metal particle are obscured by Ag(0) (see additional images in Figure S6). Additional data (see below) confirmed that the dark “dots” randomly distributed throughout the remainder of the visual field in Figure 3B are freely solvated POM anions.

The Raman spectrum of pure K₉I (solid) and the surface-enhanced Raman (SER) spectrum of the **1**-protected Ag(0) NP solution are compared in Figure 4.

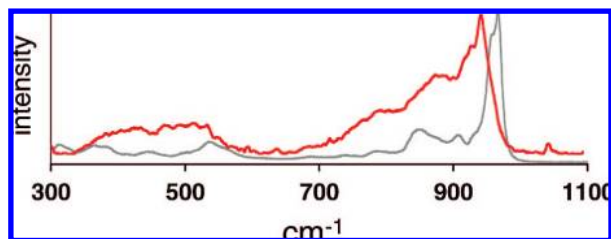


Figure 4. Raman spectrum of solid K₉I (gray line) and SER spectrum of an aqueous solution of **1**-protected Ag(0) NPs (red line). Due to low solubility (~ 2 g/100 mL), no discernible features are observed in Raman spectra of saturated solutions of pure K₉I.

Based on Figure 3B, the SER spectrum provided here can, more confidently than ever before, be assigned to scattering from the POM anions directly bound to a metal NP surface.¹¹ Comparison of Raman, SER, and FTIR spectra (Figure S1) provides additional evidence that the POMs bound to Ag(0) are indeed intact clusters of **1**. The SER bands are red-shifted and selectively enhanced. Additional SERS studies, involving Au(0) and Ag(0), and other POM structures, may enable us to determine the orientation of **1** relative to the M(0) NP surfaces (for more discussion, see the Supporting Information).¹²

A second line of evidence that the ordered features on the surface of Ag(0) in Figure 3B are due to **1** was obtained using citrate-protected Ag(0). Tong¹³ reacted these with α -PW₁₁O₃₉⁷⁻ (**2**) and provided UV-vis and SERS data consistent with the displacement of citrate by **2**. We now present cryo-TEM images of the actual solution-state structures involved.

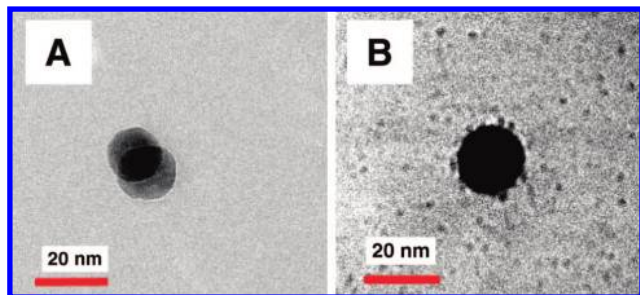


Figure 5. Cryo-TEM images of a solution of citrate-protected Ag(0) particles, before (A) and after (B) addition of α -PW₁₁O₃₉ (K₇2).¹³

Before the addition of **2** (Figure 5A), the surfaces of Ag(0) are featureless, as the organic ligands are not observed.¹⁴ Several days after the addition of **2**, POM anions are seen on the surface of Ag(0) (Figure 5B) and randomly distributed about the visual field. By analogy, this provides additional evidence that the objects on the surface of Ag(0) in Figure 3B, and randomly distributed about the visual field in that image, are individual molecules of **1**. It appears

that fewer POM anions are associated with Ag(0) in Figure 5B, than in Figure 3B, where no citrate was present. This may suggest that not all the citrate is displaced.¹⁵ *To our knowledge, these are the first direct images of anion exchange (and/or competitive association) on a metal NP in solution.*¹⁶

In summary, a representative heteropolytungstate anion and cryogenic sample preparation were combined to obtain the first reported TEM images of a self-assembled monolayer (SAM) of anions on a colloidal metal(0) nanoparticle. The herein demonstrated use of cryo-TEM¹⁷ to obtain these “solution-state” images is an important step forward in efforts to better understand how electric double layers stabilize metal(0) colloids,^{1,18} as well as to establish structure/reactivity relationships for POM-protected metal(0) nanoparticles,^{2,13} a large and growing class of catalytically active nanostructures.

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Supporting Information Available: Synthesis, analytical data, additional images, and discussion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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