Real-time Simulation of the Atomistic Ostwald Ripening of TiO_2 Supported Au Nanoparticles

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Content

DFT settings

All calculations were carried out using spin-unrestricted DFT in VASP code with generalized gradient approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) form.[1, 2] The valence electronic states were expanded in the basis of plane waves with the core-valence interaction represented using the projector augmented wave (PAW) approach and a cutoff energy of 400 eV.[3] The energy barriers shown in Fig. S6 was searched using the climbing image nudget elastic band (CI-NEB) method.[4] To dispel the interaction among the Au cluster and its periodic images, the large (4×4) and (5×5) surface unit cells with a vacuum layer of 30 Å was used for optimizing the structure of the supported Au clusters. The *k*-point sampling is set as the Γ point to the large supercell. The TiO_2(101) 2-D periodic slab contained 3 TiO_2(101) layers. The bottom TiO_2(101) layer was fixed to their lattice position as mimetic bulk structure and the rest TiO_2 layers were allowed to relax during geometry optimizations. The force convergence criterion for the geometrical optimization was set at 0.05 eV/Å and the electronic self-consistent is set to be 10^{-5}.

Kinetic Monte Carlo algorism

The standard "rejection-free" KMC algorism is adopted in this work, in which the time occurrence of a jump (Δt) is decided by the below formula:

$$\Delta t = -\frac{\ln(R)}{r_{tot}} = -\frac{ln(R)}{\sum_{i=1}^{N_a}\sum_{j=1}^{NN_i^*} r_{ij}} \quad (1),$$

where *R* is a random number in (0, 1), r_{tot} is the sum of all the possible jumping rates, N_a is the total number of metal atoms, NN_i^* is the number of empty NN sites of *i*. r_{ij} is the jumping rate as calculated below:

$$r_{ij} = \frac{k_b T}{h} exp(-\frac{E_a}{k_b T}) \quad (2),$$

where k_b is the Boltzmann constant, *h* is the Planck constant, T is the temperature, and E_a is the activation energy of the jump. In this work, E_a is estimated by the formula below that satisfies the principle of microscopic reversibility by fitting with the Brönsted-Evans-Polanyi relations and has been successfully used in real-time simulations of nanocrystal transformation:[5, 6]

$$E_a = E_f - E_b - \frac{E_f}{E_b + E_f} E_f \quad (3).$$

E_f and E_b is defined as the formation and broken energy during one atomic jump, which are negative.

Table S1. The DFT results of formation energy per atom of Au clusters supported on TiO_2(101) surface, which is calculated by $E_f = -(E_{coh} + E_{adh})/N_a$

clusters	E_f (eV)
Au_1	**0.37**
Au_2	**1.57**
Au_3	**1.77**

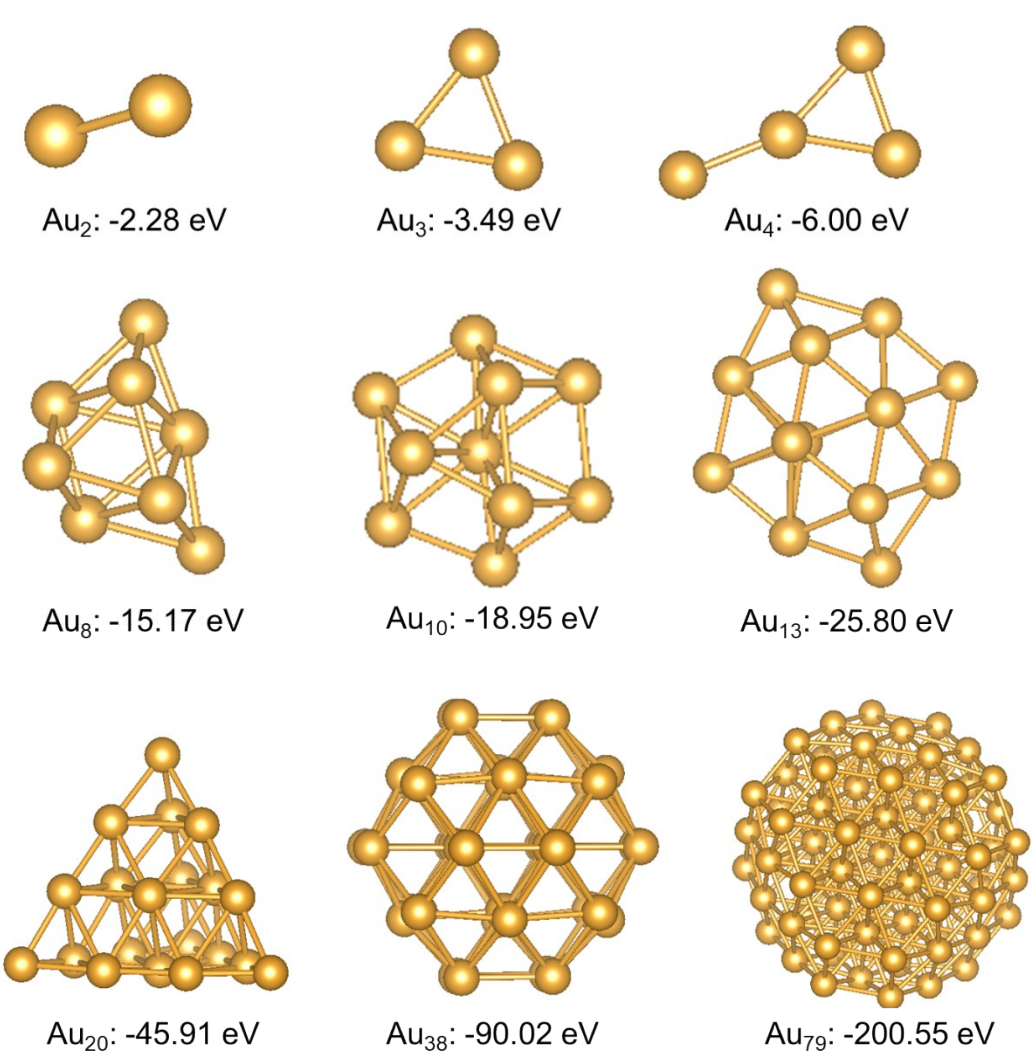

Figure S1. Optimized structures and calculated cohesive energies of Au clusters. The cluster structures of Au_8, Au_{10}, and Au_{13} were referred from Ref. 7.

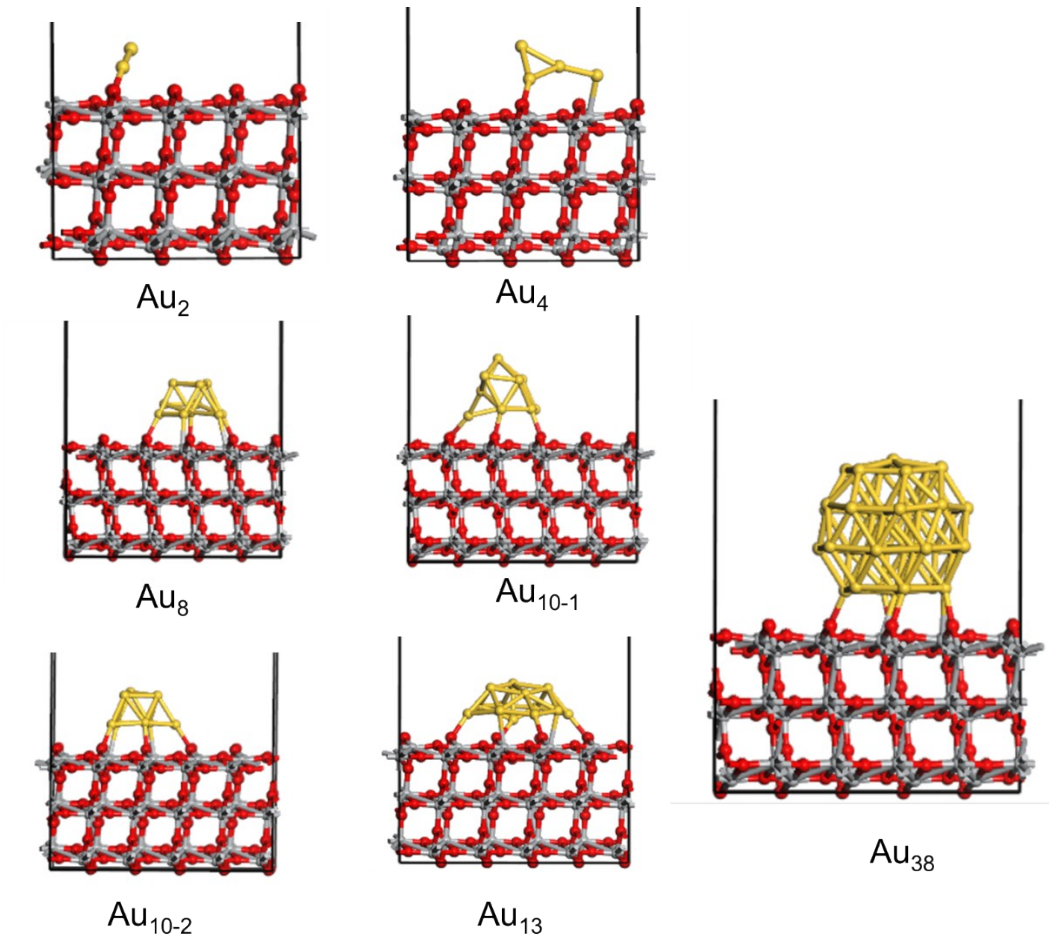

Figure S2. Optimized structures of supported Au clusters on the TiO2(101) surface. The corresponding result of Au79 used in this work was taken from our previous work (Ref. 8).

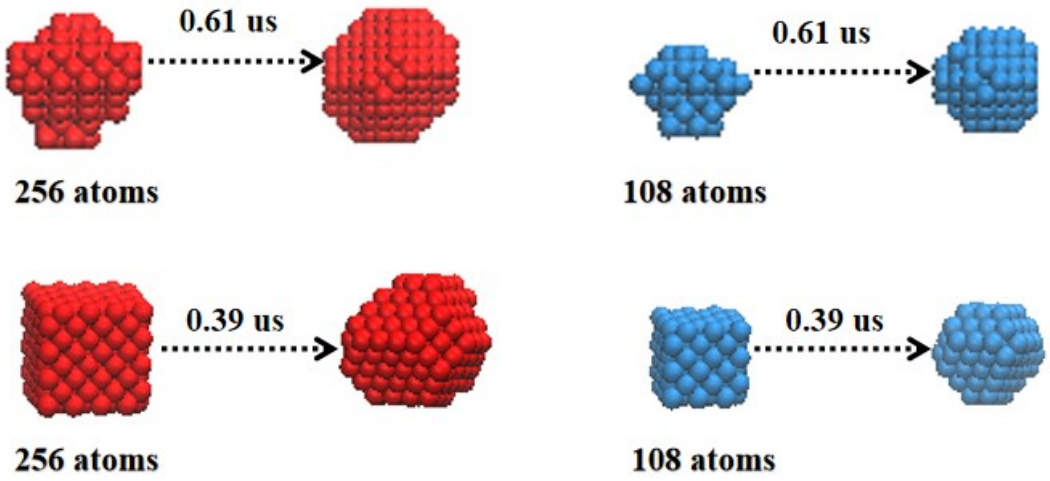

Figure S3. The morphologic change of different initial shapes over a short period of time.

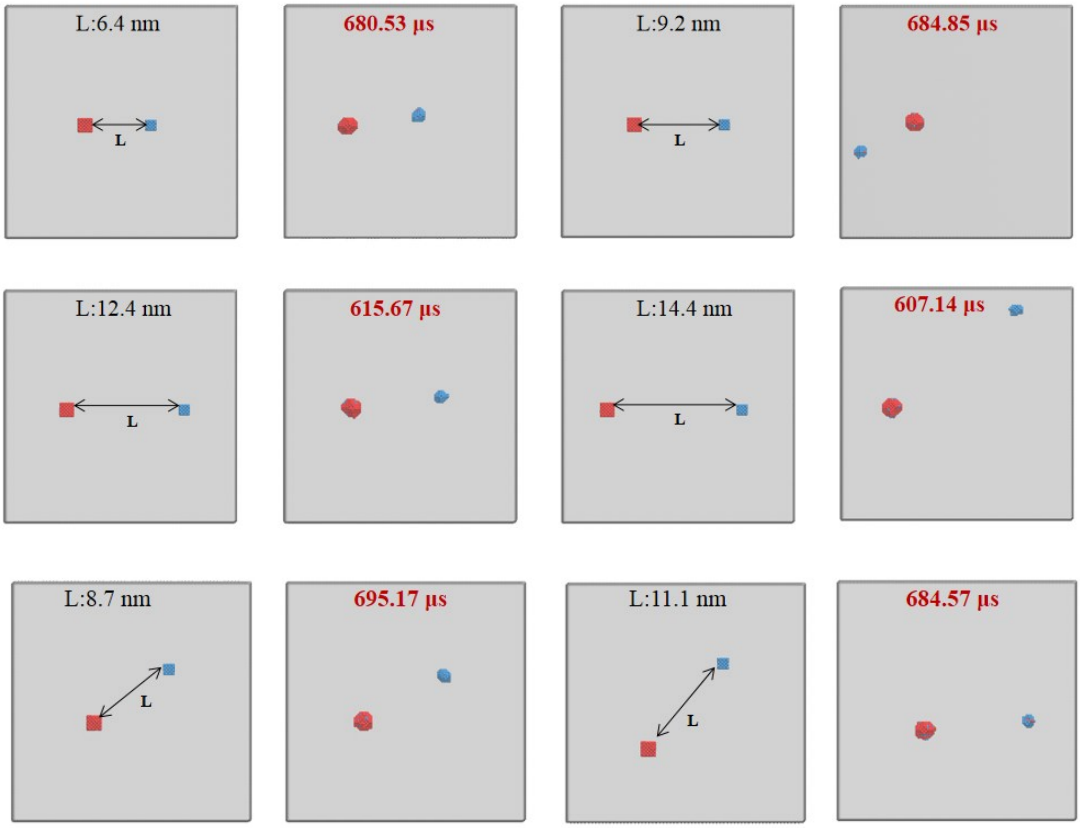

Figure S4. Simulations of the two NPs on different initial positions.

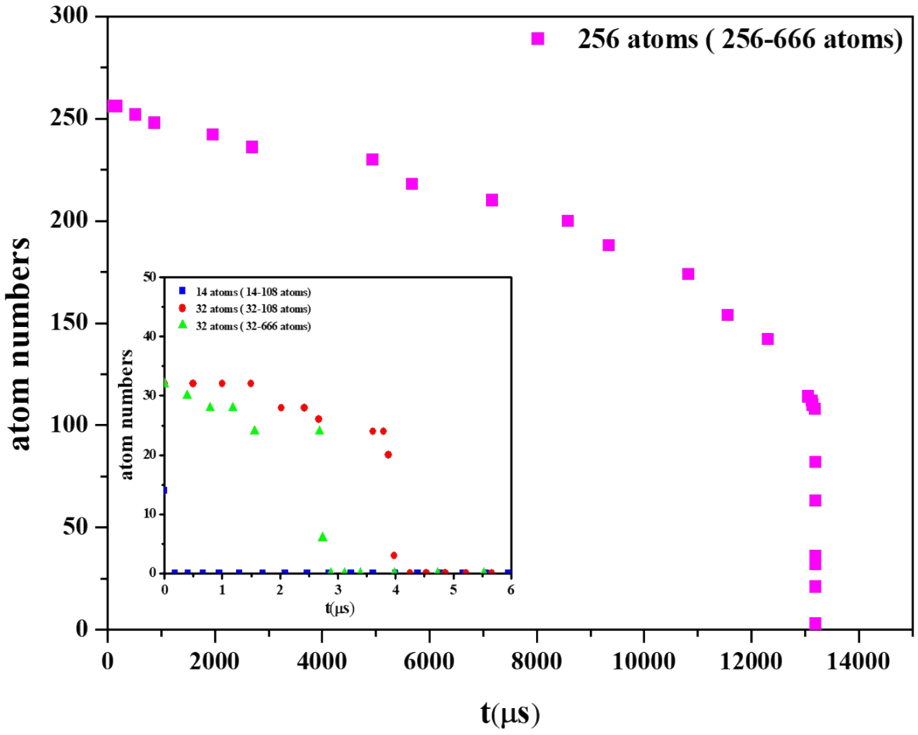

Figure S5. Simulated size evolutions of supported Au NPs with different initial atom numbers as functions of time.

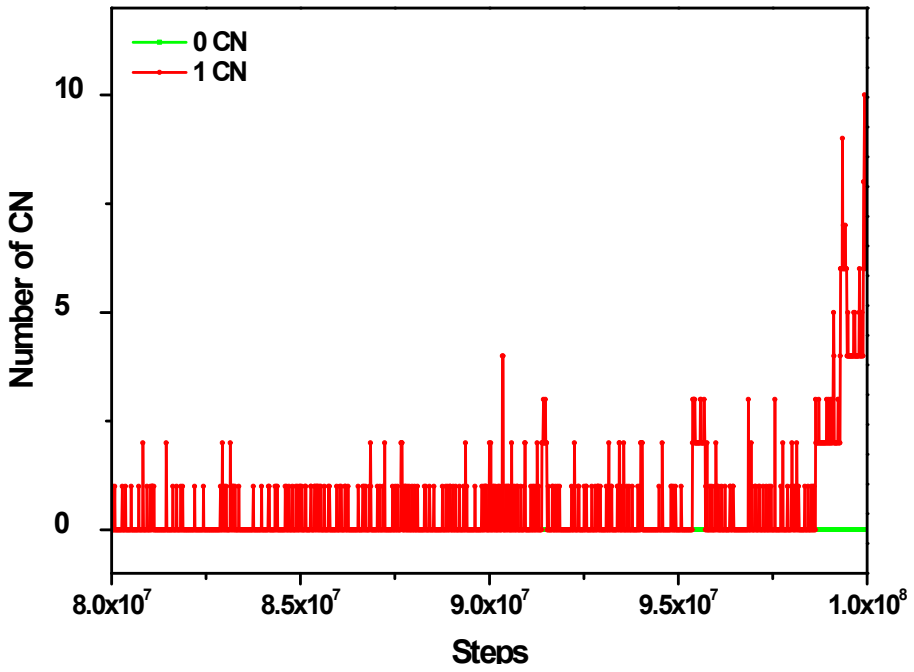

Figure S6. Frequency of occurrence of Au atoms with CN=0 and CN=1 during the OR simulation.

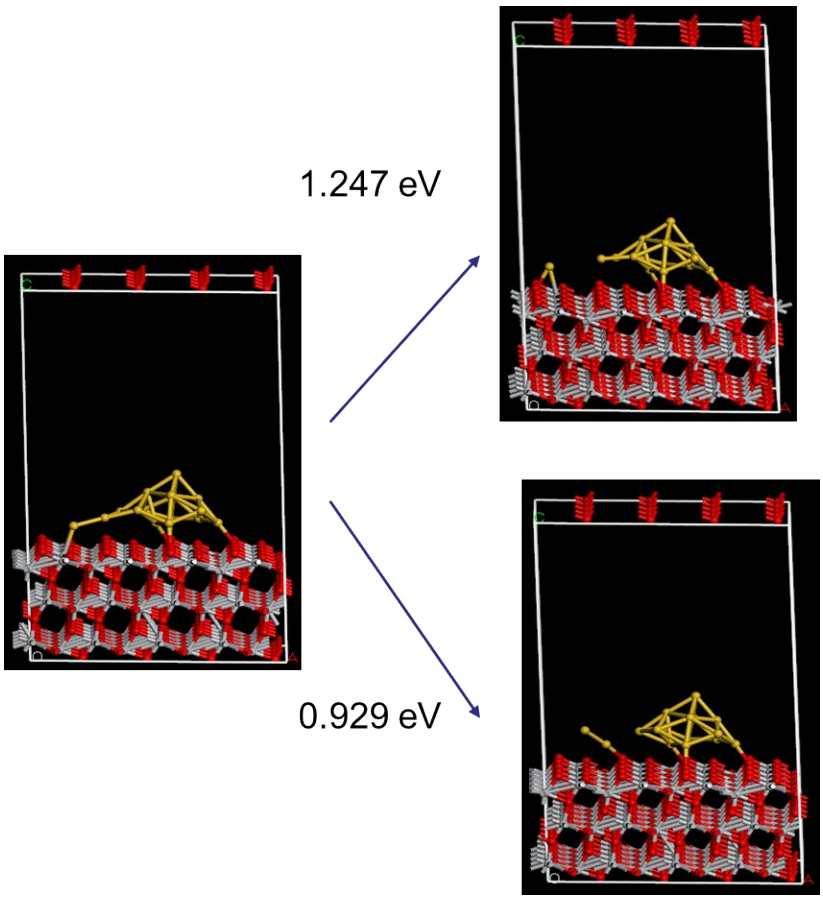

Figure S7. Two energy barriers of detaching a monomer and a dimer from the same NP calculated at the DFT level. The initial structure was obtained from the KMC simulation.

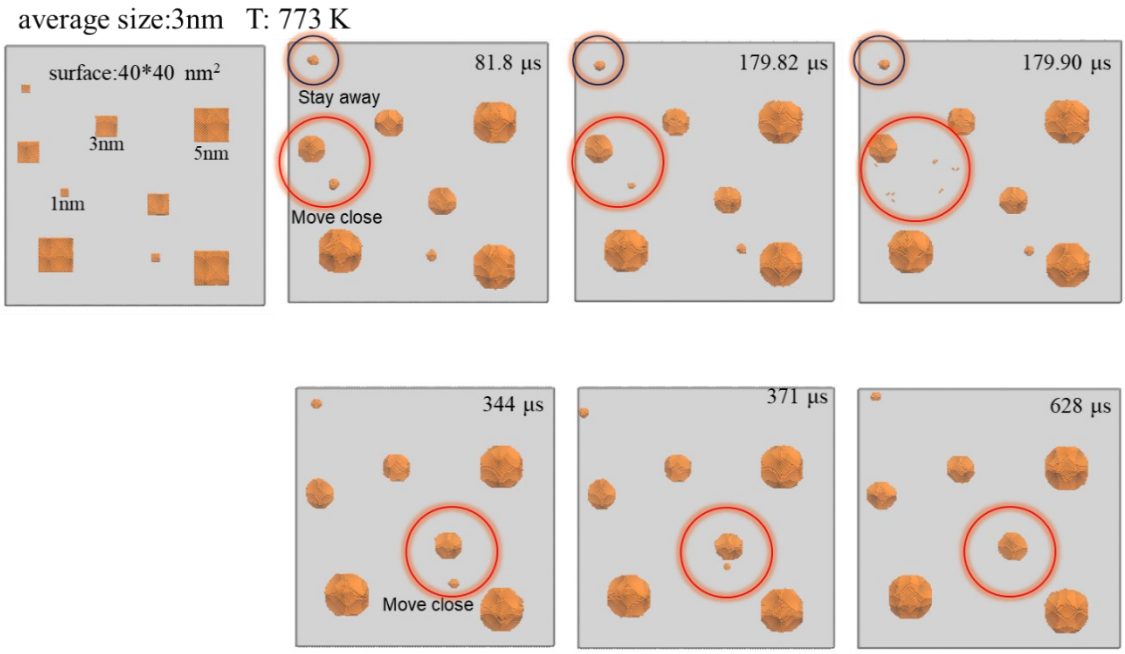

Figure S8. Simulated sintering of Au NPs on the TiO_2(101) surface with multiple initial sizes. The surface area is 40×40 nm^2.

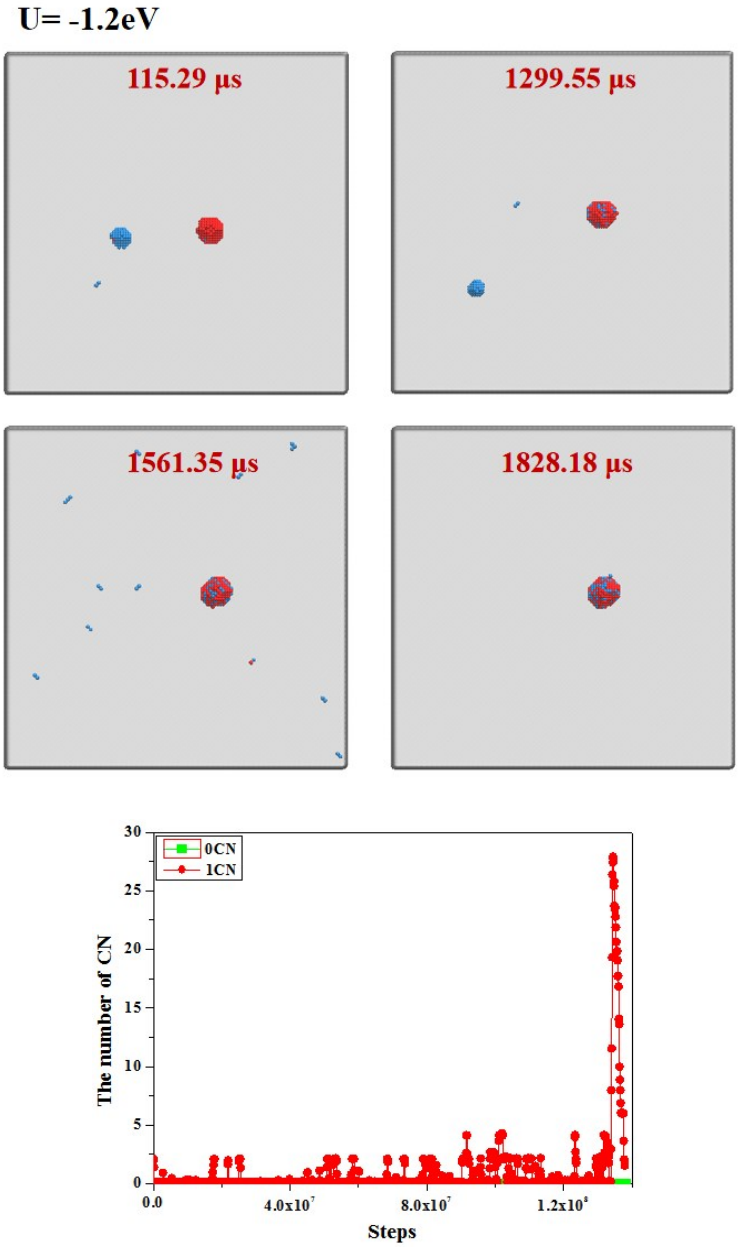

Figure S9. Snapshots (top) and CN statistical analysis during the OR simulation using smaller U.

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