Adaptive Kinetic Monte Carlo Simulations of Surface Segregation in PdAu Nanoparticles

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Supplementary Information

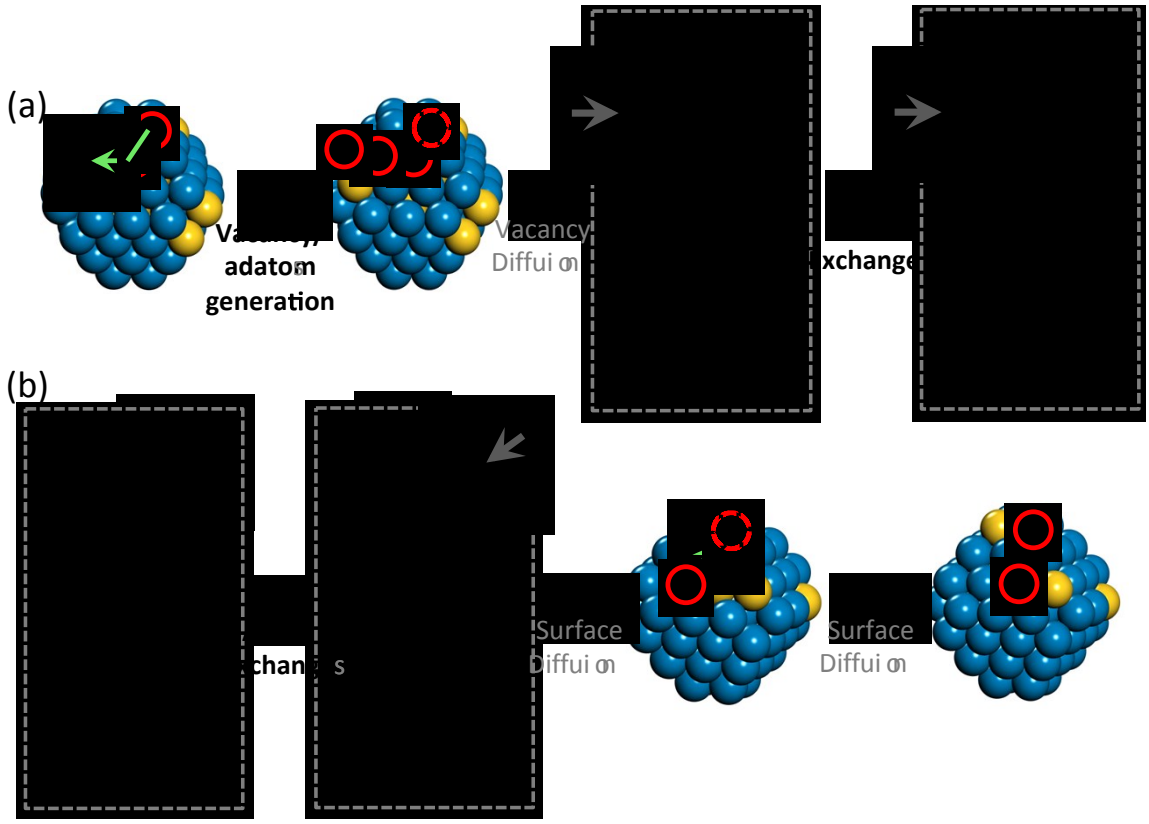

Figure S1. Schematic illustration of (a) vacancy-mediated and (b) concerted mechanism in the $Au_{19}@Pd_{60}$ core@shell NP. The lower-panel images in the grey boxes are cross-section view of the corresponding upper-panel images through the direction indicated by the grey arrows. The dashed and the solid circles highlight the vacancy site and the atoms participating in surface segregation. The green arrows indicate the migration direction of the atoms participating in the reaction.

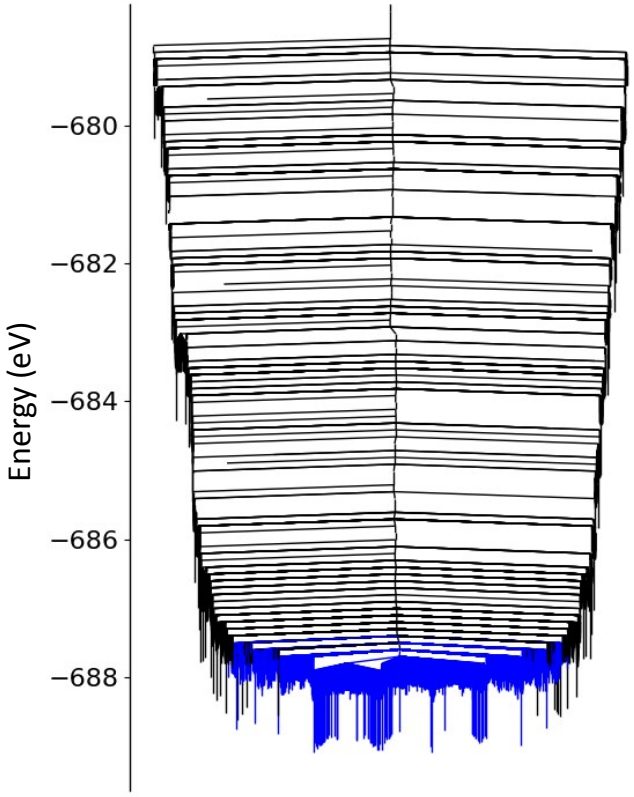

Figure S2. A disconnectivity graph constructed from the first 10,000 unique states visited in the AKMC simulation of the $Au_{79}@Pd_{122}$ core@shell NP at 400 K. The black portion indicates the transition between n=0 and n=24; the blue portion represents surface rearrangement at the n=24 state where the system becomes kinetically trapped.

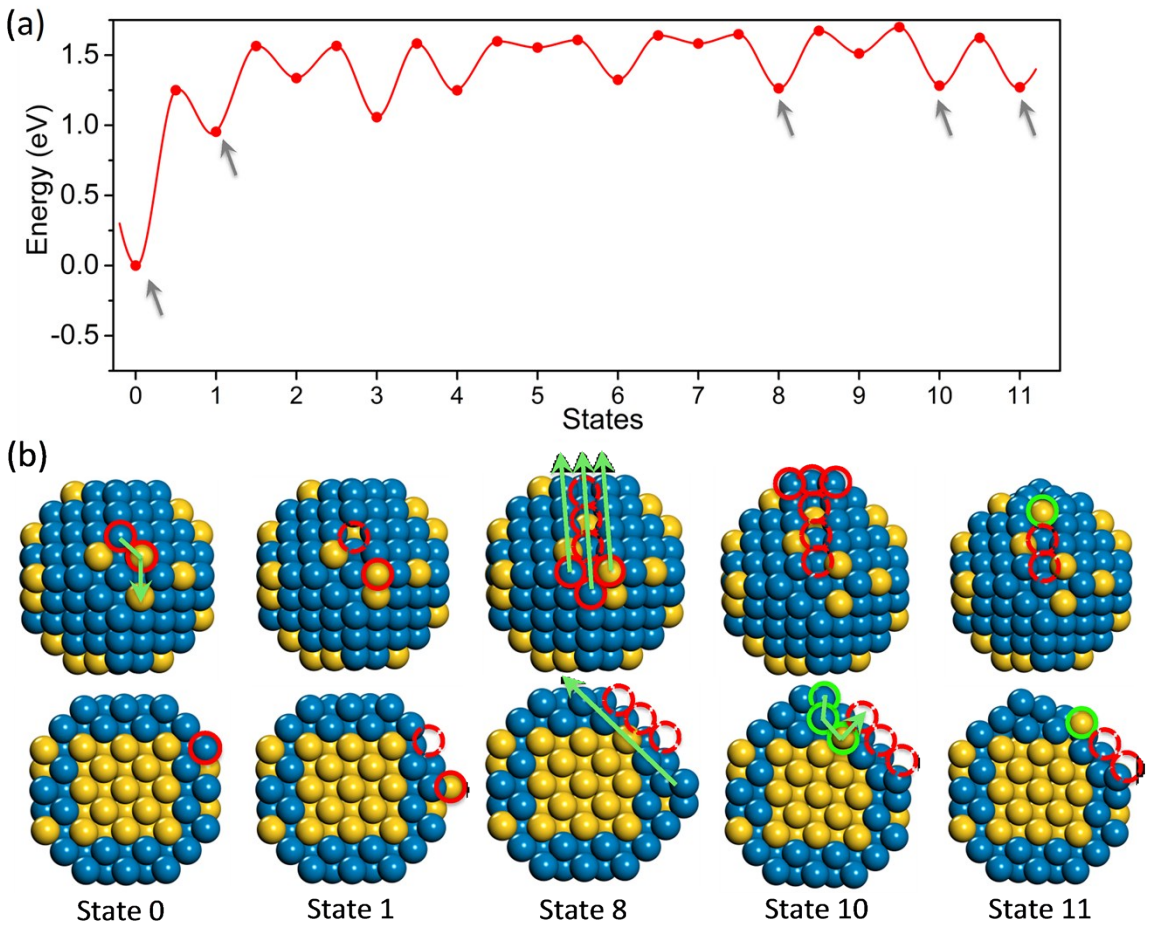

Figure S3. (a) The energy profile for the n=24→25 transition in the $Au_{79}@Pd_{122}$ core@shell NP. The geometric structures (upper panel) and the corresponding cross-section view (lower panel) of the key states highlighted with grey arrows are presented in (b). The dashed and the solid circles indicate the vacancy sites and the atoms that participate in surface segregation. The green arrows show the migration direction of the atoms participating in the reaction. Briefly, the n=24→25 transition involves four key steps, the generation of a vacancy/adatom pair (state 0→1), the formation of a highly defected truncated octahedral structure (state 1→8), the sliding of three rows of PdAu atoms (state 8→10, as indicated by green arrows in State 8) and the Au-Pd core-shell exchange (state 10→11, involving the migration of a three-atom group highlighted in green circles).

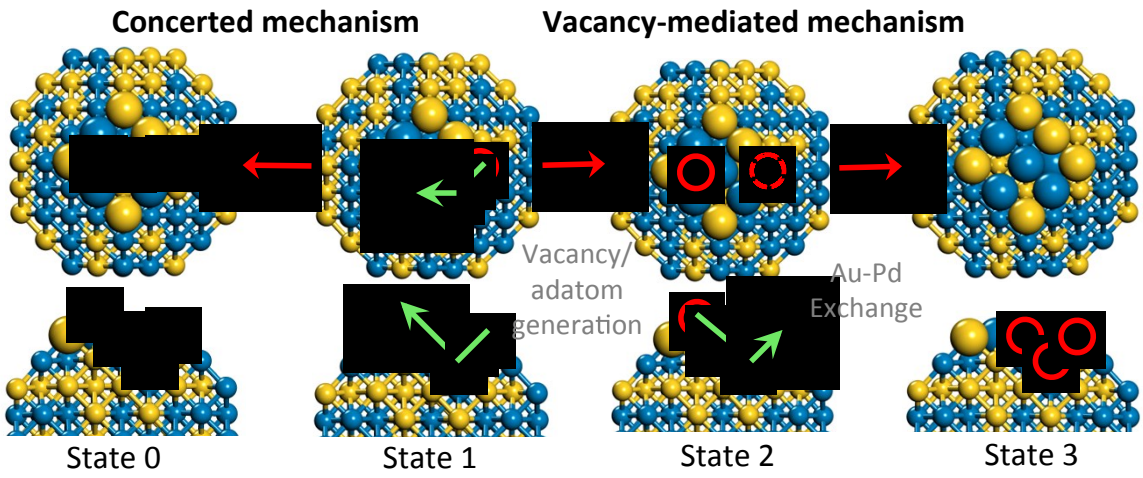

Figure S4. Schematic illustration of the concerted (state 1→0) and the vacancy-mediated (state 1→3) mechanism in the $Au_{79}Pd_{122}$ alloy NP.

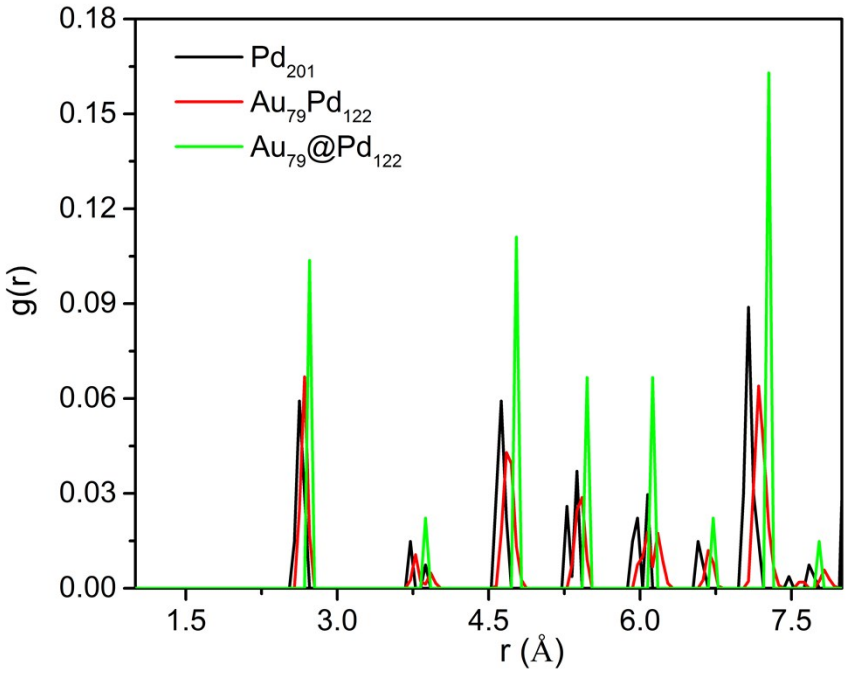

Figure S5. Pair distribution function, g(r), of the bond lengths in the shell of the Pd_{201}, $Au_{79}Pd_{122}$ alloy, and $Au_{79}@Pd_{122}$ core@shell NPs.

Movie S1. Surface segregation of Au in $Au_{19}Pd_{60}$ core@shell NPs at 400 K. The letter 'n' represents the number of Au atoms in the NP shell. The blue and the gold spheres represent the Pd and the Au atoms, respectively.

Movie S2. Surface segregation of Au in $Au_{79}Pd_{122}$ core@shell NPs at 400 K. The letter 'n' represents the number of Au atoms in the NP shell. The blue and the gold spheres represent the Pd and the Au atoms, respectively.