Nanowire Self-Assembly

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On the Mechanism of Formation of Metal Nanowires by Self-Assembly**

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The past decade has witnessed the birth of a new type of materials, the building blocks of which—contrary to common atoms—are so large that they already belong to the nanoscale realm. These nanoscale building blocks can be of very different nature, including metals[1] semiconductors,[2] inorganic complexes,[3] and biological substances.[4] Interaction between such moieties, either induced by humans or taking place spontaneously by self-assembly, can lead to the formation of one- to three-dimensional mesostructures.[1] Nanowires are a special type thereof, which due to some unique properties are already the basis of new technologies in such important fields as electronic devices[5] and sensors.[6]

Some metallic nanowires consist of rather well-defined particles.[5,7] For instance, individual Pd nanoparticles of about 120 nm in size are clearly visible in scanning electron microscopy (SEM) images[7] of Pd nanowires that self-assembled during electroless deposition on a stainless-steel support.[8] Although the detailed structure of the particles is not resolved, SEM images suggest that Pd_n particles with face-centered cubic (fcc) packing and cuboctahedral shape are adequate models. Indeed, bulk-like fcc packing of metal atoms is already found for Pd clusters with more than 100 atoms.[9] Nanocrystallites of such size commonly exhibit (111) and (100) planes.[10] A very important finding in these experiments is that even if assembly is initiated on the steel support, the resulting nanostructures follow certain growth directions without tracking defects present on the substrate. This implies that the Pd–support interaction does not govern nanowire formation in the initial stage, which is the subject of this work.

To understand the microscopic details of the self-assembly process leading to the formation of these Pd nanowires, a clear picture of the interaction between the nanoparticles is needed. We investigated the interaction between cuboctahedral Pd_n particles of increasing size, up to 225 atoms and about 2 nm in diameter, using first-principles density functional (DF) calculations (see Methods for details). We considered linear arrays of uniform particles Pd_n ($n = 38$, 79, 140, 225).

First, each nanoparticle was placed in a large-enough cubic box to prevent interaction between them. Then, the Pd_n–Pd_n distances were gradually reduced in one direction. We chose to build the infinite one-dimensional chain by approach of two opposite (100) facets of nearby particles (Figure 1). This choice is based on the expected more-reactive character of the atoms in these facets, which is confirmed by our test calculations.[11] Moreover, a notable part of the network structures detected by SEM exhibits nodes,[7] where the nanowires are crossed perpendicular to each other, an arrangement which is compatible with interactions via (100) facets, normal to the growth direction of the nanowire, but which is not compatible with interactions via (111) facets.

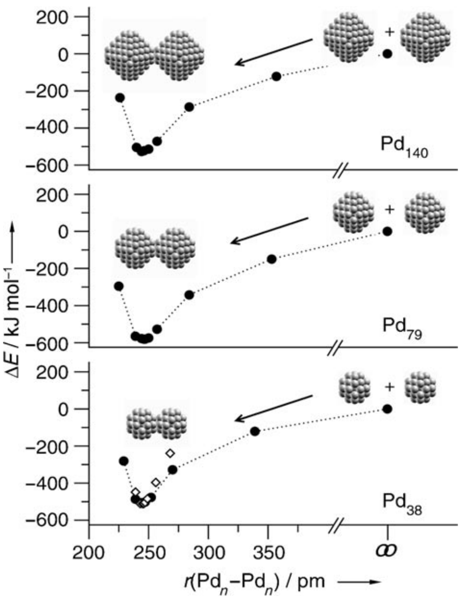

Figure 1. Interaction energy ΔE(VWN) of Pd_n clusters ($n = 38$, 79, 140) as a function of the distance $r(Pd_n–Pd_n)$ during formation of $(Pd_n)_x$ nanowires through the (100) facets for partially (●) and fully optimized (◇) interacting clusters. Dotted lines are guides to the eye.

The resulting model nanowires resemble the experimentally studied Pd nanowires formed of larger species.[7]

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Previous work[9,12,13] showing that metal particles with about 100 atoms upwards exhibit properties scalable to the bulk justifies their use as computationally tractable models of much larger species. In these nanowires the Pd_n moieties act as "designer atoms" with tunable properties and thus play the role of conventional atoms in common chemical structures. Herein we show that the elasticity of metal particles is a key to understanding the mechanism of self-assembly. On the other hand, at equilibrium the local character of the strong interparticle interactions is demonstrated. In the nanowires, rather large particles are required for cluster-size convergence of the interaction energy.

An important issue is alteration of the atomic structure of the interacting particles as the distance between them is reduced and the nanowire is formed. Ideally, one would allow for full geometry reoptimization at each distance between centers of the neighboring clusters, defined by the axial lattice parameter. However, for the quite large nanoparticles studied, the necessary computational resources are excessive even for modern supercomputers. In fact, DF calculations on the Pd_{225} particle are at the limit of contemporary computational facilities.

For the Pd_{38} nanoparticle, the geometry was completely relaxed at each point of nanowire formation ("all-relaxed", Table 1, Figure 1). In another approach to geometry optimization, only the presumably most active Pd_4–Pd_4 atoms of the interacting (100) facets were allowed to relax from their positions in fully optimized single particles ("relaxed", Table 1). For the nanowire $(Pd_{38})_x$ featuring the smallest building block, the nearest distances $r(Pd_{38}–Pd_{38})$ obtained using the all-relaxed and relaxed schemes are nearly the same (245.8 and 244.8 pm, respectively). Moreover, the corresponding interaction energies per Pd_{38} moiety differ by only 4 kJ mol^{-1}. Thus, at the nanowire equilibrium, the interaction between Pd_{38} monomers is essentially quantitatively described already by merely allowing for geometry reoptimization of the Pd_4–Pd_4 subsystems. For the nanowires formed from larger Pd_n building blocks, the effect of the full geometry relaxation is expected to be even smaller; therefore, we refrained from studying them at the all-relaxed level. Note, that even using the totally unrelaxed ("fixed", Table 1) geometry of Pd_n moieties, fully optimized as single particles, allows one to approximate equilibrium distances and interaction energies in the nanowires rather accurately.

Table 1: Equilibrium distances between Pd_n units [pm] and interaction energies per Pd_n unit [kJ mol^{-1}] in $(Pd_n)_x$ nanowires.[a]

Nanowire	$r(Pd_n–Pd_n)$	ΔE(VWN)	ΔE(PW91)
$(Pd_{38})_x$			
fixed[b]	245.0	496	322
relaxed[c]	244.8	505	365
all-relaxed[d]	245.8	509	369
$(Pd_{79})_x$			
fixed[b]	246.0	578	392
relaxed[c]	246.1	581	403
$(Pd_{140})_x$			
fixed[b]	245.0	520	334
relaxed[c]	244.4	526	336
$(Pd_{225})_x$			
relaxed[c]	245.7	545	360

[a] $r(Pd_n–Pd_n)$: equilibrium distance between the nearest atoms of the Pd_4 subunits of two Pd_n monomers approaching each other in the $(Pd_n)_x$ array; ΔE(VWN) and ΔE(PW91): VWN and PW91 Pd_n–Pd_n interaction energies per Pd_n cluster, respectively. [b] Structure of the interacting clusters kept fixed as optimized for the isolated species. [c] As in [b], but atomic coordinates of the Pd_4 subunits ((100) facets) of each cluster facing the approaching Pd_n neighbors were allowed to relax. [d] Geometry of the interacting clusters was fully reoptimized.

The first question concerning the structure of the Pd nanowires is convergence of the equilibrium distances $r(Pd_n–Pd_n)$ and the interaction energies ΔE per Pd_n particle as a function of particle size (Table 1). Variation of the distances $r(Pd_n–Pd_n)$ over the whole range of systems under scrutiny is very small (± 1 pm). This implies a local character of the Pd_n–Pd_n interactions in the nanowires. On the other hand, energies of interaction with metal nanoparticles are known to be much more sensitive to their global properties and size than the distances.[13] Indeed, the variations in binding energy between the arrays composed of relaxed clusters are notable, for example, ΔE(PW91) values (PW91: Perdew–Wang 91) change by 38 kJ mol^{-1} from Pd_{38} to Pd_{79} and by -67 kJ mol^{-1} from Pd_{79} to Pd_{140}. This dependence of energy on the number of atoms is a clear manifestation of the limited size of the interacting particles. It is corroborated by a rather small energy change of only 24 kJ mol^{-1} from Pd_{140} to Pd_{225}; this value can be considered to be an indication of approaching size convergence. Thus, the convergence of the ΔE values with cluster size requires the building blocks to be at least as large as Pd_{140}; the same picture emerges from the ΔE(VWN) values (VWN: Vosko–Wilk–Nusair). This particle size is larger than that for converged adsorption energies for probe molecules on Pd nanoparticles,[13] for which species with about 80 Pd atoms were concluded to be sufficiently large.

The cluster–cluster energy ΔE(PW91) in the nanowires formed via Pd_4 subunits for the largest clusters Pd_{140} and Pd_{225} is 340–360 kJ mol^{-1} or 85–90 kJ mol^{-1} per Pd–Pd bond. The latter value is about three times larger than that for a Pd–Pd bond in the bulk metal;[13] this reflects a low coordination number of the Pd atoms in the interacting Pd_4 fragments. For two single square Pd_4 moieties interacting in the same way the energy per Pd–Pd bond is 79 kJ mol^{-1}, in line with a predominantly local character of Pd_n–Pd_n bonding. Note that mutual rotations of the Pd_n units in the nanowires do not appear to alter the interaction mechanism.[14]

The second important issue is the influence of nanowire assembly on the electronic structure of Pd_n clusters and its dependence on cluster size. Total density of state (DOS) plots of isolated Pd_n clusters and of their chain at equilibrium (not shown) do not reveal any noticeable difference. This is one more indication of a rather local character of the interactions, which leaves more-distant parts of the interacting nanoparticles almost unperturbed. To make the effect visible, we examined DOS plots projected (PDOS) on the two sets of Pd_4 atoms of each cluster directly involved in nanowire formation (Figure 2); due to the reduced coordination number of the Pd_4 atoms these PDOSs are rather different from the DOS

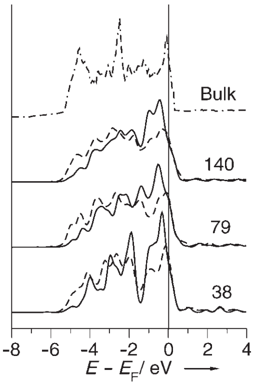

Figure 2. PDOSs of Pd_4–Pd_4 atoms on the (100) facets of Pd_n clusters ($n=38$, 79, 140) which directly take part in the formation of model nanowires $(Pd_n)_x$. Solid lines: isolated clusters. Dashed lines: clusters at the equilibrium distances in the nanowires. The DOS plot calculated for bulk Pd is also shown (dash-dotted line). Energies are given with respect to the Fermi level E_F.

plot of bulk Pd. The most significant effect of nanoparticle aggregation in nanowires on the PDOS is a considerable decrease in the number of states slightly below the Fermi level with a concomitant increase in the energy range of −2 to −5 eV. The latter are bonding states formed by the neighboring interacting clusters, and thus the PDOS features nicely reflect the chemical bonding that keeps the nanoparticles together in the nanowires.

A distinctive feature of the Pd_n building blocks of the Pd nanowires compared to common atoms is that these Pd_n units can alter their structure, for instance, by deformation due to interactions in the nanowire. It is instructive to examine peculiarities related to such a new degree of freedom in more detail.

We characterized cluster deformation by the distances between the most remote Pd atoms in equivalent positions along the array axis, r_a, and perpendicular to it, r_p. In line with previously discussed results, the deformation of clusters in the nanowires at equilibrium is negligible. Nevertheless, at intermediate distances, when Pd_n clusters begin to interact with their axial neighbors and the cluster–cluster distances shrink (see Figure 1), cluster deformation becomes noticeable, especially for the nanowires composed of the smaller species. Calculations on the partially relaxed $(Pd_{38})_x$ array at intermediate distances between centers of nearby clusters of 1.071 nm (axial lattice parameter) result in $r(Pd_{38}–Pd_{38}) =$ 270 pm and a deformation of $r_a/r_p = 800/729$. Fully relaxed clusters exhibit considerably stronger deformation (852/717) and basically the same bond length of $r(Pd_{38}–Pd_{38}) = 268$ pm but at significantly longer distances between the cluster centers (1.121 nm). This is a clear manifestation of noticeable elasticity of interacting metal nanoparticles.

Such elasticity also clarifies a seemingly counterintuitive result (Figure 1, bottom panel) that at $r(Pd_{38}–Pd_{38}) \approx 270$ pm the array built of fully relaxed clusters appears to be less stable than that formed from partially relaxed ones. In fact, in Figure 1 we plot only the distances $r(Pd_n–Pd_n)$, which become erroneous for comparison due to different degrees of the deformation taken into account at the fully and partially relaxed levels of the geometry optimization (see above; the distances between centers of the nearby clusters at $r(Pd_{38}–Pd_{38}) \approx 270$ pm differ by about 50 pm).

When Pd_n blocks in the nanowires become larger (Figure 1, middle and upper panels), the dimension r_p remains unchanged to within 1 pm over the whole range of cluster–cluster contacts, from "infinitely" long to equilibrium. This implies that the spatially limited axial interaction between Pd_n particles with $n \geq 79$ solely affects part of their atoms. In other words, more-distant surface atoms in the clusters with $n \geq 79$ do not "communicate" with each other. The maximum r_a values calculated for the $(Pd_{79})_x$ and $(Pd_{140})_x$ arrays are 1.157 and 1.529 nm, respectively, both at $r(Pd_n–Pd_n) \approx 284$ pm, and the corresponding distances between centers of the nearby clusters are 1.441 and 1.814 nm. The maximum absolute cluster deformation values $r_a - r_p$ are very similar for these two nanowires (40–41 pm), which indicates size convergence of structural parameters of the arrays under scrutiny.

An important finding is that the nanoparticles "feel" the presence of their neighbors at quite long distances of about 375 pm (compare $r(Pd–Pd) = 275$ pm in the bulk). This interaction not only governs nanowire formation by self-assembly but is also related to the phenomenon of particle sintering, for example, in supported metal catalysts.[15] In this sense, sintering is a particular type of (undesirable and uncontrolled) self-assembly process. Furthermore, one can speculate that the pronounced capability of Pd nanoparticles to be easily locally deformed is the origin of the slight curvature experimentally detected for some Pd nanowires.[7]

In summary, motivated by the innovative preparation of Pd nanowires,[7] we computationally studied the structure and bonding mechanism of one-dimensional arrays made of Pd nanoparticles of increasing size, up to Pd_{225}. Using a supercell DF approach we analyzed the evolution with size of structural parameters and of the interaction energy between the clusters leading to the formation of Pd nanowires which mimic those prepared experimentally. We demonstrated that the convergence of the interaction energy requires larger particles (Pd_{140} or Pd_{225}) than those of about 80 Pd atoms, previously shown to be sufficient for yielding converged adsorption energies. Structural perturbation of the nanoparticles in the arrays at equilibrium is shown to be small, whereas at intermediate cluster–cluster distances particle deformation is noticeable and plays a key role in the self-assembly process. Peculiarities of the nanoparticles as building blocks compared to atoms, such as their elasticity and tunable size-dependent properties, are quantified. We also outlined implications of the cluster–cluster interaction for the sintering of nanoparticles, a common problem in catalysis by supported metals.

Metal particles of the studied size and shape can be considered as precursors of the ligand-stabilized quantum dots that are widely used chemical building blocks of nanomaterials with fascinating properties.[16] Thus, this study also contributes to bridging the gap between the contemporary simplified theoretical description of assemblies of quantum dots[17] and the still-remote target of their strict quantum mechanical treatment.

Methods

The DF calculations have been carried out with the Vienna ab initio simulation package (VASP)[18] by using local density (LDA) and generalized gradient (GGA) approximations. The VWN exchange-correlation functional was employed for the LDA calculations,[19] and the PW91 functional for the GGA calculations.[20] A plane-wave basis set with kinetic energy up to 415 eV (250 eV for Pd_{225}) was used. The effect of the Pd $1s^2$–$4p^6$ core electrons on the valence electron density was taken into account by using the projector augmented wave method.[21] All calculations were performed at the Γ k-point. As justified elsewhere,[13] reported geometries are optimized at the LDA level; the GGA energies for these were computed in a single-point fashion. LDA optimization of bulk Pd leads to r(Pd–Pd) = 273 pm, close to the experimental value of 275 pm; the GGA value is notably longer (r(Pd–Pd) = 281 pm). The LDA cohesive energy per Pd atom in the bulk of 485 kJ mol^{-1} is strongly overestimated with respect to the experimentally determined 377 kJ mol^{-1}. The GGA energy computed in a single-point fashion at the VWN optimized bulk structure is much more accurate (358 kJ mol^{-1}).

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