hcp metal nanoclusters with hexagonal A-A bilayer stacking stabilized by enhanced covalent bonding

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First-principles total energy calculations within density functional theory have been performed to study the geometric and electronic structures of Ruₙ nanoclusters of varying size n (14≤n≤42). Strikingly, for the size range of n=14 to 38, the clusters always prefer a hexagonal bilayer structure with A-A stacking, rather than some of the more closely packed forms, or bilayer with A-B stacking. Such an intriguing “molecular double-wheel” form is stabilized by substantially enhanced interlayer covalent bonding associated with strong s-d hybridization. Similar A-A stacking is also observed in the ground states or low-lying isomers of the clusters composed of other hcp elements, such as Os, Tc, Re, and Co. Note that these “molecular double-wheels” show enhanced chemical activity toward H₂O splitting relative to their bulk counterpart, implying its potential applications as nanocatalysts.

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Since the discovery of fullerenes1 and their subsequent bulk synthesis,2 the structure and stability of nanoclusters have been the subjects of intensive study. One motivating factor is that such nanoclusters may exhibit novel and exotic structures in contrast to their bulk counterparts, thereby offering opportunities for elucidating new types of chemical bonding. These forms of clusters and/or cluster-assembled materials, in turn, may possess unique physical and chemical properties with potential applications, e.g., in energy storage, sensing, spintronics, and catalysis. As an example, C₆₀ may serve as a high-capacity medium for hydrogen storage upon Ca coating, due to strong electrostatic polarization and enhanced binding of molecular hydrogen.3 Au prefers an fcc structure in bulk form, but due to relativistic effects Auₙ clusters prefer planar, cage-like, or core-shell structures when n is small,4,5 and such open structures of gold may exhibit outstanding catalytic properties.5 Despite the predominance of three-dimensional structures found in bulk boron and its compounds,7 eight- and nine-atom boron clusters are perfectly planar molecular wheels with double (σ and π) aromaticity,8 attributed to their extreme coordination environments.

Recently, considerable attention has been paid to the structural properties of clusters of hcp and fcc transition metals (TM), a class of elements with important catalytic and magnetic applications.4-6,9-13 In particular, it was found that Ruₙ clusters of sizes (2≤n≤13) prefer a simple cubic structure, rather than the icosahedral-like (Iₖ₃) or buckled planar (BBP) structures (Ref. 9) predicted for related systems. Additionally, Coₙ clusters of sizes (13≤n≤23) were shown to prefer multilayer structures with fcc or hcp stacking, and the enhanced stability of the layerlike structure was attributed to enhanced magnetization of the systems.11

In this paper, we report the discovery of a and unexpected structural form of hcp metal nanoclusters, the hexagonal bilayer structure with A-A stacking, as revealed by first-principles studies of Ruₙ clusters of varying size n (14≤n≤42). We identify that, for the whole size range of n=14 to 38, the clusters always prefer the hexagonal bilayer structure with A-A stacking, rather than some of the more closely packed forms, or a bilayer with A-B stacking. We further attribute the stabilizing force of the intriguing “molecular double-wheel” structure to the substantially enhanced interlayer covalent bonding associated with strong s-d hybridization. Similar A-A stacking is also observed in the ground states or low-lying isomers of the clusters composed of other hcp elements, such as Os, Tc, Re, and Co. These findings may have broad applicability in the areas of atomic binding, nanostructure formation, nanocatalysis, and molecular devices.

Our calculations are carried out using density-functional theory (DFT)14 with the spin-polarized generalized gradient approximations (GGA),15 as implemented in the VASP code.16 The wave functions are expanded in a plane wave basis with an energy cutoff of 213.3 eV. The interaction of valence electrons with the core is described with projector augmented wave (PAW) method.17 The atomic positions are optimized with the energy convergence up to 0.001 eV. We use a simple cubic supercell with large size of 18–23 Å to make the interactions between the cluster and its periodic images negligible. Only the Γ point is used in the summation of the Brillouin zone of the simulation cell. The accuracy of the present calculation was checked by calculating the bond length of Ru₂ dimer and the lattice constant of Ru bulk. The present PAW pseudopotential method can correctly predict the binding properties of the dimer and the bulk. Simulated annealing and conjugate gradient method were used to optimize the global structures.

We performed theoretical calculations on a wide variety of structures for Ruₙ (n=14–42) in search of the

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FIG. 1. (Color online) Ground-state and low-lying structures of Ruₙ clusters (n=14–42).

global minimum, including the icosahedral-like and nonicosahedral-like structures of other species such as the recently reported Coₙ (Ref. 11) and some metastable closely packed configurations from the simulated annealing method implemented by empirical potential.18

The ground-state structures and some low-lying isomers of Ruₙ (n=14–38) are shown in Fig. 1. It is clear that up to n=38, the even-sized Ruₙ clusters prefer bilayer hexagonal structures in A-A sequence, which are subsequently termed as the A-A structure. Figure 2(a) compares the average binding energies, Eᵣ/atom=−[∑E(Ruₙ)-nE(Ruatom)]/n, of the A-A structures and those of the most stable low-lying isomers with hcp/fcc multilayered (ML) fragments. The total energy difference is typically larger than 1.333 eV, except for Ru₃₄, where the A-A structure is more stable by 0.086 eV. The largest total energy difference is 4.355 eV for Ru₂₀. From Ru₄₀, closely packed ML structures are favored (Fig. 1) and the A-A structures become low-lying isomers. Here, we note that for the low-lying isomers (except for Ru₁₄ and Ru₁₅ preferring bilayer A-B structures) up to Ru₃₈, trilayer structures of hcp/fcc fragments are favored. For odd-sized clusters within the range of (n=15–37), the structures can be simply obtained by placing the extra atom at the outer edge of the even-sized structures of size (n−1).

Now, we address the detailed properties of the A-A structures and the structural evolution from the A-A sequence to ML closely packed. In the bilayer hexagonal Ru₁₄ cluster presented in Fig. 1, all the bond lengths in the hexagonal plane are 2.524 Å, and the layer-layer distance is 2.203 Å. As mentioned, Coₙ clusters (Ref. 11) are also identified to exhibit a layerlike structure, but our calculations show that the A-A structure of Ru₁₄ is 3.481 eV more stable than the bilayer (A-B) structure of Co₁₄. It is also found to be 4.769 eV more stable than the form obtained directly from the addition of a Ru atom on the I₄Ru₁₃ unit, though this is indeed the ground state for many other TMₙ₄ species. As noted earlier, our previous results show that small Ruₙ clusters (n=2–13) favor the cubic growth mode, and the Ru₁₃ cluster shows a low-symmetry relaxed by the capping of one Ru atom on the surface of the Ru₁₂ cuboid (Ref. 9). Ru₁₅ can be obtained by capping one Ru atom on the rectangular facet (other sites are much higher in energy) of the A-A Ru₁₄ structure, forming four equilateral bonds of 2.56 Å in length, and the bilayer A-A hexagonal Ru₁₄ unit is well maintained.

The addition of one dimer on the rectangular facet of Ru₁₄ yields the most stable Ru₁₆ with a bilayer A-A structure, Fig. 1. When compared to Ru₁₅ with an average bond length, R ≈ 2.470 Å, Ru₁₆ shows a slightly reduced R of 2.458 Å, implying an enhanced binding energy and stability (the enhanced stability is indicated by the second-order difference of the total energy with respect to cluster size). This even-odd variation in stability also agrees well with the stability oscillations observed in smaller Ruₙ clusters (n=2–13) reported recently (Ref. 9). Thus, in later sections we focus on the representative even-sized cases.

By symmetrically growing a Ru₂ dimer on Ru₁₆, the ground state of Ru₁₆ is obtained with an A-A stacking. The ground state of Ru₂₀ is identified to result from the simple addition of another Ru₂ dimer to the A-A Ru₁₆, Fig. 1, which can be seen as two hexagonal bilayer A-A building blocks (14-atoms) penetrating into each other with the R slightly extended to 2.476 Å, as compared with 2.453 Å of Ru₁₄. In fact, if one Ru atom rather than a Ru₂ dimer is added on the same site of Ru₁₆, the most stable structure of Ru₁₉ is obtained, which is about 4.532 eV more stable than a closely packed structure relaxed upon two I₄ units penetrating into each other. Furthermore, the ground-state A-A structure of Ru₁₉ is found to be 1.366 eV more stable than a trilayer configuration with a perfect regular octahedron of the O₈ atom, which was verified as the ground state of Co₁₉ (Ref. 11).

From n=22 to 38, the growth of the Ruₙ clusters follows a perfect hexagonal bilayer A-A framework upon the Ru₁₄ core unit, as shown in Fig. 1. We have also calculated a wide variety of other structures and found that the hcp/fcc-like fragment structures possess significantly higher energies, typically by 3.464 eV in Ru₃₄. The cubic growth mode in small Ruₙ (Ref. 9) and Rhₙ,12 as well as the I₄ structures in other TMₙ (Refs. 11–13), are also both significantly unfavorable. However, as the cluster size increases, the energy difference between the A-A structures and the most stable low-lying ML structures becomes small, as seen in Fig. 2(a). The largest cluster of a perfect hexagonal A-A configuration is Ru₃₈, which is about 1.451 eV more stable than the most...
stable trilayer fcc fragment with an atomic packing of 12–14–12, as shown in Fig. 1. 38(II). The A-A Ru38 is also 2.291 eV more stable than a perfect octahedron, 38(III), which has also been found as the ground-state of many other TM38 clusters, such as Co38 (Ref. 11) and Ni38.13

We find that the A-A stacking is preferred only until Ru38. For Ru40, a more stable structure is formed by placing one Ru atom on each of two neighboring (100) facets of the Oh-Ru38 structure (as shown in Fig. 1), which is about 0.228 eV more stable than the bilayer A-A structure. Addition of two more Ru atoms on the subsequent (100) facets of the octahedron yields an optimized ground-state structure of Ru42, Fig. 1. Relative to the most stable A-A stacking, the energy difference is raised to 1.174 eV, showing a significant structural transition from bilayered A-A to multilayered closely packed stacking. We also note that compared to Co3 clusters, these Ru3 clusters possess significantly small magnetic moments (MM) and the MM decreases with increasing the cluster size except for Ru15, which displays the largest MM of 9.82 μB; Ru38 (n = 18, 26, 30, 38, and 40) clusters carry negligible magnetism and the other clusters under present study show an MM from 2.0 to 4.0 μB with negligible magnetic moments (Ref. 11).

The total electronic density of states (DOS) of the Ru3 clusters (n = 14–42) are presented in Fig. 3, which shows high peaks near the Fermi energy (Ef), indicating metallic properties and highly catalytic tendencies. Here, we also note that Ru3 clusters begin to exhibit metallic properties from n ~ 10, see Ref. 9. For small sizes, the even-sized clusters with a perfect A-A bilayer structure display simple DOS, Fig. 3, with clear sharp peaks, e.g., for Ru14 (Ru18), compared with Ru15 (Ru17). Ru38 possesses more complex DOS than both Ru10 and Ru20, due to the geometric effect, i.e., its imperfect hexagonal A-A bilayer stacking. From Ru20 to Ru38, sharp peaks occur at about 3.0 eV below the Ef, due to symmetric growth of the bilayer structure, particularly in the case of Ru14 and Ru20. From Ru38, the peaks at ~3.0 eV are gradually broadened; however, peaks at about ~5.6 eV become much more distinguished. For the cases of Ru14 to Ru38, there are two sharp peaks at about ~1.5 and ~2.0 eV, particularly for Ru38 with a highly symmetric hexagonal A-A bilayer structure. Ru40 possesses similar DOS to that of Ru42 due to their very similar close-packed structures; however, it is evidently different from the DOS of Ru38, strongly suggesting a change in their geometric structures. We stress that the profile of the DOS (the dotted) of an Oh-Ru38 is significantly different from that of the ground state structure of a bilayer A-A stacking (solid lines), due to considerable difference in their structures. We also note that the anions of all the studied Ru3 clusters maintain almost the same configurations as their neutral counterparts, leading to similar DOSs in both cases, which may be valuable for further experimental verification of these structures, such as by photoelectron spectroscopy.

These hexagonal-like A-A bilayer structures, particularly for the cases of Ru14 and Ru38, can be viewed as “molecular double-wheel” structures: the former and the latter possess atomic packing of 7–7 and 19–19, respectively. In each single-wheel, the bonding between the central Ru atoms and the outer rings can be viewed as “spokes” of the molecular wheels. One intriguing question is why these clusters adopt such an unusual A-A stacking. To answer this question, we first analyze the bonding properties of the A-A structures. The results are shown in Fig. 2(b). The A-A structures always possess shorter R by about 0.1 Å relative to other ML structures and the layer-layer distances are significantly shorter than the bonding lengths in each layer, indicating significant covalent characteristics in these A-A structures though the DOSs in Fig. 3 reveal metallic characteristic.

The enhanced covalency is further supported by the electronic charge-difference (Δρ) analysis defined by Δρ = ρ(SC) − ρ(SP). Here, ρ(SC) is obtained by a self-consistent calculation and ρ(SP) by the superposition of the atomic charge for the same structure. First, taking the A-A Ru14 as an example, the three-dimensional (3D) Δρ pattern as inserted in Fig. 4(a) reveals that the in-layer Ru atoms display evident covalent bonding, i.e., the “spokes” are of covalent nature. To further analyze the covalent bonding nature of the interlayer and perform comparisons between different sizes and structures, we have also calculated Δρ along the axis of the bonds between the two layers, i.e., we summed all the line Δρ together along the axis of the bonds between the two layers and then divided by the number of bonds. As presented in Fig. 4(a), charge density accumulates considerably at the bond center, revealing a significant level of covalent bonding of the interlayer. With the size decreases from infinite 3D A-A Ru bulk through A-A Ru38 to A-A Ru14, the covalent bonding of the interlayer becomes stronger and stronger. We also stress that for the cases of a bilayer A-B Ru14 isomer and hcp Ru bulk, the covalent bonding of the interlayers are considerably weaker than those of the “molecular double-wheel,” implying the unique bonding properties in these unusual nanostructures. To support the strong covalent bonding in these Ru3 clusters, we also select an A-A Mg38 isomer (the ground state Oh-Mg38 is about...
4.945 eV more stable) for comparison, and one can see that there is a negligible peak in the line $\Delta \rho$. Although bulk Mg possesses an hcp structure, due to the weak covalent bonding nature, Mg$_n$ clusters within the current size range still prefer the close packed structure$^{19}$ rather than the A-A packing.

The competition between the covalent bonding and the coordination number determines the structural evolution from A-A to ML configurations. For a given cluster, its stability depends on both the average bonding strength and the total number of the bonds ($N_{\text{bond}}$) involved. In Fig. 2(c), we present the $s$-$d$ hybridization indices, $H_{s,d}$ (for definition, see Ref. 9), of the ground-state structures of Ru$_n$ clusters. Evidently, the $H_{s,d}$ values of the A-A Ru$_n$ clusters ($n=14$–38) are considerably larger than those of the smaller Ru$_{12}$ and larger Ru$_{40}$ clusters ($n=40$ and 42), indicating a stronger binding in the former cases. Figure 2(d) presents the $N_{\text{bond}}$ as a function of cluster size. Clearly, in the small size range, the number of bonds in A-A structures is comparable with that of the multilayer fcc or hcp fragments, thus the A-A growth mode is preferred due to relatively strong covalent bonding. With increasing cluster size, the number of bonds in ML structure dramatically increases relative to that of A-A structure, mainly as a result of the increased number of encapsulated atoms. These encapsulated inner atoms [type III atoms in Fig. 4(b)] have a higher coordination number and possess larger binding energies, subsequently lowering the total energy, as implied by the much enhanced (reduced) peaks in the deep (shallow) energy levels in the local projected DOS of the $O_p$-like Ru$_{40}$ [see Fig. 4(b)]. We also note that the covalent bonding is gradually weakened with the increasing size, and the metallic bonding begins to dominate the stability. Thus beyond a critical size ($n=38$), more closely packed ML fragments become more stable.

We have also checked the stabilities of the A-A structure for some other hcp transition-metal elements near Ru in the periodic table. We find that almost all the Os$_n$ clusters in the current studied size range also prefer the A-A stacking, by a typical energy difference of 0.363 eV for Os$_{30}$, if compared to that of other stacking forms (such as A-B, A-B-A, or A-B-C). For smaller Tc$_n$ clusters, structures with A-A stacking are essentially degenerate in energy compared with those of other closely packed structures. For Re$_n$ and Co$_n$, the structures with A-A stacking are also found to be low-lying isomers. Furthermore, relatively strong covalent bonding is also clearly observed in the A-A bilayer structures of Os$_{38}$, Tc$_{40}$, and the layerlike structures of Co$_n$ (Ref. 11). However, in the current size range studied, the slightly weaker covalent bonding properties involved in Fe$_n$, Co$_n$, and Tc$_n$, relative to Ru$_n$, resulting in the low-lying isomers of A-A stacking for the former cases.

Finally, we identify that relative to their bulk counterpart, these A-A bilayer Ru$_n$ nanostructures possess significantly enhanced chemical activities toward H$_2$O splitting. Recently, both dissociation and non-dissociation observations were identified for H$_2$O adsorption on the Ru(0001) surface$^{20–24}$, indicating that Ru(0001) is on the border of active and inactive metal surfaces with respect to dissociation of water. The underlying essential point may be that the barrier for desorption of the nondissociated adsorbed water is comparable with the dissociation barrier$^{23,24}$ on the Ru(0001) surface. However, this observation may change in the nanoscale.

Here, we simply report the adsorption and dissociation behaviors for a H$_2$O molecule on Ru$_{14}$, the smallest double-wheel in our findings. In our calculations$^{25}$, the optimized H$_2$O molecule possess $R(\text{H-O})=0.973 \text{ Å}$ and $\angle \text{H-O-H} = 104.61^\circ$, in close agreement with previous calculations. As presented in Fig. 5(a), we find that H$_2$O favors to adsorb on the top of the edge Ru atom with an adsorption energy $E_{\text{ads}}=[E(\text{H}_2\text{O/Ru}_{14})-E(\text{H}_2\text{O})-E(\text{Ru}_{14})]$ of 0.671 eV, bond length $R(\text{O-Ru})=2.231 \text{ Å}$, $R(\text{H-Ru})=0.978 \text{ Å}$, and $\angle \text{H-O-H}=108.03^\circ$, respectively. We note that the H$_2$O monomer possesses a significantly larger $E_{\text{ads}}$ on the cluster than that on the Ru(0001) surface, 0.409 eV$^{24}$ and the enlarged $\angle \text{H-O-H}$ along with this larger adsorption energy indicates a stronger activation of the H$_2$O molecule in the former case. On this site, splitting the H$_2$O species further
identify that the energy barrier involved in the dissociation lowers the total energy by 0.596 eV, resulting in the configuration as shown in Fig. 5(c). Importantly, with the improved climbing image nudged-elastic-band (NEB) method, we identify that the energy barrier involved in the dissociation process is only 0.592 eV [see Fig. 5(b) for the configuration of the saddle point, \( R(O-Ru) = 2.102 \text{ Å}, R(O-H1) = 0.981 \text{ Å}, R(O-H2) = 1.332 \text{ Å}, \) and \( \angle H-O-H = 112.39^\circ \)], which is considerably smaller than the adsorption energy of 0.653 eV, i.e., the desorption barrier. Therefore, the above results strongly suggest that these novel double-wheel Ru nanostructures possess superior chemical activity to their bulk counterpart for water splitting due to their intriguing atomic bonding and chemical properties in the nanoscale. In fact, the observed enhanced chemical activity of these Ru bilayer nanostructures can be readily understood from the \( d \) band theory. Our calculations show that the \( d \) band center of the first-layer surface atoms of Ru(0001) simulated with a six-layer slab model is located at \(-1.971 \text{ eV} \). However, the Ru\(_{14}\) cluster possesses a \( d \) band center of \(-1.910 \text{ eV} \), particularly, the \( d \) band center of the edge atoms with less coordination numbers is even higher, \(-1.844 \text{ eV} \), in close agreement with the density of state analysis as presented in Fig. 4(b), rendering these sites more active for molecular adsorption.

In summary, we have carried out a systematic first-principles study of the geometric and electronic structures of Ru clusters of varying size \( n \) \((14 < n < 42)\). Our studies lead to the surprising finding that, for the size range of \( n = 14 \) to 38, the clusters always prefer a hexagonal bilayer structure with \( A-A \) stacking, rather than some of the more closely packed structures, or bilayer with \( A-B \) stacking. The intriguing “molecular double-wheel” structure is stabilized by the substantially enhanced interlayer covalent bonding associated with strong \( s-d \) hybridization. Similar covalent-bonding stabilized \( A-A \) stacking is also observed in the ground states or low-lying isomers of clusters composed of other hcp elements, such as Os, Tc, Re, and Co. These findings, predicting the first transition-metal based “molecular double-wheel” structures, may be instrumental in the design of new forms of nanocatalysts and molecular nanodevices.

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In our calculations, to obtain the adsorption energy and the dissociation path for $\text{H}_2\text{O}$ on Ru$_{14}$ cluster, we use PAW-PBE potential, which is generally regarded as more accurate to describe an adsorption process, though our test shows that PAW-GGA give almost the same data.
