Direct imaging of lattice planes in atomically precise noble metal cluster crystals using a conventional transmission electron microscope†

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Imaging finer structural details of atomically precise noble metal cluster crystals has been difficult with electron microscopy, owing to their extreme beam sensitivity. Here we present a simple method whereby lattice planes in single crystals of nanoclusters can be observed using a conventional transmission electron microscope, enabling further expansion of cluster research.

Atomically precise noble metal clusters (APNMCs) belong to an emerging class of materials with unusual properties.1–3 Over one hundred nanocluster molecules have been understood with single crystal diffraction leading to their atomic structures.4–11 Consequently, the application of quantum chemical simulations has allowed us to unravel their spectroscopic properties.12 A large number of other clusters are known today with their compositions being determined by advanced mass spectrometry.13 While spectroscopy,14,15 chemistry,16–18 catalysis,19,20 and applications21,22 of all of them are intensely pursued, absence of precise structures makes a thorough understanding of their properties difficult.

Single crystal diffraction, the preeminent tool for structural elucidation, requires high quality single crystals. While micro-crystal electron diffraction and single particle reconstruction coupled with computer modelling have revealed the structures of many molecules including clusters,23–26 they are still not commonly used in cluster science, excepting the report on Au68.24 The traditional transmission electron microscope (TEM), available in most of the research institutions, is generally not adequate for routine characterization of APNMCs and their crystals, in view of the extreme beam sensitivity of fragile clusters, which transforms them to nanoparticles instantaneously upon electron beam exposure.27 A method to observe clusters under such conditions for precise determination of their lattice parameters would facilitate the growth of cluster science.

In this communication, we present a simple way to image cluster crystals using a traditional transmission electron microscope where beam induced damage is minimized. Through this methodology, we have successfully imaged various lattice planes in three APNMCs

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whose structure has been solved previously using single crystal X-ray
diffraction, namely – cubic (C) \([\text{Ag}_{29} (\text{BDT})_{12} (\text{TPP})_4]^{-}\) (ref. 7), it’s
trigonal (T) polymorph\(^\text{28}\), and \([\text{Ag}_{25} (\text{DMBT})_{18}]^{-}\) (ref. 9), where BDT,
TPP, and DMBT are 1,3-benzenedithiol, triphenylphosphine, and
2,4-dimethylbenzenethiol, respectively. The method is schematically
illustrated in Fig. 1 with \([\text{Ag}_{29} (\text{BDT})_{12} (\text{TPP})_4]^{-}\) (abbreviated as
\(\text{Ag}_{29} \text{C}\), C refers to cubic polymorph) as a model. We start with
\(\text{Ag}_{29} \text{C}\) single crystals of edge length varying from around 0.1 \(\mu\text{m}\) to
80 \(\mu\text{m}\), which are routinely crystallized in the laboratory by solvent
evaporation (see the experimental section in ESI\(^\dagger\) for further
details). All the clusters discussed here were fully characterized
using UV-Vis spectroscopy, and ESI MS (Fig. S1–S3, ESI\(^\dagger\)). Results
were in agreement with the reported data. The single crystal
morphology was as per literature and the structural parameters
were checked with SCXRD (Tables S2 and S3, ESI\(^\dagger\)). About 100 such
single crystals weighing around 0.5 mg were carefully transferred
from a glass slide used for crystal growth and were ground
thoroughly with a mortar and pestle, to make a powder composed
of 0.02 \(\mu\text{m}\) to 0.7 \(\mu\text{m}\) particles (see ESI\(^\dagger\) Fig. S4, for further details
and an optical micrograph of the powder). This cluster crystal
powder was suspended in methanol, in which the cluster was
insoluble, and was sonicated for 10 s. About 10 \(\mu\text{l}\) of this suspension
was drop-casted on a carbon coated 300 mesh copper grid. After
drying for 2 h, the sample was imaged under 100 kV electron beam
using a JEOL 3010 TEM, with a LaB\(_6\) filament, having 1.2 Å point-to-
point resolution. Cluster crystals were noticed immediately under
the electron beam while continuous exposure of more than 60 s
damages the crystals. This time may be used to optimize parameters
for better imaging. By moving the beam to an adjacent crystal, it was
possible to collect more than 10 images without beam induced
damage.

While examining such crystallites, we observe the various
lattice structures of \(\text{Ag}_{29} \text{C}\), as shown in Fig. 2(A–C). These
correspond to (110), (111), and (200) planes with lattice con-
stants of 2.42 nm, 1.97 nm and 1.71 nm, respectively. Due to
the cubic symmetry of \(\text{Ag}_{29} \text{C}\), these may also correspond to
equivalent planes in other directions (ESI\(^\dagger\) Table S4). Several
other adjacent \(\text{Ag}_{29} \text{C}\) crystallites on the grid are also presented
in the ESI\(^\dagger\) (Fig. S5). These lattice parameters match well with
the crystallographic data reported by AbdulHalim, et al.\(^8\) We
compare the TEM images with the crystal structures in
Fig. 2(D–F).

Once beam induced damage sets in, nanoclusters coalesce
to form larger nanoparticles. To understand the optimum time
during which measurements can be done, before beam
induced damages occur, we exposed the sample to the electron
beam for an extended period of time. As mentioned previously,
images can be collected for about 60 s from one crystallite,
without noticeable beam induced damage, during which approximately 10 images could be collected for each area. However, beam induced damages set in the course of time and the lattice transforms continuously after 60 s. The systematic transformation is captured in ESI† (Fig. S6 and S8), and two of those images are presented in Fig. 3. As observed, beyond 60 s (Fig. S8, ESI†), the sample undergoes permanent changes and lattice planes are no more visible. Particles up to approximately 3.8 nm diameter were observed till 56 s (Fig. S7, ESI†). Bigger particles (410 nm) were formed up on exposure beyond 2 min (Fig. S9, ESI†). It is to be noted that the direction of growth of these particles is not yet clear and is beyond the scope of experiments discussed here. In this methodology, by reducing the accelerating voltage, we have managed to delay the damages happening to APNMCs. This creates a time window to image lattice planes, before beam induced damages become predominant. We believe that the success of this imaging methodology is also related to the thickness of the sample as well as the relative orientation of crystals on the TEM grid, with enhanced thermal contact with the grid. Therefore, removing those crystallites without proper contact by gentle tapping or inverting the grid, after drying the sample on the grid, can enhance the success of imaging. Improving thermal contact may be possible with grids such as ultra thin carbon film, microgrid, and those with supports such as molybdenum mesh and gold mesh. Thicker crystallites were opaque to electron beam (Fig. S10, ESI†). Note that images were collected at room temperature. When an acceleration potential greater than 100 kV was used, the crystallites got damaged sooner and the very first images showed signs of particle formation. With 100 kV voltage, all our attempts were successful in obtaining high quality images. The conditions used for imaging are presented as Table S1 in ESI†.

In order to ensure that this methodology is applicable for other crystals, we examined trigonal single crystals of \([\text{Ag}_{29}(\text{BDT})_{12}(\text{TPP})_{4}]^{-}\) cluster (abbreviated as \(\text{Ag}_{29}\)T), which was a polymorph reported by our group.28 The images correlated exactly to the single crystal structure of crystal of \(\text{Ag}_{29}\)T, as seen in Fig. 4(A–D). The lattice planes observed were (011) and (012) with interplanar spacings of 2.12 nm and 1.68 nm, respectively. Additional images from adjacent \(\text{Ag}_{29}\)T crystallites

![Image](http://example.com/image.png)

**Fig. 3** (A) TEM image of an \(\text{Ag}_{29}\)C crystallite imaged without any noticeable damages. (B) Nanoparticle growth that happened over the region, after an exposure of nearly 56 s.

![Image](http://example.com/image.png)

**Fig. 4** TEM images of various crystallites representing different lattice planes of \(\text{Ag}_{29}\)T and \(\text{Ag}_{25}\). (A and C) represent TEM images of \(\text{Ag}_{29}\)T crystallites and (B and D) are representative images of corresponding planes in a 2 × 2 × 2 unit cell of the same crystal. Inset in A represents the expanded image of the crystallite. Insets (i and ii) show an expanded area of the crystallite and beam induced damage from another area after nearly 60 s of exposure. (E and G) represent TEM images from \(\text{Ag}_{25}\) crystallites and (F and H) are representative images of corresponding planes in a 3 × 3 × 3 unit cell. Insets in (E and G) show expanded views of the crystallites. The scale bars in all insets are 25 nm, except for (iii), where it is 10 nm.
and beam induced damages on one of them are presented in ESL† as Fig. S11 and S12, respectively. Ag$_{29}$T shows beam induced damage after 60 s of beam exposure (Fig. C(ii)).

Furthermore, we observed single crystals of [Ag$_{25}$DMBT)$_{18}$]$-$ (abbreviated as Ag$_{25}$) as well. The lattice spacings observed in these images were consistent with the expected distances in Ag$_{25}$ crystallites, which are triclinic, as depicted in Fig. 4(E–H). Additional images of the Ag$_{25}$ crystallites are presented as Fig. S13 (ESI†). Ag$_{25}$ also shows beam induced damage, as shown in the inset of Fig. 4G. As in the case of Ag$_{25}$C, the planes may correspond to equivalent ones in other directions, due to the trigonal and triclinic symmetries of Ag$_{25}$T and Ag$_{25}$, respectively (Tables S5–S6, ESI†).

We had also performed this experiment by using water as a solvent to disperse the cluster crystal powder. Both Ag$_{25}$C and Ag$_{29}$T are insoluble in water. While using water as a solvent, the grid was dried for an extended period of 6 h before imaging. Similar results were obtained and are presented as Fig. S14 in the ESL†. Detailed analysis followed for obtaining the lattice spacing in the crystallites, is described in ESL† (Tables S4–S6 and Fig. S15).

In conclusion, we show that a simple methodology can make cluster crystals observable with regular transmission electron microscopes available in most research laboratories. Generally, APNMCs grow in size and their structure gets transformed upon exposure to electron beam. We demonstrate that with careful sample preparation and optimized imaging parameters, finer structural details of nanocluster single crystals can be obtained, without causing damages, using electron microscope models that are employed for routine imaging. This will ensure more details of such fragile materials to be examined in many labs across the world. If this methodology were to be applied with improved instrumentation like low-dose imaging, cryo-cooling, etc., we anticipate that even the ligands will be observable. Consequently, we hope that crystal structures of unknown clusters will be determined more routinely.

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Conflicts of interest

There are no conflicts to declare.

References