SUPPLEMENTAL MATERIALS

Building with Ions: Direct Write of 3D Platinum Nanostructures using In-Situ Liquid Cell Helium Ion Microscopy

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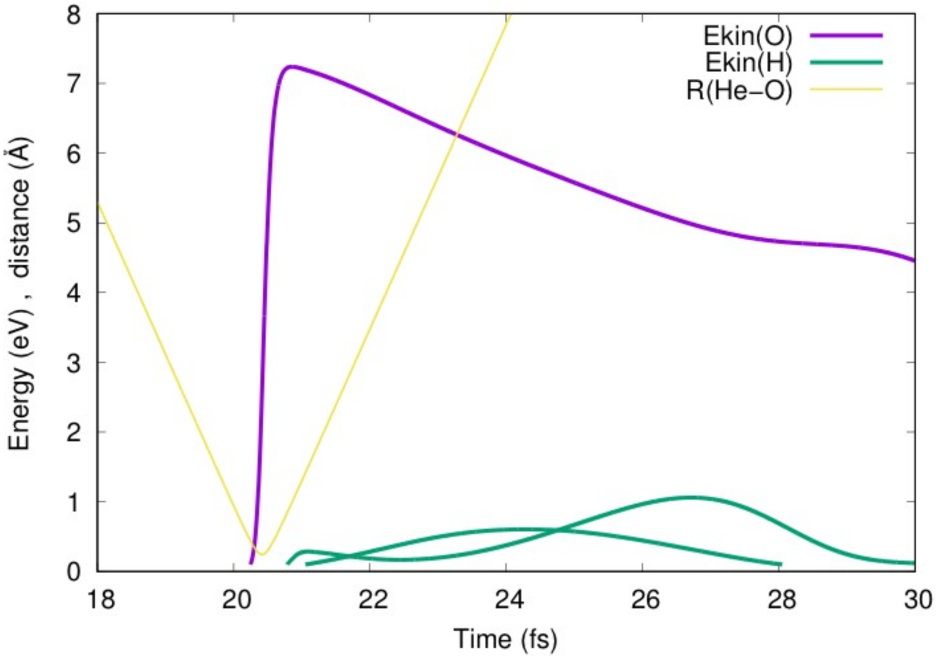

Figure. S1. Kinetic energy of single water molecule irradiated with 1keV He+ beam as a function of time of flight of He+ ion. All energy is delivered to oxygen atom (blue curve). Subsequently kinetic energy is redistributed to hydrogen and surrounding waters. Distance of He+ from O atom (in Angstrooms) is show in green.

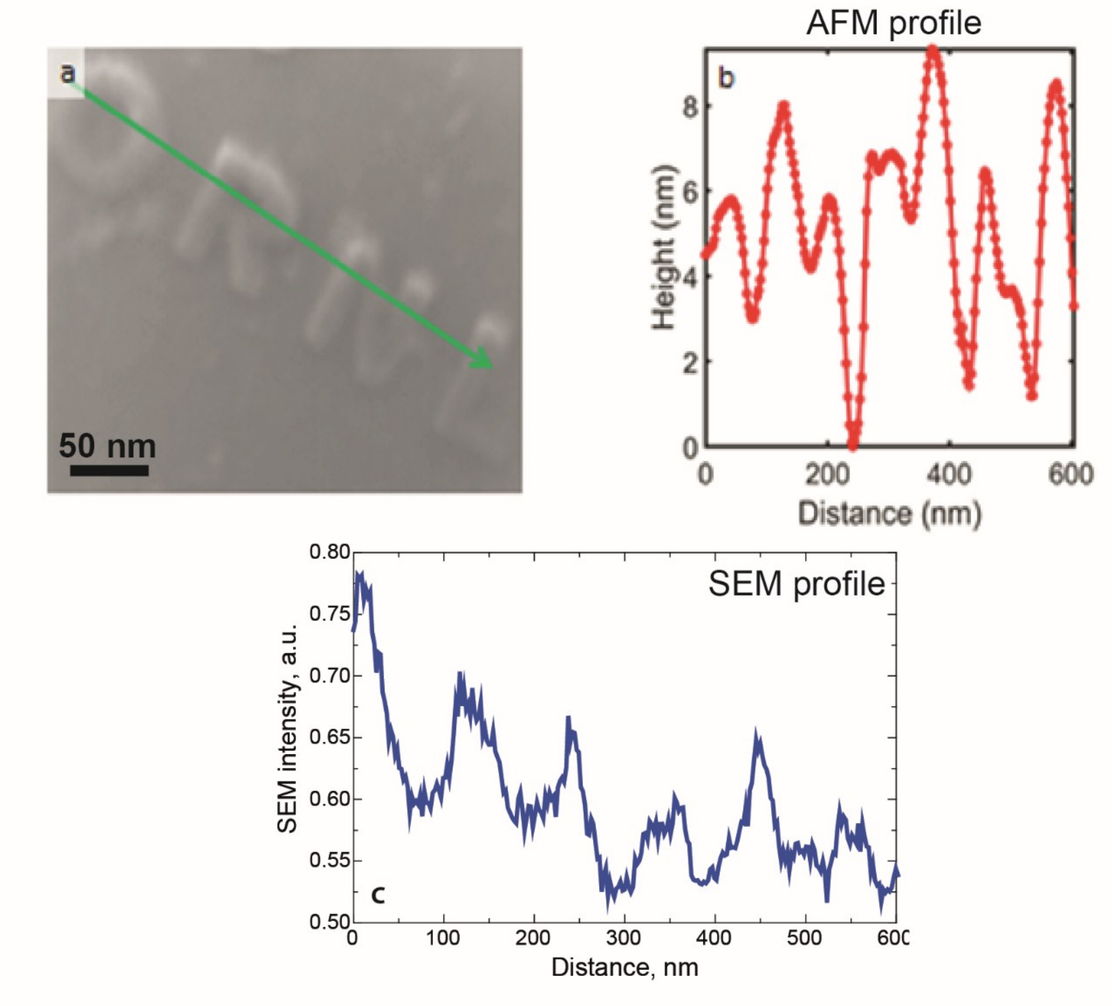

Figure S2. SEM Imaging of the ORNL logo and AFM line profile. (a) SEM Image of the ORNL logo made in the liquid cell, with the green line indicating the position and direction of the line profile; (b) AFM and (c) SEM line profiles of the area indicated in the SEM image in (a).

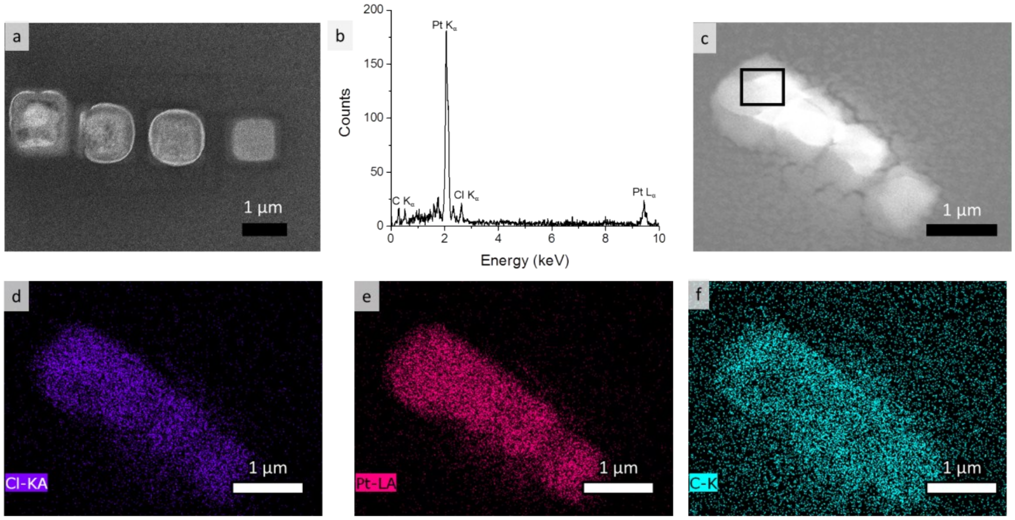

Figure S3. A helium ion micrograph of the (a) liquid grown structures with the respective EDX spectra shown in (b) with the area analyzed in the SEM micrograph in (c). (d), (e), and (f) show the relative distribution of the k-edge for each element Cl, Pt, and C, respectively.

Supplemental section A. Modeling and simulations details

Born-Oppenheimer molecular dynamics (BOMD) and real-time electron dynamics (RTED) simulations are performed with density functional tight-biding (DFTB) framework for electronic structure. DFTB is an approximate density functional theory in which only the valence electrons are treated quantum mechanically while all core electrons and nuclei are approximated via pairwise interatomic repulsive potential Erep. It is based on the Hubbard extension of a tight-binding Hamiltonian in which additional long-range coulomb interaction terms (~1/R) are included. RTED simulations are based of real-time propagation of electronic densities in the field moving point charge. The details of DFTB can be found elsewhere.[1-5]

The Slater Koster parameters required for current RTED and BOMD studies with DFTB are based on modified MIO-1-1 set with customized parameters for He^+ ion included. The onsite energies of He^+ ion were shifted up to ensure that the charge of He ion is always +1 were performed with MIO. This approach is valid for fast moving ions for which the probability of capturing an electron is nearly zero. The time step used for the BOMD and RTED was set to 0.02 fs.

The molecular system consists of ~500 water molecules (random) within the 2x2x4 nm^3 box (see Figure 5a) and simulations were performed in the microcanonical ensemble (constant energy). The initial velocities in BOMD case were set to zero for all water molecules. The interaction time between the He^+ and any specific water molecule in the simulation box is much shorter than the water response time and hence the motion of the water molecules is a minor factor. In fact, the time for He^+ penetration of the entire 4nm thick time water box is on the order of ~10fs (Fig. S1). In the RTED case all water molecules were kept frozen for the same reason. To account for electronic excitation due to the time-dependent electrostatic (Coulomb) interaction with the moving charge of He^+ we employed the quantum dynamical approach for electrons

In quantum dynamics for electrons we solve the time-dependent Schroedinger equation for electrons in the von Neumann, density matrix representation:

$$i\hbar\frac{dP(t)}{dt} = [F(t), P(t)]$$

where the right hand side expression represents matrix commutator *[F,P] =FP-PF*. This is usually achieved by a formation of complex valued exponential time-evolution operator $U(t,\Delta t) = \exp\left(-\frac{1}{\hbar}\Delta t\, F\right)$ from the eigenstates of the F-matrix. The matrix operator $U(t,\Delta t)$ is, then, directly applied to the density matrix to find its values at the next time step:

$P(t+\Delta t) = U(t+\Delta t)^{+}\ P(t)U(t,\Delta t)$ where “+” is a self-adjoint matrix. This procedure has to be repeated for every time step using the updated Fock matrix F(t). We have recently proposed and numerically tested an alternative solution which is based on Baker-Campbell-Hausdorff expansion in which diagonalization is replaced by the matrix-matrix multiplications:

$$P(t+\Delta t) = P(t) - it[\bar{F},P] - \frac{\Delta t^2}{2!}[\bar{F},[\bar{F},P]] + i\frac{\Delta t^3}{3!}[\bar{F},[\bar{F},[\bar{F},P]]] + \frac{\Delta t^4}{4!}[\bar{F},[\bar{F},[\bar{F},[\bar{F},P]]]] + \ldots$$

The symbol operator F is obtained from the electronic Hamiltonian through Magnus expansion (time-ordering) of time-evolution operator. The details are presented in Refs [2-6]

References

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