Supplementary Information:

Structural evolution of Pt-Au nanoalloys during heating process:

Comparison of random and core-shell orderings

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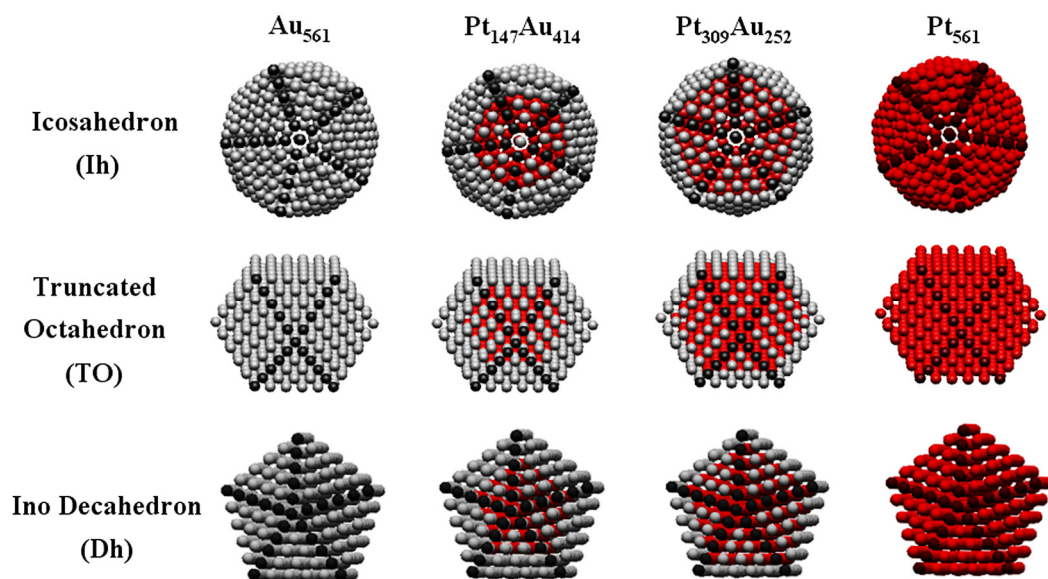* Author to whom any correspondence should be addressed.

Fig. S1 Snapshots of the Pt-Au 561-atom nanoalloys with different geometrical shapes after optimization with Sutton-Chen potential.

Table S1 The corresponding total configuration energies (eV) of Pt-Au 561-atom nanoalloys with Sutton-Chen potential.

Shape	Au_{561}	$Pt_{147}Au_{414}$	$Pt_{309}Au_{252}$	Pt_{561}
Ih	−2031.714	−2349.303	−2692.864	−3149.841
TO	−2031.677	−2343.914	−2689.014	−3149.783
Dh	−2032.192	−2345.202	−2690.120	−3150.581

To justify the validity of choice of icosahedral structures for Pt-Au nanoalloys in this work, the configuration energies of nanoalloys with several typical geometries have been compared. As shown in Table S1, the lowest configuration energies (labeled by red color) of pure nanoparticles (Au or Pt) with decahedral shape imply that the decahedron is favored at the size of 561 atoms for Au and Pt monometallic

nanoparticles. However, the lowest energies of core-shell nanoalloys at the same size correspond to the icosahedron. The phenomena may be attributed to the competition between surface energy and internal strain. The surface energy of icosahedron is lowest but its internal strain is largest, while the internal strain of decahedron is less than icosahedron, and the truncated octahedron presents a largest surface energy but lacks internal strain.[1] Hence, the monometallic nanoparticles prefer to display decahedral shape at intermediate sizes since the internal strain gradually dominates the structure of nanoparticle rather than surface energy as the particle size increases. Nevertheless, for the Pt-Au core-shell nanoalloys, the smaller Pt atoms located in the core of icosahedral nanoparticle can effectively reduce the internal strain,[2] which is favorable for the Pt-Au core-shell nanoalloys with icosahedron. Therefore, the choice of icosahedron for the Pt-Au nanoalloys is reasonable in this work.

References

1   F. Baletto, R. Ferrando, A. Fortunelli, F. Montalenti, C. Mottet, *J. Chem. Phys.*, 2002, **116**, 3856.

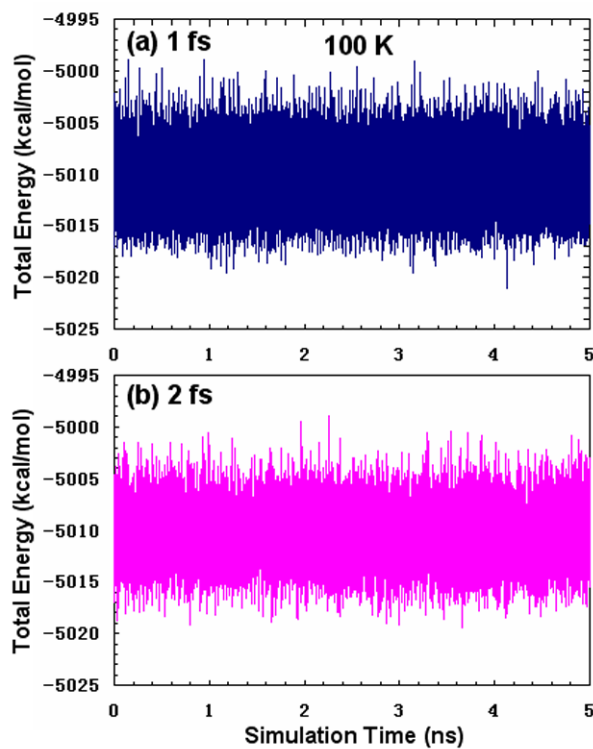2   C. Mottet, G. Rossi, F. Baletto and R. Ferrando, *Phys. Rev. Lett.*, 2005, **95**, 035501.

Fig. S2 Comparison between total energies from 1 and 2 fs for the $Pt_{13}Au_{42}$ CS
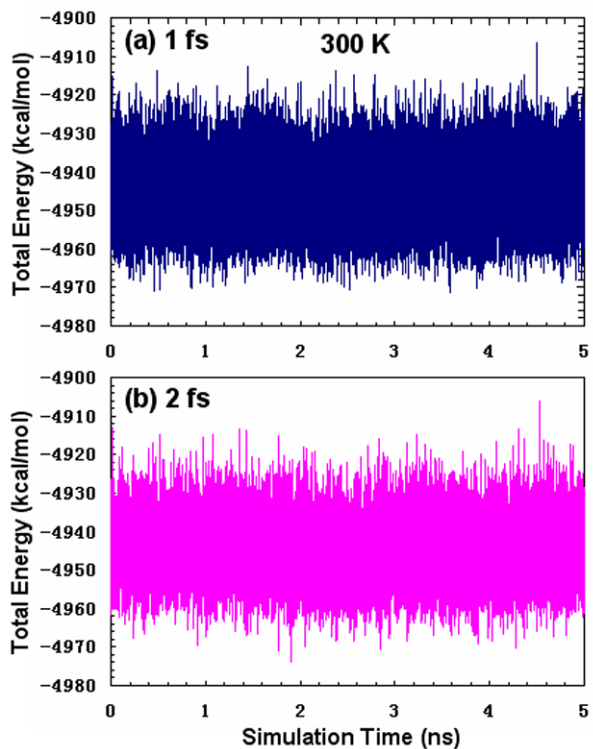
nanoalloy at 100 K.

Fig. S3 Comparison between total energies from 1 and 2 fs for the $Pt_{13}Au_{42}$ CS
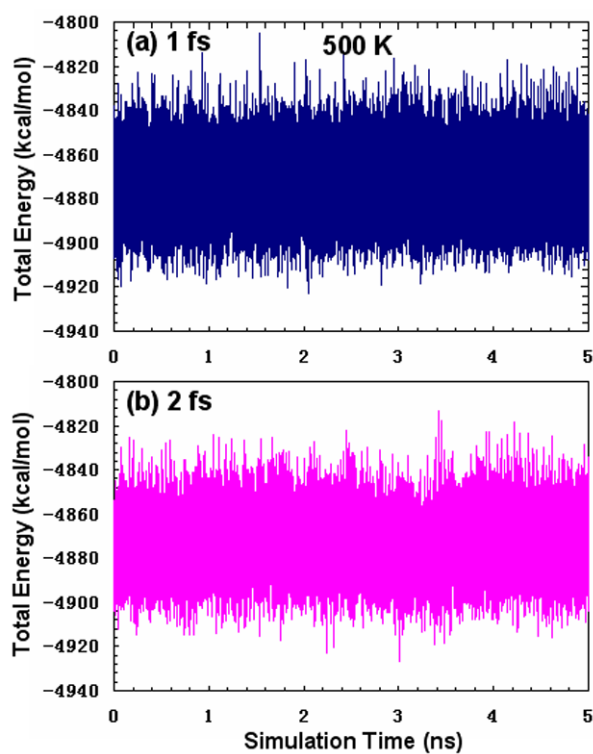
nanoalloy at 300 K.

Fig. S4 Comparison between total energies from simulation with the time step of 1 and 2 fs for the $Pt_{13}Au_{42}$ CS nanoalloy at 500 K.
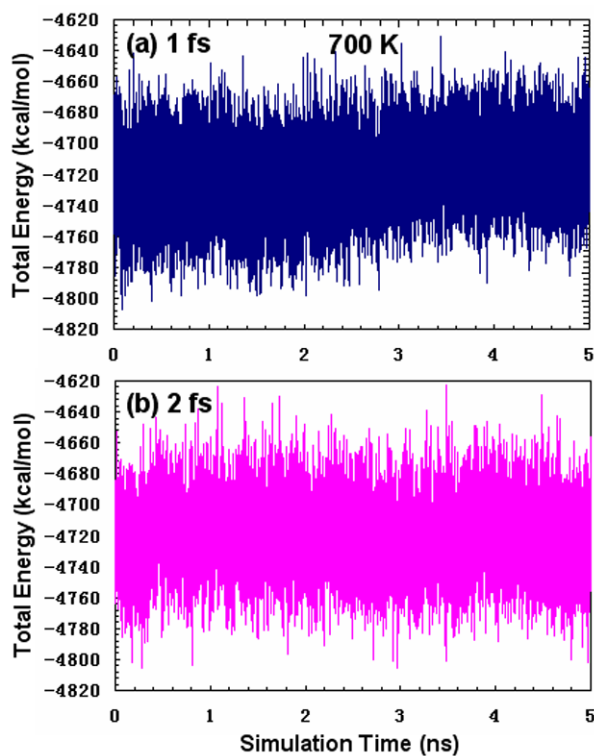
Fig. S5 Comparison between total energies from 1 and 2 fs for the $Pt_{13}Au_{42}$ CS

nanoalloy at 700 K.

To test validity of the time step of 2 fs, we performed a series of runs with the

timestep of 1 fs at several temperatures for the $Pt_{13}Au_{42}$ core-shell (CS) nanoparticle

over the temperature range of heating, viz., 100, 300, 500, and 700 K. As shown in

Figs. S2–S5, the comparison results shows that the timestep of 2 fs used in this paper

is reasonable and enough to keep the stability of the Hamiltonian (contributions from
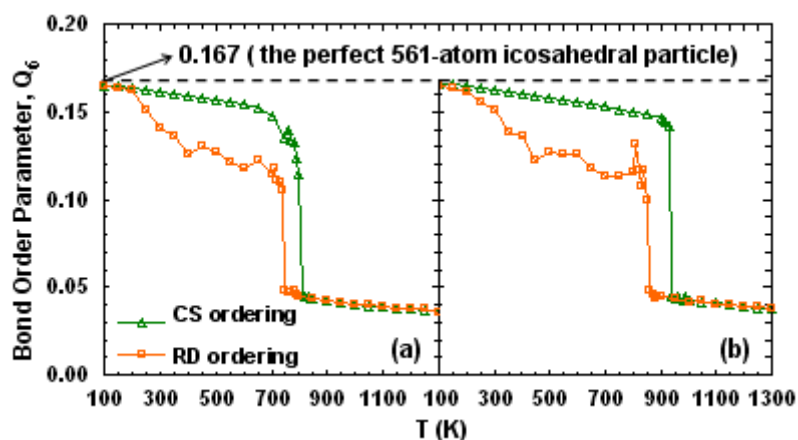
both kinetic and potential energies).

Fig. S6 The bond order parameter as a function of temperature for the (a) $Pt_{147}Au_{414}$

and (b) $Pt_{309}Au_{252}$ nanoalloys with the core-shell and random orderings.