Subnano Pt Particles from a First-Principles Stochastic Surface Walking Global Search

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Supporting Information

ABSTRACT: Subnano transition metal particles have wide applications in chemistry. For the complexity of their potential energy surface, it has long been a great challenge for both theory and experiment to determine the structure of subnano clusters and thus predict their physiochemical properties. Here we explore the structure configurations for 35 subnano Pt_N (N = 12-46) clusters using a first-principles Stochastic Surface Walking (SSW) global search. For each cluster, thousands of structure candidates are collected from a parallel SSW search. This leads to the finding of 20 new global minima in 35 clusters, which reflects the essence of a first-principles global



search for revealing the structure of subnano transition metal clusters. P_{t_N} subnano clusters with *N* being 14, 18, 22, 27, 36, and 44 have higher stability than their neighboring size clusters and are characterized as magic number clusters. These P_{t_N} subnano clusters exhibit metallic characteristics with a diminishing HOMO–LUMO gap, much poorer binding energy (by 1–1.7 eV), and a much higher Fermi level (by 1–1.5 eV) than bulk metal, implying their high chemical activity. By analyzing their structures, we observe the presence of a rigid core and a soft shell for P_{t_N} clusters and find that the core–shell 3-D architecture evolves as early as N > 22. For these core–shell clusters, a good core–shell lattice match is the key to achieve the high stability.

1. INTRODUCTION

Platinum subnano- and nanoparticles are of great importance for their applications in many fields.¹⁻⁷ In heterogeneous catalysis,⁵⁻⁸ for example, subnano Pt particles (from several atoms to 1 nm) exhibit significantly better catalytic performance than large nanoparticles and chunky metals in oxidative dehydrogenation of propane,⁹ electrocatalytic oxygen reduction,^{10,11} and photocatalytic hydrogen evolution.¹² These interesting phenomena are often attributed to the unique geometrical and electronic structures of small Pt clusters. The optimum structure of transition metal clusters, even containing only a few atoms, was long a great challenge to solve for both theory and experiment. Theoretically, this is not least because of the complexity of the potential energy surface (PES) of transition metal particles, which involves both long-range metallic bonding and strong highly directional d-d covalent bondings, in particular, on the particle surfaces. The current understanding on transition metal particles is thus limited due to the overwhelming computational costs of first-principlesbased PES exploration method. More efficient global search methods are thus highly desirable to resolve the structure of transition metal particles and to provide insights into their unique physicochemical properties.

The last 20 years have seen significant efforts to identify the magic size Pt clusters, which are defined as the particles that are thermodynamically more stable than their neighboring sizes. It however turns out to be technically difficult and scientifically controversial. Pt₁₃ and Pt₅₅ are perhaps the two most studied Pt clusters, simply because these two sizes are the magic number in well-studied Lennard-Jones clusters.¹³⁻²⁴ For Pt₁₃, Watari et al. using density functional theory (DFT) calculations first showed that the cuboctahedron structure is more stable than the icosahedron isomer,¹³ the analogous of LJ_{13} . Later studies however found that other low symmetry structures, e.g. a buckled biplanar layered structure, ¹⁴ can be more stable than the cuboctahedron structure. Pt_{13} is now believed to be disordered after the work by Da Silva et al.¹⁵ and Bunau et al.¹⁶ Similarly, for Pt₅₅, the global minimum (GM) was initially proposed to be an icosahedral structure, $^{19-21,25}$ similar to LJ₅₅, ²⁶ but it was soon proved to be incorrect.^{23,27} Apra et al.²³ found that Pt₅₅ has a strong tendency to become amorphous, which has also been confirmed by other groups.^{27,28} It is therefore interesting to ask whether the high-symmetry structures are present as the magic size for Pt subnano particles.

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Using plane-wave DFT calculations, Kumar and Kawazoe²⁹ suggested 6, 9, 10, 14, 18, 22, 27, and 36 as the magic size clusters based on the guessed high symmetry structures. On the other hand, the later study by Tian and co-workers³⁰ found very different magic number clusters, i.e. 15, 18, and 24. In their study, the genetic algorithm is combined with several types of many-body potential, i.e. Gupta-like potential^{31–33} and Sutton–Chen potential,³⁴ for the initial screening of the possible configurations, which were finally examined using DFT calculations with localized basis set. These results imply that the energy spacing between different isomers is generally small for small Pt clusters and the exact GM could be rather sensitive to the candidate structures and the computational method utilized. The global optimization based on first-principles,^{35–37}

although highly computational demanding, is thus highly desirable for resolving the structure of transition metal clusters.

In this work, we utilize the recently developed Stochastic Surface Walking (SSW) global optimization method^{37,38} in combination with spin-polarized plane-wave DFT calculations to investigate the structure of subnano Pt clusters, i.e. Pt_N (N = 12-46). Our structure search, unlike most previous studies, is grounded on first-principles global optimizations that are seeded mainly from unbiased empirical force field global optimization, which has led to the identification of 20 new GMs. By focusing on magic number clusters, we discuss the geometrical structure and the electronic structure of the subnano Pt clusters. Finally, we also discuss the general relationship between the GM and the second-lowest energy minimum (SLM), between the core—shell architecture and the cluster stability.

2. CALCULATION DETAILS

2.1. SSW Global Structure Search. The PES of Pt clusters is explored using a DFT based SSW global structure search (SSW-DFT). The SSW method is capable of surmounting the high barrier on PES and identifying low energy minima. The efficiency of the method for exploring PES has been demonstrated for both aperiodic (molecules,³⁹ clusters⁴⁰⁻⁴²) and periodic (surfaces,⁴³ crystals^{44,45}) systems. The algorithm of the SSW global optimization method can be found in our previous papers^{37,40,41} and also in the Supporting Information. The key SSW parameters utilized are the same with those utilized previously for exploring PES of carbon and boron clusters,^{42,46} i.e. the Gaussian width being 0.6 Å, the number of Gaussian bias potential being 10. The temperature utilized in Metropolis Monte Carlo (MC) is varied from 3000 to 5000 K. The high temperatures are utilized to verify the obtained GM structure since the structure search is less likely to be trapped in local minimum but tends to explore structures with higher energy at higher MC temperature, e.g. 5000 K.

The initial guess structures (seed) of Pt clusters are taken from three possible pools: (i) the global minima from the SSW search based on empirical Gupta force field,^{47,48} which are obtained by extensive SSW exploration from random initial structures for up to 10^5 minima for each cluster size; (ii) the proposed global minima from the literature, mainly from refs 29 and 30; and (iii) the manually constructed high symmetry structures by adding or subtracting atoms of neighboring size cluster (e.g., an octahedron-like structure of Pt₁₈ as initial guess by subtracting one apex atom from octahedron Pt₁₉).

In the SSW search, we in general performed a series of parallel runs (4-10 depending on the system) starting from the initial guess structures, and up to 300 minima are collected at

the first stage, from which the most stable configuration is obtained. Next, we verified the result from the most stable configuration of the first stage and collect another 300 minima. This process is repeated until no more stable configuration is identified at the stage of verification. The symmetry of the cluster is determined according to the previous numerical approach.⁴⁹ For Pt₄₄, where the GM is a high symmetry octahedron, an extensive structure search has been conducted, and up to 4788 minima have been collected to confirm no more stable configuration.

2.2. DFT Calculations. All DFT calculations in combination with the SSW search were performed using the SIESTA package^{50,51} with Troullier-Martins norm conserving pseudopotentials⁵² and numerical local basis sets. The exchangecorrelation functional utilized was at the generalized gradient approximation level, known as GGA-PBE.53 The optimized double- ζ plus (DZP) polarization basis set with extra diffuse function was employed for Pt. The orbital-confining cutoff was determined from an energy shift of 0.010 eV. The energy cutoff for the real space grid used to represent the density was set as 150 Ry. The Quasi-Newton L-BFGS method is used for geometry relaxation until the maximal force on each relaxed atom is less than 0.01 eV/Å. All clusters are placed in large cubic unit cells to allow a large separation (>10 Å) between neighboring images: the unit cell edge is 20 Å for $Pt_{N<40}$, and it increases to 30 Å for $Pt_{N>40}$.

Finally, at least four lowest-lying configurations obtained from the SSW-DFT/SIESTA search were optimized and checked using the spin-polarized plane wave calculations with projected augmented wave (PAW) pseudopotentials, ^{54,55} as implemented in VASP.⁵⁶ The plane-wave kinetic energy cutoff of 400 eV was used, and the exchange-correlation functional utilized was at the generalized gradient approximation level, GGA-PBE.⁵³ We found that these small Pt clusters are generally spin polarized, but the contribution of spin-polarization to the total energy of the Pt cluster is diminished for clusters above Pt₂₉ (<0.06 eV per cluster).

3. RESULTS

Table 1 lists our main results on the most stable structure we have identified for Pt_N clusters (N = 12-46) using SSW-DFT calculations, which includes the energetics, the average coordination of Pt (N_c defined by the first neighbor distance below 3.1 Å), the average Pt–Pt bond length, the magnetic moment of the cluster (Mag), and the symmetry point group (Sym). Following the convention, we term these most stable structures as the GM, although they are only the best available structure from the current searching database and, strictly speaking, not guaranteed to be the true GM. The binding energy of the cluster (E_B) is reference to the bulk Pt metal, which is also compared with the data in the literature, if available.^{29,30} The E_B is plotted against the cluster size N in Figure 1a. In Figure 2, we compile all the structures for the GM (acronym as Na in the figure) and the SLM (acronym as Nb) of Pt_N clusters.

In the 35 Pt_N (N = 12-46) clusters studied, we found 20 new GMs (see Table 1) that are either never reported or more stable than those reported in the previous works, ^{15,29,30,57} including Pt₁₅, Pt₁₇, Pt₂₄₋₂₅, Pt₂₈₋₂₉, Pt₃₀₋₃₉, Pt₄₁, Pt₄₃, Pt₄₅, and Pt₄₆ (also see the structures in Figure 2). About half of these newly identified GM structures are low-symmetry (C_1), implying the PESs of these clusters are complex with multiple low energy structures. For the rest of the Pt clusters, including

Table 1. Properties of the Global Minimum for Subnano Pt_N (N = 12-46) Clusters from the First-Principles SSW Global Structure Search

Ν	$\frac{E_{\rm B}}{({\rm eV})}^{a}$	$\frac{\Delta E^{o}}{(eV)}$	$\frac{\Delta E_{gap}}{(eV)}^{c}$	$N_{\rm cor}^{d}$	BL ^e (Å)	$Mag'(\mu_B)$	Sym
12	3.83	0 ^a	0.01	4.17	2.60	2	C,
13	3.89	0 ^a	0.10	4.46	2.62	2	<i>C</i> ,
14	3.95	0 ^b	0.19	5.14	2.68	0	C_{4v}
15	3.97	0.09 ^c	0.09	5.20	2.68	2	$C_{s}^{\pi \nu}$
16	4.00	0^{b}	0.31	4.88	2.64	4	C_{3v}
17	4.05	0.24 ^b	0.24	4.35	2.61	6	C_s
18	4.11	0 ^{b, c}	0.29	4.33	2.60	6	D_{3k}
19	4.11	0 ^b	0.40	4.42	2.60	6	C_s
20	4.13	0 ^b	0.21	4.80	2.63	4	C_s
21	4.15	0 ^b	0.14	5.62	2.65	6	$C_{2\nu}$
22	4.20	0 ^b	0.30	5.91	2.66	4	D_{5k}
23	4.22	0 ^b	0.18	6.26	2.69	6	D_{5k}
24	4.23	0.30 ^b	0.09	6.25	2.69	6	C_s
25	4.25	0.04 ^b	0.04	4.56	2.60	4	C_1
26	4.30	0 ^b	0.44	4.23	2.56	2	$C_{2\nu}$
27	4.33	0^{b}	0.61	4.00	2.54	6	O_h
28	4.32	/	0.49	4.14	2.56	6	C_s
29	4.33	/	0.18	6.21	2.68	2	C_s
30	4.32	0.16 ^b	0.03	6.40	2.69	2	C_1
31	4.35	0.67 ^b	0.07	6.71	2.71	0	C_1
32	4.37	0.68 ^b	0.13	6.44	2.69	4	C_1
33	4.39	1.28 ^b	0.24	6.73	2.70	4	D_{3k}
34	4.41	1.25 ^b	0.22	6.35	2.68	4	C_1
35	4.42	1.05 ^b	0.24	6.29	2.67	8	$C_{2\nu}$
36	4.45	1.51 ^b	0.13	6.17	2.66	4	D_{3k}
37	4.44	1.27 ^b	0.11	6.54	2.69	2	C_1
38	4.45	1.96 ^b	0.01	6.58	2.69	2	C_1
39	4.46	/	0.54	6.77	2.69	2	$C_{2\nu}$
40	4.47	0 ^b	0.08	7.60	2.74	4	D_{4k}
41	4.49	/	0.03	6.88	2.70	4	C_1
42	4.51	0 ^b	0.13	7.62	2.74	4	D_{4k}
43	4.53	/	0.37	7.63	2.74	4	$C_{4\nu}$
44	4.55	0 ^b	0.08	7.64	2.74	2	O_h
45	4.55	/	0.25	6.80	2.69	2	C_s
46	4.55	/	0.52	6.83	2.70	2	C_1

 ${}^{a}E_{\rm B}$: the binding energy per atom, which is defined with reference to the free Pt atom. With the increase of the cluster size, $E_{\rm B}$ approaches the bulk cohesive energy (cal. 5.54 eV/atom). ${}^{b}\Delta E$: the energy difference between the GM identified in this work and lowest energy structures reported previously (a: Da Silva;^{15,57} b: Kumar;²⁹ c: Wang³⁰). The symbol '/' indicates that the structure is not studied previously. ${}^{c}\Delta E_{\rm gap}$: the energy difference between GM and SLM ($E_{\rm a}$ - $E_{\rm b}$). ${}^{d}N_{\rm cor}$: the average coordination number of Pt. e BL: the average Pt-Pt bond length. f Mag: magnetic moment (μ B). g Sym: the symmetry point group.

 Pt_{14} , Pt_{16-23} , Pt_{26} , Pt_{27} , Pt_{40} , Pt_{42} , and Pt_{44} , our results for the GM are consistent with those reported in the literature.^{15,29,30}

As seen in Table 1, we also analyzed the Pt–Pt bond length and the average Pt coordination number (N_{cor}) for these GM Pt clusters. The Pt–Pt bond lengths (BL) of small clusters, e.g. Pt_N (N < 29) are generally shorter than those of large ones Pt_N ($N \ge 29$): the average BL of Pt_N (N < 29) clusters is about 2.54–2.69 Å, while the average BL of Pt_N ($N \ge 29$) clusters is in the range of 2.68–2.74 Å. The Pt–Pt contraction in ultrasmall clusters is mainly caused by the fact that Pt atoms are generally exposed as surface atoms in the small clusters and the Pt–Pt bond is shortened in response to the reduced



Figure 1. (a) The binding energy $E_{\rm B}$ (data listed in Table 1) of subnano Pt_N clusters (N = 12-46). By fitting $E_{\rm B}$ with respect to N we arrived at $E_{\rm B}^{0} = 7.72642 - 41.8086 N^{-1} + 45.4882 N^{-2/3} - 20.8106 N^{-1/3}$. The inset shows the binding energy of the Pt clusters approach the bulk cohesive energy (cal. 5.54 eV/atom) as the Pt clusters increase. (b) The relative binding energies of clusters calculated by $E_{\rm B}-E_{\rm B}^{0}$. (c) The second finite energy differences (D₂E) of subnano Pt_N clusters, as defined by eq 2.

coordination on the surface. Consistently, due to the low Pt coordination in small Pt clusters we found that their magnetic moments are generally nonzero. We noted that above Pt_{36} , the nonmagnetic ground state becomes energetically nearly degenerate with the magnetic ground state, and thus the spin-polarization does not alter the stability ordering of isomer configurations. For example, for Pt₄₄, the magnetic ground state ($\mu_B = 2$) is only 0.12 meV per atom more stable than the nonmagnetic ground state. In the following, we will elaborate the geometrical and electronic structures of these clusters, particularly, magic number clusters.

3.1. Magic Number Clusters. Knowing the GM structures, we are able to identify the magic number size of the Pt clusters. This is based on a standard energy fitting procedure proposed previously, e.g. Northby et al.,⁵⁸ Lee and Stein,⁵⁹ and Sebetci.⁶⁰ As shown in Figure 1a, we fit a $E_B^{0} \sim N$ curve from the binding energy E_B of the clusters using a polynomial function.

$$E_{\rm B}^{0} = aN^{-1} + bN^{-2/3} + bN^{-1/3} + d \tag{1}$$

In the equation, the fitting parameters, *a*, *b*, *c*, and *d*, are designed to describe the contributions of volume, surface, edge,

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Figure 2. GM (Na) and SLM (Nb) structures of Pt_N (N = 12-46) clusters obtained from the first-principles SSW global structure search. The energy relative to the GM and the symmetry of the clusters are indicated in the parentheses.

and vertex to the energy, respectively. The relative binding energies of clusters as $E_{\rm B}-E_{\rm B}^{\ 0}$ are thus plotted against N in Figure 1b, which shows clearly cluster sizes that are more stable than their neighbors. The other quantity often used to assess the cluster stability is the second finite difference, D_2E , which is the energy released by migrating one Pt atom from Pt_{N+1} to Pt_{N+1} to form two Pt_N clusters, and it is defined in eq 2.

$$D_2 E_N = E_{N+1} + E_{N-1} - 2E_N \tag{2}$$

 E_N is the calculated energy of the Pt_N cluster. In general, a large D_2E would indicate the high stability of the cluster, which should thus be abundant in experiment (e.g., as found from mass spectra). The $D_2E \sim N$ plot is shown in Figure 1c.

The magic number of the Pt clusters can be identified from Figure 1b and c, namely, N = 14, 18, 22, 27, 36, and 44. Among them, only the GM of Pt₁₄ and Pt₄₄ is the face-centered cubic (fcc) packing, which is identical to Pt bulk (In fact, in 35 Pt_N clusters studied only 5 of them (N = 14, 40, 42, 43, 44) are fcc packing). Pt₃₆ has the highest peak in the $D_2E \sim N$ plot and

thus could be the most abundant one among the subnano clusters. Interestingly, these magic numbers except for Pt_{44} have been suggested by Kumar and Kawazoe²⁹ by manually structure enumeration and DFT calculations, despite that the most stable structures in their work are still not correct (see Table 1).

For Pt clusters with N = 12-28 that have been studied extensively in the previous work,^{29,30} the GM structures identified from SSW-DFT for 13a, 14a, 16–23a, and 26–28a are consistent with the best structure reported. However, four new GM structures, i.e. 12a, 15a, 24, and 25a, are identified for the first time in this work. Except for 21a and 25a (C_1 symmetry), all the GM structures in this range have at least one symmetry plane (C_s symmetry).

The large Pt clusters above N = 29 were less investigated previously, apparently owing to the exponentially increased complexity of PES. For the Pt_N clusters in this range, Kumar and Kawazoe²⁹ suggested that the lowest energy structures should be simple cubic packing or fcc packing. However, except for four clusters with the fcc GM structures (40a, 42a, 43a, and



Figure 3. Density of states of Pt_N magic clusters with N = 14, 18, 22, 27, 36, and 44. The energy levels are Lorentzian broadened with a width 0.1 eV. The vertical dashed lines show the Fermi level of the clusters.

44a), most GM structures identified in this work are neither the simple cubic nor fcc structure but mainly low symmetry structures (for example, 30-32a, 34a, 37a, 38a, 41a, and 46a have C_1 symmetry). Among these structures, 30a-32a, 34a, 35a, and 37a are Pt₃₆-like in a column shape, encapsulating a distorted structure unit mimicking the three-layer trigonal prism (18a); 41a, 45a, and 46a are low symmetry structures covered by 6-atom pentagonal pyramids on the cluster surface. The fcc packing is only preferred in Pt₄₂-Pt₄₄.

Electronic Structure of Magic Number Clusters. We have also investigated the electronic structure of the magic number clusters based on the obtained GM. The densities of states (DOS) for the valence electrons are shown in Figure 3. By comparing these DOS, we found that Pt_{14} and Pt_{44} have the similar DOS for their same fcc structure. Similarly, the DOSs of Pt_{18} and Pt_{36} are quite close as they both have a three-layer trigonal prism structure inside with a C_3 (3-fold rotational) axis.

Three general features on the electronic structure of the Pt subnano clusters can be summarized from the DOSs plots. (i) The bandwidth of valence states is wider for the larger clusters, which could be attributed to the orbital mixing of Pt delocalized s/p electrons; (ii) All clusters have a diminishing HOMO-LUMO gap with significant density distribution at the Fermi level. Obviously, Pt clusters exhibit clear metallic characteristics starting from the subnano size; (iii) The Fermi level $(E_{\rm F})$ of them are in the range of -4.0 to -4.6 eV, being much higher than that of the bulk Pt metal (cal. $\sim -5.5 \text{ eV}^{61,62}$). This supports the fact that subnano Pt clusters are chemically very active. Pt₁₈ with a three-layer trigonal prism structure has the highest $E_{\rm F}$ value (-4.07 eV), while Pt_{44} with an fcc packing octahedron structure has the lowest $E_{\rm F}$ value (-4.60 eV), which is expected since the Fermi level should reach to the bulk value with the increase of the cluster size.

3.2. Structural Features of All Clusters. Pt_{12} and Pt_{13} . Pt_{12} is the smallest Pt cluster studied in this work. The GM structure of Pt_{12} (12a) is as that reported previously by Da Silva and his co-workers,⁵⁷ having C_s symmetry. A new structure (12b) with C_s symmetry is slightly less stable (by 0.01 eV) than

12a but better energetically (0.01 eV) than the most stable structure of Pt₁₂ reported by Kumar and Kawazoe.²⁹ The structure of 12b can be obtained by rearranging the position of only one atom of 12a along its C_s symmetry plane. The Pt coordination and the average Pt-Pt bond length in 12a and 12b are about the same. For Pt_{13} , a C_s structure (13a) is identified to be the GM from the DFT-SSW search, which is exactly the lowest energy structure proposed by Da Silva et al.¹⁵ and Bunau et al.,¹⁶ but is 0.33 eV more stable than the most stable structure of Pt₁₃ reported by Kumar and Kawazoe.²⁹ It can be seen that the structure of 13a is very similar to 12a, which can be constructed by adding a four-coordinated Pt atom on the structure of 12a. The SLM of Pt_{13} , 13b (0.10 eV less stable than 13a), has a tetragonal pyramid shape with $C_{2\nu}$ symmetry, which was reported as the GM of Pt₁₃ by Zhang and Fournier.¹⁸ The average Pt coordination in 13b is even larger than that of 13a, but the average Pt-Pt bond length in 13b is 0.03 Å longer (see the Supporting Information).

 Pt_{14} and Pt_{15} . For Pt_{14} and Pt_{15} , very similar GM structures are found, apparently because Pt₁₄ is a magic number cluster. The GM structures of 14a and 15a are tetragonal pyramid (C_{4h}) and capped tetragonal pyramid (C_s) shaped structures, respectively, both belonging to the fcc packing. There are one {100} and 4 {111} facets exposed in the tetragonal pyramid 14a. This structure can be related to 13b by adding an additional Pt atom into the 8 atom plane of 13b and then slightly distorting the structure. The structure of 15a can be obtained by adding an atom on a (111) facet of 14a. Interestingly, the SLMs of both Pt14 and Pt15 have very high symmetry (O_h) . The structure of 14b is a face-centered cube, so does 15b, which can be obtained by adding a body-centered Pt atom in 14b. Comparing these SLM structures with their GM structures, the Pt coordination of 15a is slightly larger than 15b, and it is the same for 14a and 14b. The average Pt-Pt bond lengths of the SLM structures are both slightly (0.01 Å) longer than the GM structures.

 Pt_{16} to Pt_{20} . The most representative structure in this range is the magic number cluster Pt_{18} (see Figure 2). The GM

structure of Pt₁₈ is a perfect (3×6) three-layer trigonal prism with D_{3h} symmetry. This agrees with the results reported before.^{29,30} The SLM identified in this work for Pt₁₈ is however more stable than that from previous work.^{29,30} From our DFT-SSW search, the energy of the SLM of Pt₁₈, a distorted 3×6 structure with C_2 symmetry, is only 0.29 eV higher than the energy of 18a, which reduces significantly the energy gap (0.8-1.2 eV) between the GM and SLM of Pt₁₈ reported by Wang³⁰ and Kumar.²⁹

For the other clusters, the GM structures of Pt_{17} , Pt_{19} , and Pt_{20} (17a, 18a, and 19a) can obtained by removing or adding Pt atoms from the structure of 18a. The GM of Pt_{16} is a trigonal prism isomer (16a) with $C_{3\nu}$ symmetry, which can be described as a plane-sharing composite between a 2 × 6 triangular prism (12b) and a 10-atom tetrahedron. Except for the low symmetry structure of 20b, the SLM structures of Pt_{17-20} are all the distorted structures from their GMs.

 Pt_{21} to Pt_{24} . The GM structures of Pt_{21} , Pt_{22} , and Pt_{23} are consistent with the results reported by Kumer and Kawazoe.²⁹ Among them, Pt_{22} is the magic number cluster. The structure of 21a with $C_{2\nu}$ symmetry can be obtained from the pentagonal bipyramid cage of 22a by removing an atom from the edge. By adding a core atom into the cage of 22a, we can get the structure of 23a. The structures of 22a, 23a, and 23b all have a 5-fold rotational symmetry (D_{5h} or D_{5d}). For $Pt_{24\nu}$ its GM structure can be obtained by adding an atom on the surface of 23b and slightly reconstructing the structure. We noted that the pentagonal bipyramid structure with D_{5h} symmetry of 23a is the smallest GM structure with a core—shell structure, where the core contains only one atom.

 Pt_{25} to Pt_{28} . The GM structure of the magic number Pt_{27} contains a 3 × 3 × 3 cubic unit (3 layers with each layer contains a 3 × 3 square), and it is the representative structure in the range of Pt_{25-28} . This structure has also been suggested by Kumer and Kawazoe.²⁹ It is noticed that the simple cubic structure has been found for $Ru_8^{62,63}$ and $Ir_{12,18}^{36}$ transition metal clusters by experiment and theory. The GM structures of Pt_{26} and Pt_{28} can be obtained by reconstructing slightly Pt_{27} , i.e. removing an apex atom from the Pt_{27} cube to generate Pt_{26} , and adding a capping atom on the terrace of the Pt_{27} cube to generate Pt_{28} . For the GM of Pt_{25} , two atoms less than Pt_{27} , the structure is highly distorted away from the simple cube, and the structure has only C_1 symmetry (as shown in Figure 2).

 Pt_{29} to Pt_{39} . From Pt_{29} to Pt_{39} , the number of core atoms in the GM structure of Pt clusters increases gradually from 2 to 5. There are 2 core atoms in 29a, 3 core atoms in 30a–36a, 4 atoms in 37a and 38a, and 5 atoms in 39a. For Pt_{29} , the GM is a low symmetry structure, being 0.18 eV lower than its cubic-like SLM (29b). For the clusters with 3–4 core atoms, the GM structure of magic number Pt_{36} (36a) is representative, which is a truncated triangular prism, containing a 3-atom core and a 33atom shell with only (111) facets exposed. For the GM and SLM of the nearby clusters (Pt_{29} – Pt_{38}), they all have the similar core—shell structures with mainly (111) facets exposed. For Pt_{39} , its GM structure is a $C_{2\nu}$ structure with a 5-atom core.

 Pt_{40} to Pt_{46} . In this range, the representative cluster is Pt_{44} (44a), an octahedron with fcc packing exposing only (111) facets.^{29,63} In 44a, in total there are six core atoms and 38 shell atoms. The structures of 40a, 41b, 42a, 42b, 43a, and 45b can all be obtained from 44a by removing or adding the apex atoms. For Pt_{41} , Pt_{45} , and Pt_{46} , however, the low symmetry structures turn out to be the GM, being more stable than the fcc packing isomers. This is mainly due to the structural mismatch of the

core and shell. Although these GM structures still expose mainly the (111) facets, their core structures are generally distorted by the shell. It is a 5-atom core with a tetragonal pyramid shape in 41a and a distorted 6-atom core in 46a.

3.3. Core–Shell Structure. The above results show that the core–shell architecture turns out to be a major structural feature for N > 22. By inspecting these core–shell structures, we found that the structure for the core of the Pt_N clusters are relatively simple and belong to several major types, as shown in Figure 4. We summarize the core structures of the GM and



Figure 4. Core structures of subnano Pt_N ($N \ge 21$) clusters.

Table 2. Core Structures of Pt_N Clusters^{*a*}

core structure	GM	SLM					
no core	12–22a	12–14b, 17–19b					
single atom	23–28a	15b, 16b, 20–29b					
linear	29a						
3A	30—36a	30-36b					
4A	37a, 38a	38b					
4B		37b					
5A	39a						
5B	41a	39Ь					
6A	40a, 42–45a	40-45b					
6B	46a						
7A	46b						
See Figure 4 for the notation of core structures.							

SLM identified in this work in Table 2. For these GM and SLM, the single-atom, triangle (3A) and octahedron (6A) are dominant cores, occurring 18, 14, and 11 times, respectively, while the other core structures occur no more than 3 times. This implies that simple, high-symmetry cores are critical to stabilize the cluster.

For the magic number clusters, Pt_{27} , Pt_{36} , and Pt_{44} have the most popular core structures. Pt_{27} has the one-atom core, forming a high symmetry cube. Pt_{36} and Pt_{44} are more interesting, where the symmetry of the core is exactly the same as the symmetry of the shell, which reaches a good lattice match between the core and shell. For example, the GM of Pt_{44} (44a in Figure 2) has a 6-atom octahedron core, and its 38-atom shell has the same O_h symmetry. This suggests that the close-packed core structure becomes dominant in the large size Pt clusters, and the shell has the tendency to structurally match with the core.

For the Pt subnano clusters investigated, the shell structure is generally versatile. When the cluster size increases, the newly incoming atoms often prefer to immerse into the shell of the cluster. It is found that only after the saturation of the shell as a single layer, the core starts to grow. This can explain that the GM structures of small size Pt clusters (N < 28) are often more symmetrical (see Figure 2 shows), but the GM structures of large size Pt clusters are more likely to be asymmetrical and even amorphous-like. Apparently, with a rigid core structure, the continuous increase of shell atoms will lead to the structural mismatch between the core and shell and thus destabilize the cluster. This affects more severely on the stability of large clusters with large cores, where many more likely sites on the shell are present for incoming atoms to occupy.

4. DISCUSSION

4.1. GM and SLM. The energy difference between the GM and the SLM (ΔE_{gap} in Table 1) is generally a good indication for the structure flexibility of the cluster. A large ΔE_{gap} often suggests the high stability of the GM, while a diminishing ΔE_{gap} reflects a large density of structural conformation near GM, a typical feature in the PES of glass-like material.⁶⁴ As shown in Figure 5, ΔE_{gap} of the Pt_N clusters spans from 0.01 to 0.61 eV,



Figure 5. Energy difference between the GM and SLM (ΔE_{gap}) for subnano Pt_N clusters.

and most of them are less than 0.3 eV (28 in total 36 clusters). Among all these clusters, the average $\Delta E_{\rm gap}$ of the magic clusters (0.27 eV) is slightly higher than the other clusters (0.20 eV), but there was no clear relationship between the $\Delta E_{\rm gap}$ and the cluster size. The largest energy gap occurs at the magic number cluster Pt₂₇ (between 27a and 27b). This indicates that it needs to overcome a high energy barrier to reconstruct the GM to the SLM, and thus the cubic Pt₂₇ has a high kinetic stability. For the other magic number clusters, $\Delta E_{\rm gap}$ of Pt₁₄ and Pt₂₂ are larger than the nearby clusters, but the $\Delta E_{\rm gap}$ of Pt₁₈, Pt₃₆, and Pt₄₄ are no better than their neighborhoods.

It should be mentioned that some nonmagic clusters, such as Pt_{28} , Pt_{39} , and Pt_{46} , also have a relatively large ΔE_{gap} (≥ 0.49 eV). By inspecting the structures, we found that the GM and SLM of Pt_{28} belong to two distinct funnels, the cubic and pentagonal funnels, respectively. Similarly, the GM and SLM in Pt_{39} and Pt_{46} are also very different, having different core structures. These imply that the distinct structure of the GM and SLM, e.g. belonging to different funnels on the PES, may help to increase ΔE_{gap} . **4.2. Coordination Number of Pt.** As 20 new GM

4.2. Coordination Number of Pt. As 20 new GM structures of Pt clusters are found in this work, we are at the position to revisit the structure features in the structure evolution of Pt clusters. To this aim, we plot the average Pt coordination number $N_{\rm cor}$ for the GM and SLM of the Pt clusters against the cluster size N in Figure 6. The trend between $N_{\rm cor}$ and the cluster size N is fitted as a linear line (blue dotted) to represent the expected $N_{\rm cor}$ for the clusters.



Figure 6. Average coordination number $N_{\rm cor}$ of the GM and SLM for subnano Pt_N (N = 12-46) clusters. The dashed blue line shows the general trend for the increase of $N_{\rm cor}$ with the increase of the cluster size. The blue arrows indicate the magic clusters.

Let us first focus on the $N_{\rm cor}$ of the magic number clusters. As marked by arrows in Figure 6, N_{cor} of Pt₁₄, Pt₂₂, and Pt₄₄ are above the blue dashed line, indicating more Pt-Pt bonds are present. By contrast, less Pt-Pt bonds are present in Pt₁₈, Pt₂₇, and Pt₃₆. This interesting observation is related to the structure type of these magic clusters, as rationalized below. Both GM of Pt₁₄ and Pt₄₄ are bulk-like fcc packing, and the GM of Pt₂₂ is a pentagonal bipyramid, which is of icosahedral type. We note that the GM of most empirical potential clusters^{26,65} is associated with these two types of structures. Because the coordination number for the bulk atom in fcc truncated octahedron and icosahedron are both 12, N_{cor} of these magic clusters (Pt_{14} , Pt_{22} , and Pt_{44}) are above the expected N_{cor} in the fitted N_{cor} -N trend. On the other hand, the GM of Pt₁₈ and Pt₂₇ is a triangular prism and a simple cubic packing cube, respectively. The GM of Pt₃₆ can be viewed as the combination of a triangular prism and icosahedral caps. The N_{cor} s of the bulk atom in the triangular prism and simple cubic packing cube are only 8 and 6, respectively, which lead to the low N_{cor} for these magic number clusters.

For all the clusters, we can summarize three features for the Pt coordination with the increase of the cluster size:

(i) $N_{\rm cor}$ generally increases with the increase of size (the dotted line in Figure 6

(ii) The magnitude of $N_{\rm cor}$ cannot be used to distinguish GM from SLM.

(iii) For small clusters nearby the magic number (e.g., N = 18-21; N = 25-28), their N_{cor} tends to deviate largely from the general $N_{cor}-N$ trend.

The feature (i) is not surprising as it simply states that the stability of the cluster is proportional to the number of the bonds formed in the particle. This is a geometrical reflection of the increase of the binding energy per atom with the increase of the cluster size (Figure 1a).

For the feature (ii), although $N_{\rm cor}$ of the GM of the small clusters (from Pt₁₂ to Pt₂₀) is equal to or slightly larger than the SLM, $N_{\rm cor}$ of the GM of the larger clusters can be either much larger or smaller than the SLM. This is because the $N_{\rm cor}$ is closely related with the cluster structure, e.g. fcc packing or simple cubic packing, which however varies significantly with the change of the cluster size. For small clusters, e.g. Pt₂₇, the structure with a very low coordination number can also be highly stable.

The feature (iii) is closely related to the feature (ii). The two valleys in the $N_{\rm cor}$ -N plot are centering at Pt₁₈ and Pt₂₇, two magic number clusters. As addressed above, the clusters nearby the magic number are generally similar in their structures and the GM of Pt₁₈ and Pt₂₇ has particularly low $N_{\rm cor}$ due to the triangular prism and the simple cubic packing structure. It

should be emphasized that such a sharp reduction of the average coordination number around the magic clusters has not been found for Pt clusters determined using the Sutton–Chen⁶⁵ potential and also the Lennard-Jones²⁶ potential clusters. It indicates that the short-range d–d covalent bonding plays a critical role in stabilizing the low coordinated Pt₁₈ and Pt₂₇ clusters, which are poorly described in the empirical potential models.

5. CONCLUSION

This work represents a comprehensive survey on the structure of subnano transition metal particles, as presented by Pt. By using DFT based SSW global structure optimization, we identify all GM structures for Pt clusters from Pt_{12} to Pt_{46} , and 20 of them are not reported previously. We demonstrate that an accurate energetic description is essential in order to distinguish many energetically low-lying structural conformations on the complex PES of transition metal clusters. The structural versatility of transition metal clusters shown here provides a solid theoretical foundation to understand the unique physicochemical properties of Pt subnano clusters. Our main results are outlined in the following.

(i) The magic number clusters are identified at the size of 14, 18, 22, 27, 36 and 44, which generally have high symmetry (one C_{4v} : Pt₁₄, two D_{3h} : Pt₁₈ and Pt₃₆, one D_{5h} : Pt₂₂, and two O_h Pt₂₇ and Pt₄₄). This indicates strongly that even for transition metals the high symmetry magic cluster is also present.

(ii) The Pt_N subnano clusters exhibit obvious metallic characteristics with a diminishing HOMO–LUMO gap. They have much poorer binding energy (by 1–1.7 eV) and a much higher Fermi level (by 1–1.5 eV) than bulk Pt metal. It suggests that Pt subnano clusters are chemically very active.

(iii) The core-shell 3-D architecture is an important feature even in subnano clusters, which starts to appear as early as N > 22. Compared to the versatile shell, the structure of the core is relatively simple: the single atom, triangle, and octahedron are three most common cores. To achieve a high stability, a good core-shell lattice match is the key.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.6b00556.

Algorithm of the SSW global optimization method; comparison of the bond number (BN) and average bond length (BL) of the GM and SLM; XYZ coordinates for the GM of Pt_N clusters (PDF)

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Notes

The authors declare no competing financial interest.

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