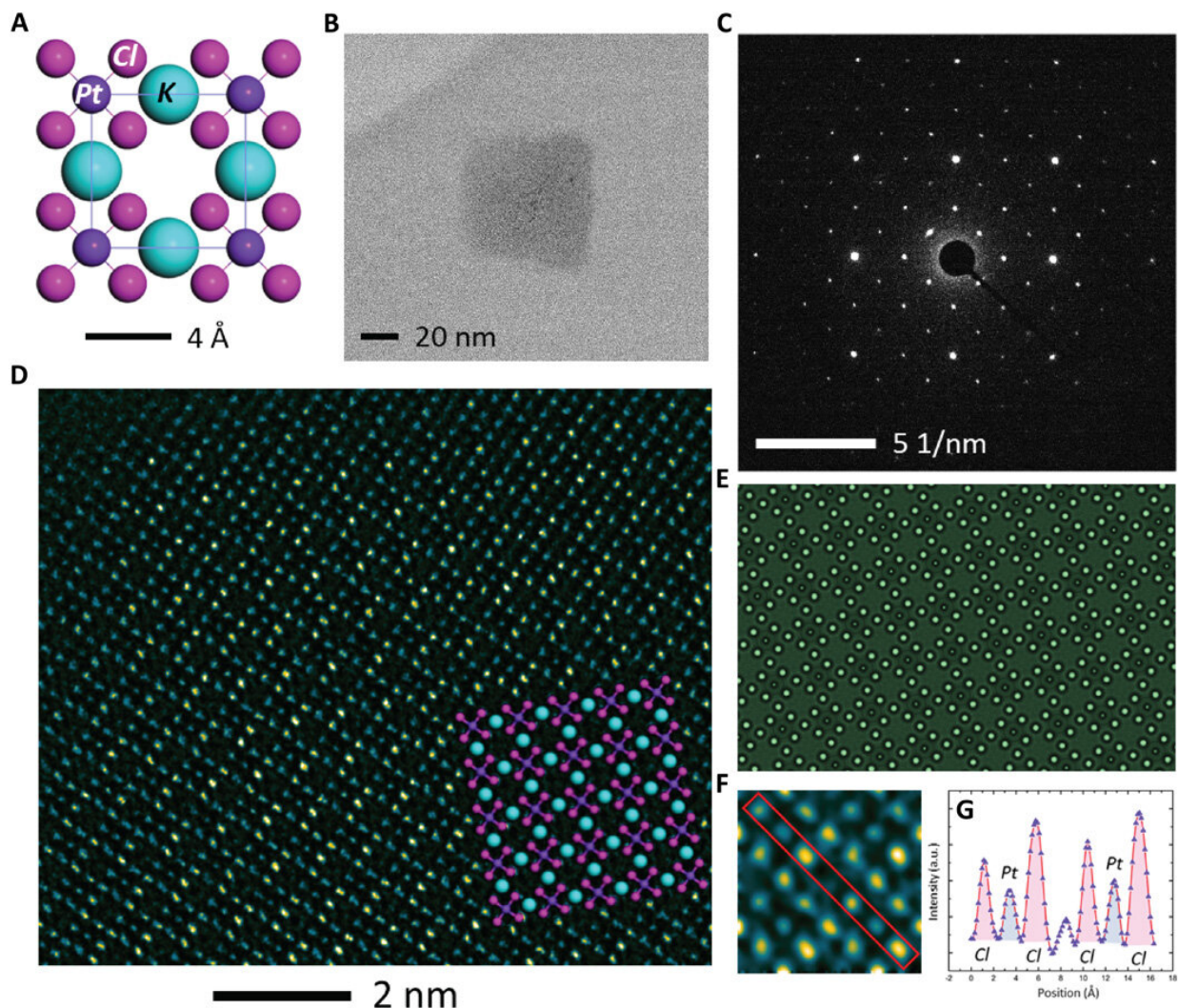


Investigating the dynamics of nanoparticle formation from a precursor at atomic resolution

January 29 2019, by Thamarasee Jeewandara



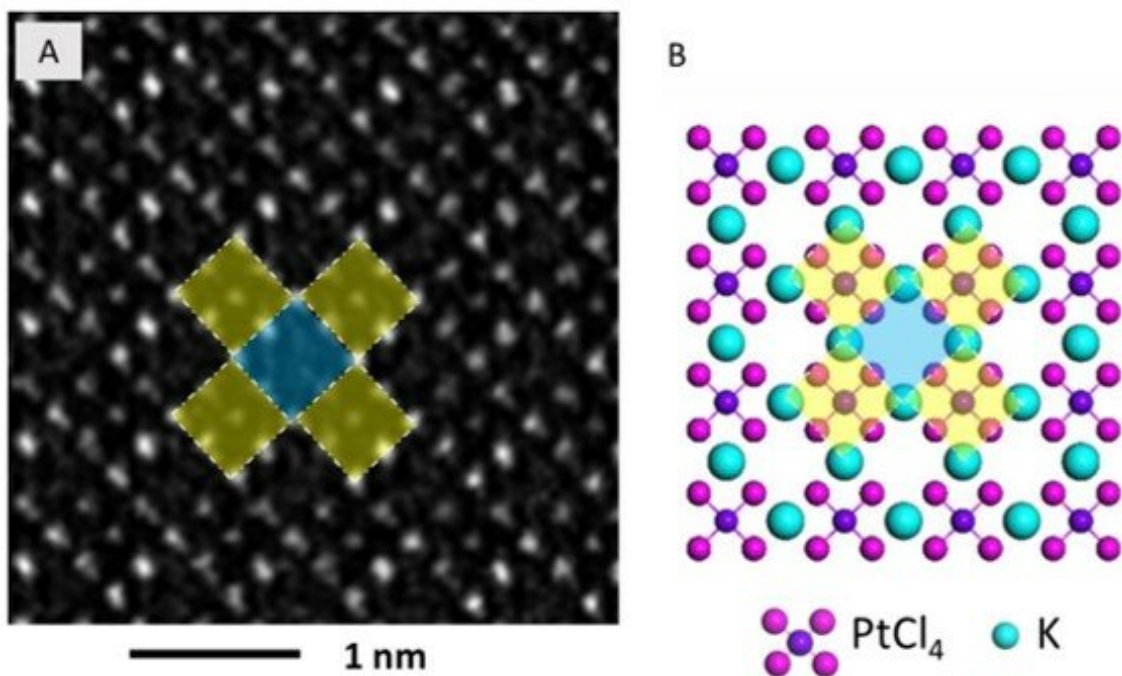
Low-dose atomic resolution imaging of K_2PtCl_4 . (A) The atomic model of the K_2PtCl_4 unit cell, with K in cyan, Pt in purple, and Cl in pink. (B) Bright-field

TEM image of a large K_2PtCl_4 crystallite. (C) Diffraction pattern of the K_2PtCl_4 crystallite in (B) after it is tilted along the (001) zone axis. (D) Atomic resolution low-dose TEM image of K_2PtCl_4 . Dose fractionation was done using an electron dose of $1 \text{ e}/\text{\AA}^2\cdot\text{s}$, with 0.1 s for each image. Sixty-four images were acquired, aligned, and averaged. The electron dose then becomes $6.4 \text{ e}/\text{\AA}^2$. The atomic model is overlaid in the inset. (E) Simulated HREM image of K_2PtCl_4 with a thickness of 12.3 nm. (F) A zoomed-in image of K_2PtCl_4 from a sub-area in (D), and the intensity line profile in arbitrary units (a.u.) from the red box, is shown in (G), where the intensity from Pt atoms is located between two Cl atoms. Credit: Science Advances, doi: 10.1126/sciadv.aau9590.

A key to materials synthesis is the ability to control the process of [reduction kinetics](#) and [nucleation](#) (phase transition) in [materials](#). Understanding the reduction dynamics during the initial stage of material synthesis is limited due to the difficulty of investigating chemical reactions at the atomic scale. This is mainly because the chemical precursors used to synthesize materials can degrade when exposed to [electron beams](#) that are typically used to image compounds at atomic resolution.

In a recent study, now published in *Science Advances*, interdisciplinary materials scientists Wenpei Gao and co-workers in the USA and China, studied the reaction kinetics of a solid-state platinum (Pt) precursor compound. In the study, they used an aberration-corrected [transmission electron microscope](#) (TEM) combined with low-dose electrons and in situ imaging. The scientists imaged the beam-sensitive Pt precursor; potassium tetrachloroplatinate (II) (K_2PtCl_4), at the atomic resolution to determine the individual atoms (K, Pt and Cl) involved in the synthesis of platinum nanoclusters. Gao et al. captured the material's transformation to Pt nanoclusters in [real time](#) to show three-stage reaction kinetics, including (1) breaking of the ionic bond, (2) formation of PtCl_2 and (3) reduction of the divalent Pt to Pt metal nanoclusters.

In the new method, the scientists combined techniques to understand the transformation of chemicals at the atomic scale in real time without damaging the substrates and provided a new platform to study reaction kinetics. Gao et al. captured, identified and revealed the dynamics at different stages of decomposition, reduction and nucleation of the material. The work allowed them to understand the transformation kinetics of platinum from precursor to nanocluster as a promising avenue to study [atomic-scale](#) reaction dynamics.



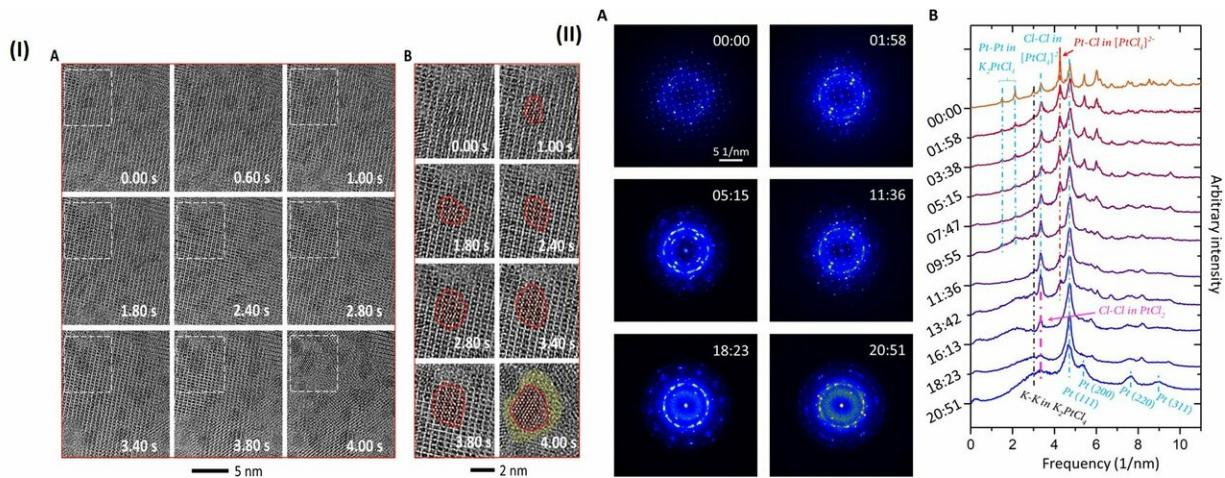
Zoomed-in image and atomic model of K_2PtCl_4 . (A) and (B) are the corresponding TEM image and atomic structure model of K_2PtCl_4 . The squares colored in yellow have one Pt atom in the center, with Cl atoms on the edge centers and K atoms on the corners. The square in blue does not have a Pt atom in the center. Credit: Science Advances, doi: 10.1126/sciadv.aau9590

In colloid and synthetic chemistry, materials scientists aim [to control the shape and size of nanoparticles](#) to achieve the desired properties of electronic, optic and [catalytic](#) materials. Nanocluster nucleation is a key process of growth kinetics in the solid state of materials synthesis. Manipulating the kinetics has allowed the synthesis of a group of [nanoparticles](#) shaped as [nanorods](#), [nanocubes](#), [octahedra](#), [octopod-shaped nanoparticles](#), [icosahedra](#) and other surface features.

While nucleation is the initial step in materials synthesis, it is difficult to control nucleation kinetics without [understanding how atoms interact](#). Platinum nanoparticles are usually synthesized in a [liquid-phase reaction](#) with C-H or Cl⁻ as a precursor. During growth in such a system, the precursor is reduced by the reducing agent to form metal monomers with [atomic arrangements](#) based on metal-metal interactions. However, a microscopic mechanism that details the intermediate reaction steps is yet unavailable.

As an alternative to materials synthesis in the liquid phase, [nanostructures](#) can also be grown in the solid phase. Studying the reduction process in the solid state can decipher materials transformation for fine control of [materials synthesis](#). Understanding the kinetics of materials transformation from precursors to nanostructures [at the atomic scale based on ionic bond breaking](#) is therefore of considerable significance.

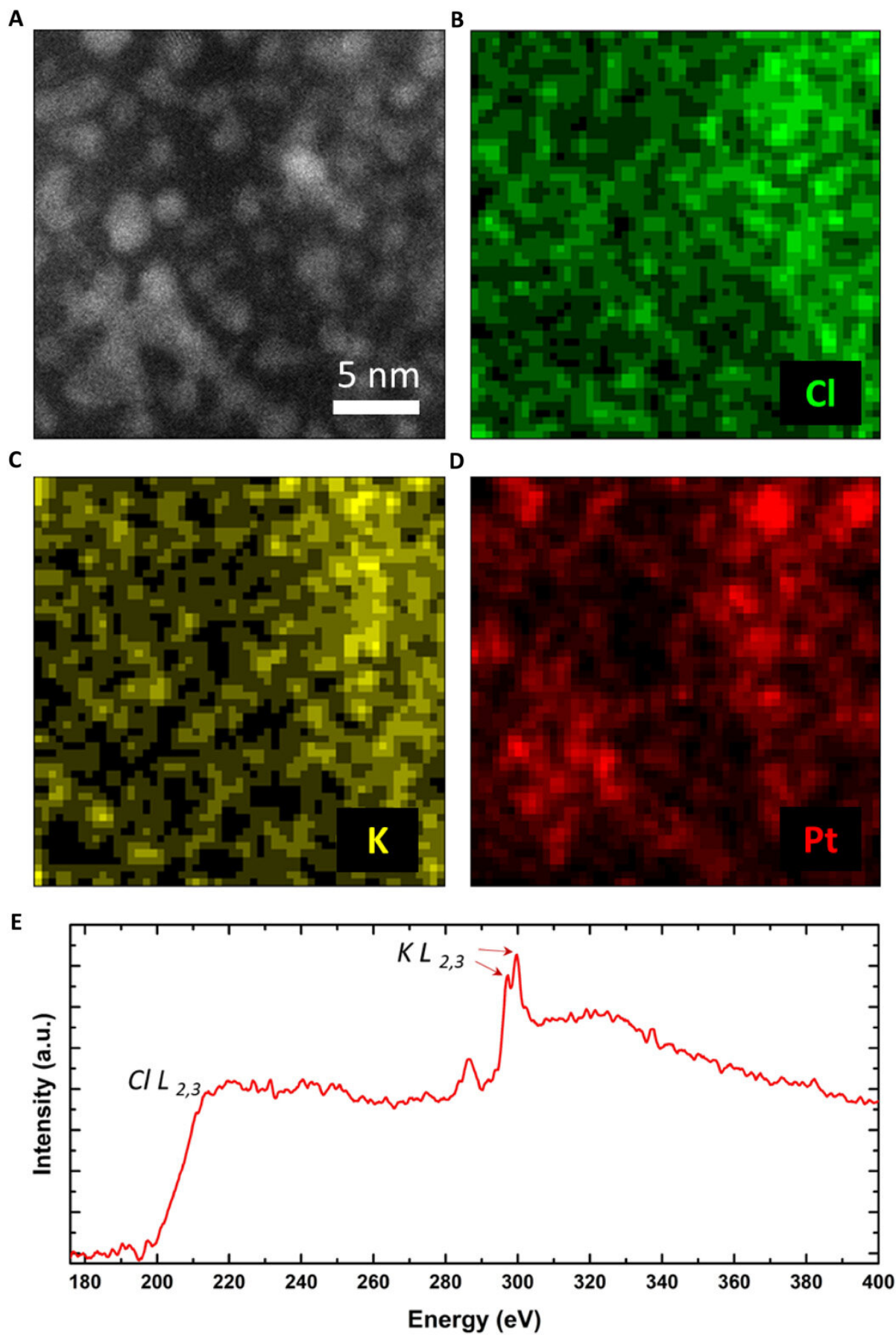
The scientists opted to study the nucleation process in the solid phase without the liquid environment using characterization tools of X-ray nanodiffraction and TEM, which offered ultra-[high resolution](#). The method resolved the evolving structures in [real and reciprocal space](#), although the sensitivity of most chemical precursors to the [electron beam](#) due to photo illumination had previously made it nearly impossible to observe the initial atomic structure of the precursor.



(I) Evolution of K_2PtCl_4 into Pt nanoparticles. (A) Sequential TEM images show the evolution of K_2PtCl_4 into Pt nanoparticles. A Pt nanoparticle nucleation process is shown in the zoomed-in images in (B), from the marked sub-area within the white dashed boxes in (A). The red contour lines indicate the edge of the newly formed Pt clusters. The region in yellow highlights the void area without lattice after the formation of a Pt cluster. (II) Sequential radial distribution function (RDF) during the transformation. (A) Time series diffraction pattern using FFT from sequential low-dose images. (B) RDF derived from the sequential diffraction pattern. Credit: Science Advances, doi: 10.1126/sciadv.aau9590

For TEM observation, K_2PtCl_4 was first dissolved in deionized water in preparation to image its crystal structure. In the bright field TEM image, the crystallite was 50 nm x 60 nm in size. Gao et al. weakened the electron beam dose to the [angstrom scale](#) for less than $1 \text{ e}/\text{Å}^2 \cdot \text{s}$ to limit beam-induced sample reduction during the process of imaging. The scientists conducted high-resolution electron microscopy (HREM) at 300,000 x magnification to obtain 64 images from the same area. By averaging the images, the atomic columns were clearly resolved in the study.

The high-resolution TEM image showed periodic lattice squares with an atom (yellow) surrounding those without bright atomic contrast (blue) in the center. Gao et al. compared the atomic resolution images with the [existing atomic structure](#) of K_2PtCl_4 to identify each individual element. The scientists identified the atoms in the corners as potassium (K), atoms in the middle of the edges of the squares as chlorine (Cl) and those in the center of the square in yellow as platinum (Pt). When Gao et al. increased the electron beam dose to $30 \text{ e}/\text{A}^2 \cdot \text{s}$, the lattice from K_2PtCl_4 , which was originally viewed across the entire area developed into individual Pt clusters. In time, the nanoclusters grew more pronounced under the microscope.

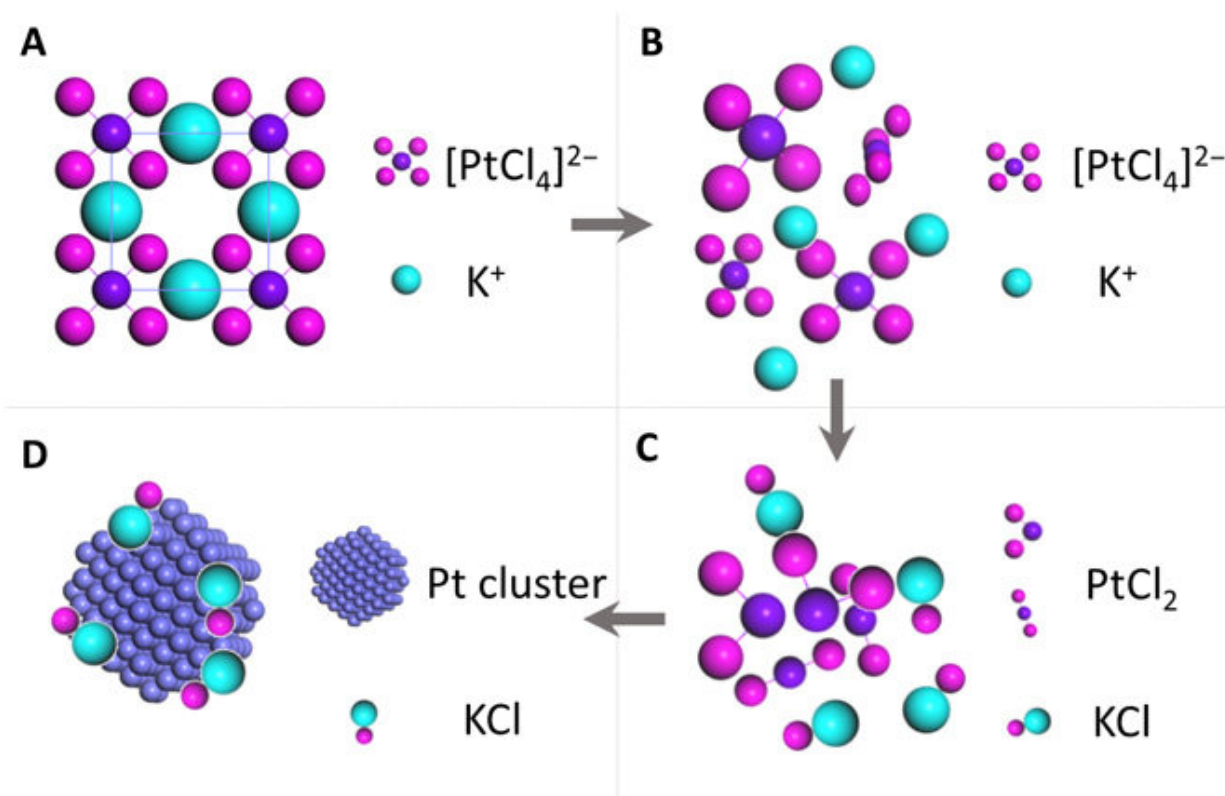


Composition analysis of the final product. (A to D) HAADF image and EDS maps of the final product of the in situ experiment and (E) EELS of the final product of the in situ experiment showing the existence of Cl and K. Credit: Science Advances, doi: 10.1126/sciadv.aau9590

They then observed further formation of the Pt nanoclusters across extended time periods under low-dose imaging conditions. The scientists selected a sub-area of the sequential images and applied a [fast Fourier transform](#) (FFT) to discern the structure and the constituents. Gao et al. were able to obtain a time series of FFT patterns in the K_2PtCl_4 lattice, which also reflected the [radial distribution function \(RDF\)](#) (to find adjacent particles). The scientists then investigated the additional surface orientation of atoms in the material, aside from the Pt nanoclusters, to understand the location of K and Cl species.

In the work, they used a series of imaging and analytical methods of materials science, starting with [high-angle annular dark-field](#) (HAADF) scanning transmission electron microscopy (STEM) and the 2-D [energy-dispersive spectra](#) (EDS) map to characterize the material. The results showed the signals from K and Cl in the background as evenly distributed across the area. When the scientists used [electron energy loss spectroscopy](#) (EELS) they further observed the existence of K and Cl from KCl, after the formation of Pt nanoparticles.

Gao et al. gathered sufficient information from the reaction dynamics captured in real space via spectroscopy and characterization techniques in materials science. They proposed a microscopic process of reduction kinetics for K_2PtCl_4 . Accordingly, the precursor K_2PtCl_4 first decomposed in to K^+ and $PtCl_4^{2-}$ by breaking the weak ionic bond.



A schematic showing the evolution of K₂PtCl₄ into Pt nanoparticles. (A) K₂PtCl₄, (B) dissociation of K⁺ and [PtCl₄]²⁻, (C) further dissociation into PtCl₂ and KCl, and (D) nucleation of Pt nanoparticles. Credit: Science Advances, doi: 10.1126/sciadv.aau9590.

Then PtCl₄²⁻ decomposed into PtCl₂ and Cl⁻, a reaction which had not previously been reported in experimental studies. Gao et al. revealed this process using FFT of the high resolution image under a low electron dose and high acquisition efficiency.

On removal of the K species from the precursor, the lattice became unstable and compounds including PtCl₂, KCl and Cl₂ could move freely. When PtCl₂ was reduced in to Pt, the molecules of Cl₂

transitioned into the gas phase for removal from the TEM column. The zerovalent Pt species formed small nuclei or migrated and grew into large Pt nanoparticles.

In this way, the scientists elegantly demonstrated the reduction kinetics in the study and illustrated the concept using atomic models. The observed findings of nucleation and reduction of Pt agreed with that of [previously calculated free energy](#) in the chemical reaction. This method can be applied to study additional material transformations in depth. The results will benefit the applications of nanostructures in nanophysics for new [materials](#) development, new energy processes in environmental remediation and in nanomedicine.

More information: Wenpei Gao et al. Probing the dynamics of nanoparticle formation from a precursor at atomic resolution, *Science Advances* (2019). [DOI: 10.1126/sciadv.aau9590](https://doi.org/10.1126/sciadv.aau9590)

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