Supplementary Information for

Relative Edge Energy in the Stability of Transition Metal Nanoclusters of different Motifs

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S1: Structures, thermal dynamic and kinetic stabilities of low energy Ru_{55} nanoclusters.

The geometric structures and relative energies of the eleven representative low-energy Ru_{55} configurations presented in Fig. 5(a):

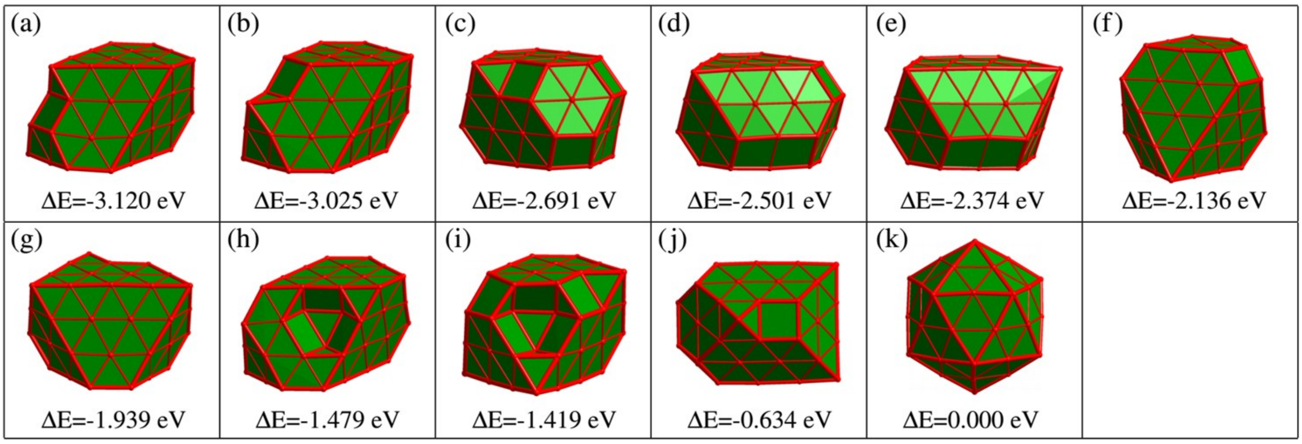

Fig. S1 *Geometric structures and relative energies of the ten representative FCCCF (a-j) and the* I_h *(k) low energy configurations of* Ru_{55}*. The* I_h *configuration is taken as the energy references, i.e.,* $\Delta E=E(Ru_{55})-E(Ru_{55}(I_h))$*. Structures in* ***(a), (c), (h),*** *and* ***(k)*** *correspond to configurations presented in* ***Fig. 3(I-a), (-b), (-d)*** *and* ***(-f)*** *of the main text, respectively.*

All the three FCCCF structures in Fig. 3(I) (or structures (a), (c) and (h) in Fig. S1) contain four layers of atoms stacked in the A-B-C-A sequence, distributed as A(13)-B(15)-C(14)-A(13), A(12)-B(16)-C(16)-A(11), and A(13)-B(15)-C(15)-A(12) for Fig. 3 (I-a), (-b), and (-d) (or Fig. S1(a), (c) and (h)) respectively, with the number of atoms in a given layer listed in the parentheses. Meanwhile, the three structures possess 5 ((a)), 3 ((b)) and 8 ((d)) fewer inner atoms than the I_h structure (Fig. 3(I-f)), resulting in enlarged fcc(111) facets in each case, as well as slightly reduced average bond length R, by ~1%. Alternatively, structures in Figs. 3(I-c) and (-e) can be optimized from a three-layered hcp crystal fragment (HCPCF). Configurations of (I-c) in A(18)-B(19)-A(18) and (I-e) in A(16)-B(23)-A(16) stacking are also lower in energy than the I_h structure (Fig. 3(I-f)), by 1.557 and 0.531 eV, respectively.

To confirm the global (or nearly-global) or local minima structures for each case, taking Ru_{55} as a representative example, we present the vibrational frequency of the most stable structure of Ru_{55} shown in **Fig. S1(a)**, see **Fig. S2**. We note that there is only negligible low-frequency (close to zero) imaginary mode. Moreover, the thermal dynamic stability of this structure is also further confirmed by constant temperature molecular dynamic (MD) simulation at 1000 K. Clearly, the most stable structure obtained for Ru_{55} keeps almost intact within the whole MD simulation time of 5 ps, as shown in **Fig. S3**. All these extensive examination can unambiguously confirm the ground state structure of **Fig. S1(a)** for Ru_{55}. By such a method, we also confirm that other structures presented in the manuscript are either global or local minima on the potential energy surfaces.

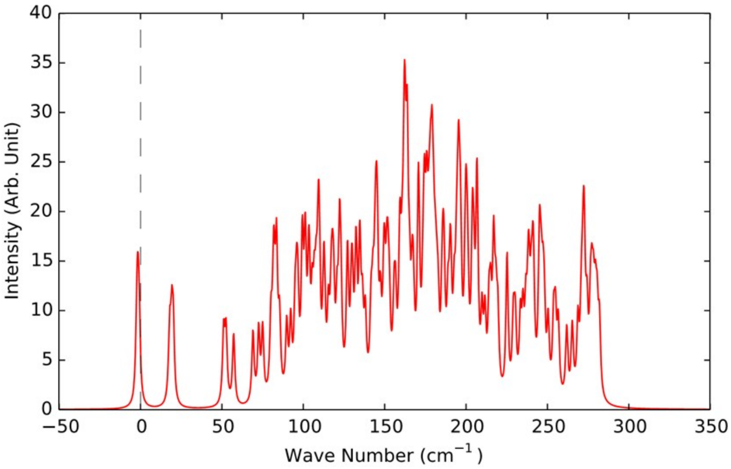

Fig. S2 *Vibrational spectrum of the most stable Ru_{55} structures in* ***Fig. S1(a)***.

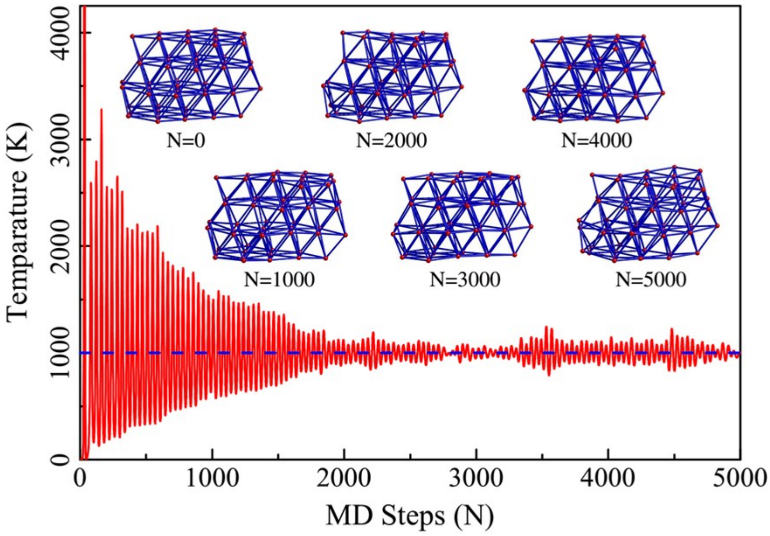

Fig. S3 *The constant temperature molecular dynamics (MD) simulations at 1000 K within 5 ps simulation time of the most stable Ru_{55} configuration presented in* ***Fig. S1(a)***.

S2: Geometric structures of four representative configurations of Ru_{54}

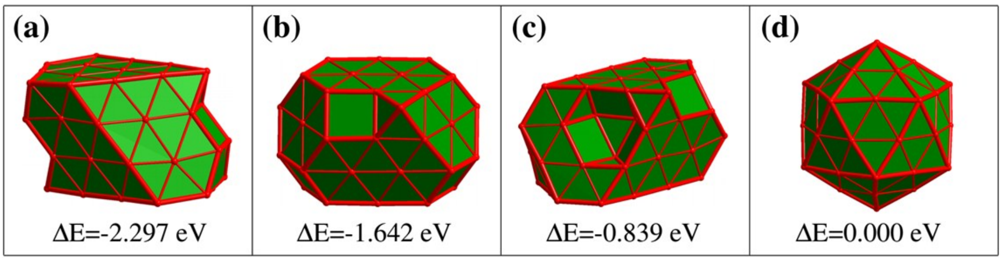

Fig. S4. *Geometric structures and relative energies of the three representative low-energy FCCCF-Ru_{54} forms (**(a)**, **(b)** and **(c)**) and the I_h-Ru_{54} configuration **(d)** optimized by removing the central atom from the I_h-Ru_{55}.*

S3: Structural properties of low energy Ru_{147} nanoclusters

In panel (II) of Fig. 3, we present six low energy structures of Ru_{147}, including three fcc-like, I_h, and two hcp-like configurations optimized mainly from various initial configurations guided by both GWCP and CWCP. The three low-symmetric FCCCF structures shown in panel (II) of Figs. 3(a), (c) and (d) are found to be still much lower in energy than the high-symmetric I_h structure presented in 3(f), by 1.715, 1.418 and 1.167 eV, respectively. Specifically, each of the three stable FCCCF structures contains 6 layers of atoms stacked in the A-B-C-A-B-C sequence, distributed as A(20)-B(29)-C(30)-A(29)-B(23)-C(16), A(18)-B(27)-C(30)-A(29)-B(25)-C(18) and A(18)-B(24)-C(19)-A(30)-B(27)-C(19) in Figs. 3(II-a), (-c) and (-d), respectively.

S4: Geometric structures and REE of Ru_{101}

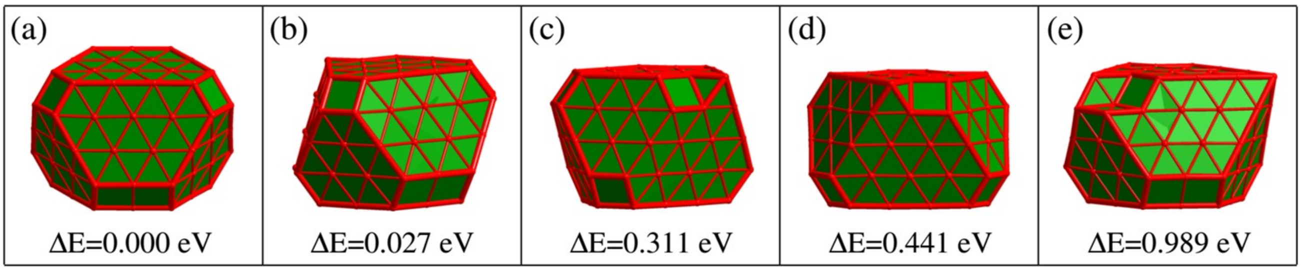

Fig. S5 *Geometric structures and relative energies of the five representative low-energy FCCCF configurations of Ru_{101}.*

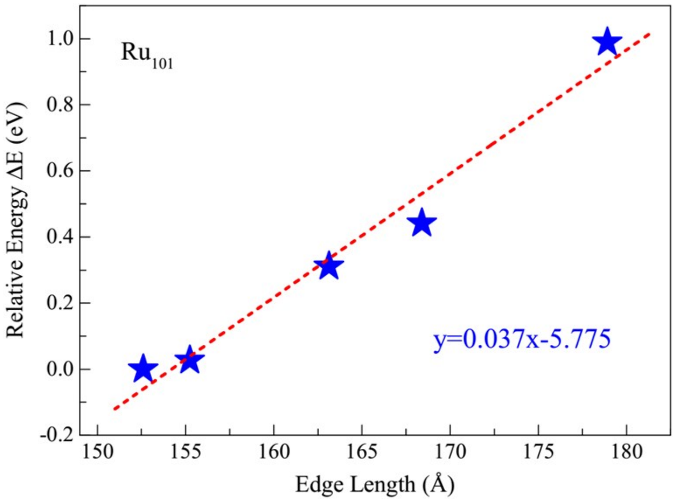

Fig. R6 *The least square fitting of the relative energies as a function of total edge length of five representative low energy structures of* Ru$_{101}$.

S5: Geometric structures and REE of Ru$_{231}$

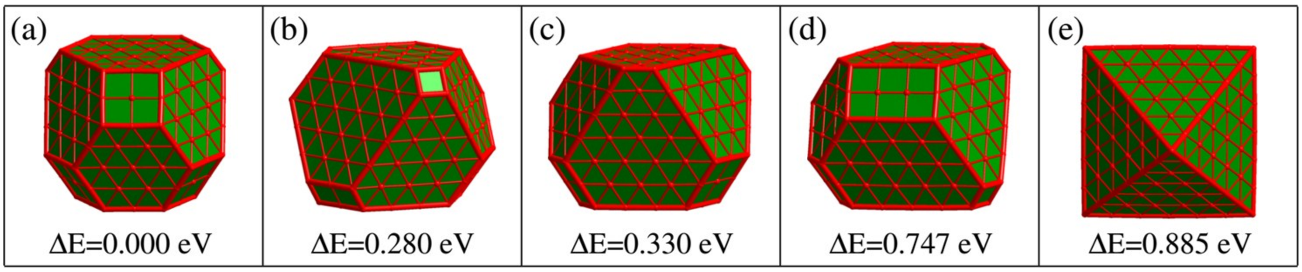

Fig. S7 *Geometric structures and relative energies of the five representative low-energy FCCCF configurations of* Ru$_{231}$.

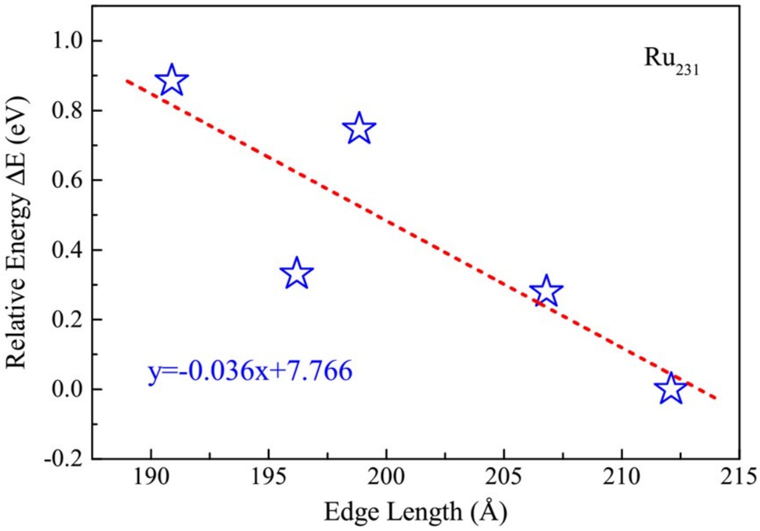

Fig. R8 The least square fitting of the relative energies as a function of total edge length of six representative low energy structures of Ru$_{231}$.

S6: Size effect on the REE

For the definition of the relative edge energy balanced by the surface variation, the term of bulk in equation (4) is implicitly an invariant for the different FCCCF isomers; otherwise, the bulk effect needs to be considered as well. Alternatively, we demonstrate that for both FCCCF and HCPCF motifs, the obtained relative edge energies are still positive for those configurations with negligible changes in the cluster cores, namely, for a given size, in these FCCCF and HCPCF isomers we observe again that overall the shorter the total edge length (the smaller the number of the edge atoms), the lower the total energy. However, for the cases presented in Fig. 6(b), these cluster configurations possess relatively larger edge length or more number of inner atoms which are high-coordinated and contribute extra stability, therefore, the obtained relative edge energy are negative.