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Sub-nanometer dimensions control of core/shell nanoparticles prepared by atomic layer deposition

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Abstract

Bimetallic core/shell nanoparticles (NPs) are the subject of intense research due to their unique electronic, optical and catalytic properties. Accurate and independent control over the dimensions of both core and shell would allow for unprecedented catalytic performance. Here, we demonstrate that both core and shell dimensions of Pd/Pt core/shell nanoparticles (NPs) supported on Al₂O₃ substrates can be controlled at the sub-nanometer level by using a novel strategy based on atomic layer deposition (ALD). From the results it is derived that the main conditions for accurate dimension control of these core/shell NPs are: (i) a difference in surface energy between the deposited core metal and the substrate to obtain island growth; (ii) a process yielding linear growth of the NP cores with ALD cycles to obtain monodispersed NPs with a narrow size distribution; (iii) a selective ALD process for the shell metal yielding a linearly increasing thickness to obtain controllable shell growth exclusively on the cores. For Pd/Pt core/shell NPs it is found that a minimum core diameter of 1 nm exists above which the NP cores are able to catalytically dissociate the precursor molecules for shell growth. In addition, initial studies on the stability of these core/shell NPs have been carried out, and it has been demonstrated that core/shell NPs can be deposited by ALD on high aspect ratio substrates such as nanowire arrays. These achievements show therefore that ALD has significant potential for the preparation of tuneable heterogeneous catalyst systems.

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Keywords: atomic layer deposition, core/shell nanoparticles, catalysis

(Some figures may appear in colour only in the online journal)

Introduction

Bimetallic nanomaterials garner much attention because they have potential applications in a large number of technologies in the fields of electronics [1, 2] and catalysis [1–3]. The ability to precisely control the size, composition and structure of metallic nanoparticles (NPs) is of high importance in order to synthesize efficient nanocatalysts [4, 5]. In this light, bimetallic core/shell NPs have attracted significant interest in the last few years [6, 7]. When compared to their alloyed counterparts or to mixtures of monometallic NPs, core/shell

NPs often show improved catalytic properties [6, 8]. For example, Pd core/Pt shell (Pd/Pt) NPs 3–6 nm in diameter synthesized by wet chemistry are known to exhibit excellent catalytic performance for oxygen reduction and for methanol electro-oxidation, which are two key reactions in methanol fuel cells [9–12]. The ability to nanotailor the core and the shell dimensions would further extend control over the NP design. This opens up new opportunities for technologies involving nanocatalysts [13–15]. For example, the core diameter is known to affect the durability [16], whereas the shell thickness has a strong influence on the overall performance of

the nanocatalyst [17]. Furthermore, placing expensive and scarce materials as an (ultra)thin shell on top of a less expensive core material can lead to a more efficient and hence a more economic use of scarce materials [11].

Various wet chemistry routes, such as impregnation or ion exchange, exist to produce supported bimetallic nanoparticles, and subsequent catalysis experiments on the resulting particles have repeatedly shown the added value of the core/shell morphology [6, 8, 18–21]. Although these wet chemistry techniques show very promising results, they also have their particular limitations. For example, purification from the wet chemicals can be elaborate, and precise control of the shell thickness remains challenging to achieve [21]. Therefore, it is relevant to explore new routes for the preparation of core–shell NPs. In this paper we will present an alternative route for the synthesis of these particles using ALD.

ALD is a thin film deposition technique based on the cycle-wise and alternate pulsing of precursor and reactant gases to a reactive surface. During the first half-cycle, the surface is exposed to the precursor molecules that adsorb on the surface through self-limiting chemical reactions. The surface becomes saturated with precursor molecules typically after a few seconds of exposure. Subsequently, the excessive amount of precursor and the reaction products generated in the half-cycle are purged out of the reactor. The second half-cycle consists of the introduction of the co-reactant, which reacts with the surface species generated in the first half-cycle. This occurs again in a self-limiting way, and after the second half-cycle the initial surface conditions before the first half-cycle are re-established. Subsequently, the reactor is purged again to remove the excess of co-reactant and the reaction products. This completes the cycle resulting in the deposition of a submonolayer of material. The targeted film thickness can be reached by repeating the cycles. Consequently, ALD is known for providing ultimate control of the thin film thickness for many materials [22, 23]. Moreover, the self-limiting surface chemistry allows for an excellent conformality and superior uniformity.

The layer-by-layer growth holds during steady state film growth by ALD. In the initial stage of film growth, however, the process behaves less ideally. More prominently, the deposition of metals by ALD on certain surfaces is known to start with the formation of islands instead of a full layer, mainly because of the difference in surface energies between the deposited metal and the support [24]. Hence, turning this drawback into an opportunity, ALD can also be considered as a new route for the synthesis of metallic NPs [25]. It allows for the deposition of highly dispersed NPs on high aspect ratio substrates [26, 27], which is very relevant for heterogeneous catalysis applications [26, 28, 29]. Various highly dispersed NPs of platinum group metals, such as Ru [30], Ir [31], Pt [27] and Pd [32], have been synthesized by ALD recently, and it has been demonstrated that their diameter can be controlled at the nanometer-level by simply tuning the number of ALD cycles applied. The composition of the NPs can be tuned as well. For example, bimetallic Pt–Ru alloyed NPs were synthesized by alternating between Ru ALD and Pt

ALD cycles [33, 34]. Moreover, by placing alloyed Pd–Pt NPs in a reducing environment, segregation could be established, leading to Pt/Pd core/shell NPs [35]. The core/shell structure was obtained by de-alloying because a Pd-rich shell is thermodynamically favored in a reducing environment. As proof for their catalytical performance, these core/shell NPs have been used for propene dehydrogenation [35].

De-alloying is an indirect method for preparing core/shell NPs for which the sub-set of combinations that can be realized is governed by thermodynamics. To gain freedom in the selection of core and shell metals, we presented a proof-of-concept method that allows for the deposition of supported bimetallic NPs with a controlled core/shell structure entirely by ALD [36]. This innovative method is a two-step process that makes use of the island growth during the initial stage of metal ALD in order to deposit the core material and of a selective ALD process to cover these cores with a shell of another metal. We presented and reported this general strategy by synthesizing supported Pt/Pd and Pd/Pt core/shell NPs on metal oxides surfaces [36]. Lu *et al* recently adopted and extended this method by preparing core/shell NPs with different combinations of noble metals, including Pd, Pt and Ru supported on metal oxides [37]. Figure 1(a) schematically illustrates the concept for the Pd/Pt core/shell system. Figure 1(b) is an atomic resolution scanning transmission electron microscopy (STEM) image clearly displaying the core/shell morphology of the NPs. Figure 1(c) presents an energy-dispersive x-ray spectroscopy (EDS) mapping of an ensemble of Pd/Pt core/shell structured NPs synthesized using this approach. The EDS mapping shows that Pd (in green) is confined to the centre of the NPs, while Pt (in red) is best visible at the NPs' edge in this 2D projection of the particles.

The island growth on oxide substrates, resulting in the NP cores, can be attributed to the difference in surface energy between the metal and the oxide [24] and is therefore relatively well understood and established [25, 38, 39]. This is however less the case for the selective ALD process used for shell growth. It has been found that the area selectivity of an ALD process toward specific materials, such as noble metals, can be achieved by tuning the process parameters, e.g. the temperature [40], the pressure [41], the nature of the co-reactant or combinations thereof [36, 37]. Key for these selective ALD processes of noble metals, such as Pt and Pd, is their catalytic activity. The selectivity stems from the dissociative chemisorption of co-reactant molecules on their surface, which does not occur on the surface of the support material [41, 42]. For example, during Pt ALD, oxygen atoms are created on the Pt surface from the dissociation of O₂ gas, which is used as a co-reactant. These oxygen atoms can decompose incoming MeCpPtMe₃ molecules during the precursor half-cycle and subsequently remove organic ligands from the surface-adsorbed species [43]. The fact that dissociative chemisorption of O₂ does take place on all platinum group metals but not on oxide support material is exploited to obtain area-selective deposition. For example, Pt can deposit selectively on Pd because Pd does dissociate O₂, while an Al₂O₃ support does not. Another important aspect for

Figure 1. (a) Schematic illustration of the two-step ALD process to deposit core/shell NPs of Pd/Pt. (b) HAADF-STEM image and (c) EDS mapping of Pd/Pt core/shell NPs (150 cycles Pd; 50 cycles Pt) on an Al_2O_3 -covered Si_3N_4 TEM window.

selective ALD of Pt is the fact that the nucleation of Pt on oxides can be controlled by the O_2 exposure [41, 42], as also has been done in the current work.

In the work on the synthesis of core/shell NPs using selective ALD published thus far [36, 37], the general strategy—successive island growth and selective growth—has been presented. However, the level of control of the dimensions of the core and the shell of NPs that can be achieved has not explicitly been addressed yet. Therefore, in this work, we here provide proof that it is possible to precisely nanotailor the dimensions of the core and shell separately. In addition, initial studies on the stability of these core/shell NPs at elevated temperatures have been carried out, and the possibility to prepare core/shell NPs on high aspect ratio substrates, such as nanowire arrays, is demonstrated as well.

Experimental section

The NPs have been prepared in an open-load ALD reactor equipped with a remote plasma source, described in detail elsewhere [44]. The precursors, methylcyclopentadienyl-(tri-methyl)platinum (MeCpPtMe_3 , 98%) and palladium hexafluoroacetylacetonate ($\text{Pd}(\text{hfac})_2$, 99%), were obtained from Sigma-Aldrich and were used as received. The substrates used were Si_3N_4 TEM windows covered by 3 nm Al_2O_3 prepared

by ALD. In one experiment, the core/shell NPs were also deposited on a substrate with an array of GaP nanowires [45] (diameter is 140 nm) in which the nanowires were covered by a 5 nm Al_2O_3 prepared by ALD. This substrate was selected as a first demonstrator for the deposition of core/shell nanoparticles on high aspect ratio nanowires because of its well-defined topography and the relatively easy sample preparation route for TEM inspection; the nanowires can easily be broken off from the substrate and collected on a carbon support film.

The work focuses on Pd/Pt core/shell NPs because the narrow size distribution obtained using this arrangement [36, 46] allows for the accurate investigation of the effect of the core dimension on the shell growth. In addition, the contrast between the core and the shell during Z-contrast STEM analysis is high using this combination of metals. Two series of experiments have been carried out. First, we fixed the Pd core diameter and varied the shell thickness in order to study the shell growth. Next, a series of samples with various Pd core sizes and constant Pt shell radii has been prepared in order to study the effect of Pd core diameters on the shell growth properties. Z-contrast STEM analysis combined with surface science and catalysis literature reports allowed us to gain more insight into the selective ALD process for shell growth. This understanding allowed us to establish the conditions for the controllable synthesis of core/shell NPs.

To deposit the Pd cores, a plasma-assisted ALD process employing Pd(hfac)₂ dosing with subsequent H₂ plasma and O₂ plasma exposure at 100 °C has been used [46]. The ALD precursor step consisted of 3 s of Pd(hfac)₂ dosing with Ar as a carrier gas, followed by a 5 s pump step. Subsequently, H₂ gas at a pressure of 7.5 mTorr was dosed for 2.5 s, followed by a H₂ plasma of 5 s at 100 W. This was followed by O₂ gas exposure for 1 s at a pressure of 7.5 mTorr before an O₂ plasma was applied for 1 s at 100 W. This O₂ step was separated from the H₂ step by a pump step of 6 s. Finally, the reactor chamber was pumped down for 8 s to complete the ALD cycle.

To deposit the Pt shell, the Pt ALD process was tuned such that selective growth of Pt on Pd NPs was obtained without any growth on the oxide surface. The ALD process was based on MeCpPtMe₃ and O₂ gas dosing at 300 °C, as developed by Aaltonen *et al* and Knoops *et al* [47, 48]. The precursor step consisted of 3 s of MeCpPtMe₃ dosing with Ar as a carrier gas followed by a 3 s pump step. The selectivity of the ALD process of Pt was achieved using an O₂ partial pressure of 7.5 mTorr during the 5 s O₂ pulse [41]. The reactor chamber was pumped down for 5 s to complete the Pt ALD cycle.

High angle annular dark field (HAADF) STEM studies were performed using a FEI Tecnai F30ST, operated at 300 kV and a Cs probe-corrected JEOL ARM 200F, operated at 200 kV. The latter system was also used for EDS mapping, which was executed by a summation of 225 maps with 0.1 ms/pixel acquisition time using a 0.5 nm probe size. During EDS mapping, HAADF images were acquired regularly to allow for drift correction. This series of images was monitored continuously to make sure the original shape remained unaltered during EDS acquisition. More details about EDS are available in the supplementary information (SI). The number of NPs and their size distribution were determined over an area of 100 × 100 nm² using the iTEM software and manual counting of the NPs. It has to be noted that only separated NPs and no merged NPs or agglomerates were used in the analysis.

It has to be noted that XPS analysis on these core/shell NPs demonstrated that the synthesized NPs were virtually 100% pure [36].

Results and discussion

Shell growth by selective ALD

First, a series of core/shell NPs with different shell thicknesses has been synthesized in order to study the growth of the Pt shell. For all the samples, the initial step consisted of depositing the Pd cores, exploiting the island growth mode taking place during the initial stage of Pd ALD. The ALD process ensures a reproducible and controllable deposition of pure Pd NPs during the nucleation stage [46]. This has been underlined by a comparison of two series of samples in which Pd NPs were deposited in the same ALD reactor with the interval of one year. It has been observed that the NPs had a

very similar density and size distribution and that in both cases the average diameter of the Pd NPs increased linearly as a function of the number of cycles with a growth in diameter of 0.02 nm/cycle (see figure SI1). This demonstrates the reproducibility and robustness of the Pd ALD process for NP synthesis.

Figure 2(a) shows Pd NPs that were prepared on Al₂O₃ substrates by applying 100 Pd ALD cycles. HAADF-STEM was used to visualize the NPs as it enables high-contrast imaging of high-Z elements, such as Pd or Pt, against the lower-Z background of oxides such as Al₂O₃. The NPs are highly dispersed with a narrow size distribution, and they are round in shape. After 100 ALD cycles, the Pd NPs have an average diameter of 2.2 ± 0.4 nm, and their surface density is $(1.0 \pm 0.1) \times 10^{12}$ NPs cm⁻².

Using the Pd NPs obtained after 100 ALD cycles as cores, subsequently, Pt shells of different thicknesses were deposited by selective ALD employing 25, 50 and 75 cycles of Pt ALD. The Z-contrast STEM images in figures 2(b)–(d) yield insight into the core/shell structure of these bimetallic NPs. There is a clear contrast between the Pd core and the Pt shell, confirming the formation of core/shell NPs through selective growth of Pt on the Pd cores while not depositing on the oxide surface. The TEM images clearly demonstrate the increase of the shell thickness.

Figure 3(a) presents the NPs' size distribution, as extracted from the TEM images presented in figure 2, as a function of the number of Pt ALD cycles applied. The figure shows that the size distributions are unimodal and stay narrow for all the samples studied, which is of particular interest for many catalysis applications since a precise definition of the NP size allows for optimum control of the catalytic activity and/or selectivity [49, 50]. A reduction of the density of core/shell NPs can be observed, which can be attributed to the merging of NPs as they grow bigger. However, the Pd core's density stays constant in the whole series with values of $(0.9 \pm 0.2) \times 10^{12}$ NPs cm⁻². This corroborates the good reproducibility of the Pd ALD process, and it also illustrates the successful application of selective ALD, i.e. no new NPs have been formed on the oxide during shell growth.

Figure 3(b) shows the evolution of the NP diameter as a function of the number of Pt ALD cycles applied. The average diameter of the NPs increases linearly with the number of Pt ALD cycles, implying that the Pt shell thickness grows at a constant rate. This behavior provides additional information on the surface processes active during shell growth. If Pt atoms would also be deposited on the oxide surface, their diffusion to the NPs could contribute to the growth of the NPs. Obviously, this contribution would decrease as a function of the number of ALD cycles, as the fraction of oxide surface area decreases upon island growth. Thus, the linear increase in shell thickness is further proof for the high selectivity of the ALD growth process for which this increase only depends on the availability of catalytically active surface sites. As these sites are only present at the NPs' surface, these NPs grow at a constant rate. The diameter of the NPs increases with 0.06 ± 0.02 nm/cycle, which corresponds to an increase of the shell thickness of 0.03 ± 0.01 nm/cycle. This

Figure 2. HAADF-STEM images of (a) Pd NPs obtained after 100 Pd ALD cycles. Pd/Pt NPs with increasing shell thicknesses obtained by (b) 25, (c) 50 and (d) 75 cycles of Pt ALD on Pd cores obtained by 100 Pd ALD cycles. The substrates were Si_3N_4 TEM windows covered by 3 nm Al_2O_3 prepared by ALD. The scale bar in (a) applies also for (b)–(d).

thickness increase of the shell can be compared to the growth-per-cycle of 0.045 nm/cycle typically observed for ALD of planar Pt films [41, 51]. It shows that the Pt shell can be tailored with control of the thickness through the choice of the number of ALD cycles and with a thickness precision of 0.03 nm. Moreover, the linearly increasing shell thickness indicates that the Pd core acts as a good catalyst for O_2 dissociation. This O_2 dissociation is required for Pt ALD growth, and there is no indication of a delay of Pt growth on the initial surface of the Pd core.

The size distribution remains narrow and similar in shape with the increase of the shell thickness. This trend, combined with the observation that the NP core density remains constant, indicates the absence of significant Oswald ripening, i.e. the process of net diffusion of atoms from small NPs to larger NPs. This mechanism would lead to an enhanced growth of larger NPs at the expense of smaller NPs. We thus believe that the surface diffusion of metal atoms over the Al_2O_3 surface has a limited role during the selective ALD growth of the shell. This allows for optimal control of the diameter of the NPs.

The round shape of the core/shell NPs can reflect the selective ALD growth of the Pt shell on the Pd cores, which are round in shape, but it can also imply fast diffusion of Pt atoms along the Pd NP edge. The latter leads to a round and compact shape of the NPs by the minimization of the total free energy of each NP as the driving force [52]. A close examination of figure 2(d) of the particles that have merged through shell growth reveals that atomic diffusion along the particle edges does play a significant role. If two NPs merge, a double-core/shell structure is created, and a concave curvature results at the position where they merge. However, as is clear from figure 2(d), for several merged core/shell structures with a small distance between their cores, the concave parts of the edge have been eliminated. This is a sign of atoms diffusing along the NPs' edges, enabling a reduction in surface energy. However, this process also reduces the (catalytic) surface area. Consequently, in catalytic systems in which a high NPs density—and more importantly a large effective surface—is desired, a minimal distance between the core/shell NPs is essential to optimize this effective surface.

Figure 3. (a) Size distribution and (b) average diameter of the NPs determined from the TEM images presented in figure 2 over a surface area of $100 \times 100 \text{ nm}^2$. The error bars correspond to the standard deviations extracted from the NPs' size distributions. The dashed line is a linear fit of the data.

Influence of the core size on the shell growth

In a second series of samples, the effect of the diameter of the Pd core on the shell growth by selective ALD was studied. The Pd core diameter was varied by varying the number of Pd ALD cycles, while the number of Pt cycles was kept constant. The number of Pd ALD cycles was 50, 100, 125 and 175, and the number of cycles applied for the Pt shell was 50 cycles. Figure 4 presents the HAADF-STEM images of the resulting Pd/Pt core/shell NPs with various core diameters.

From the Z-contrast imaging the Pd cores can again be well distinguished from the Pt shells. Similarly as for the samples presented in figure 2, the Pd/Pt core/shell NPs are round in shape when not merged. Merged NPs with multiple cores are observed in figures 4(c) and (d). No signs of asymmetrical shell development can be observed, which could have been the result of a mismatch between the Pd and Pt crystal lattices or a high interfacial energy between Pd and Pt. The fact that the Pt shells are compactly formed

around the Pd cores reveals that the minimization of surface energy of the NPs plays a major role in the Pt ALD process.

Figure 5(a) presents the size distribution of the core/shell NPs with various core diameters, as extracted from the TEM images in figure 4. As can be seen in figure 5(a), the core/shell NPs with Pd cores prepared by applying 100, 125 and 175 Pd ALD cycles (shown in figure 4(b)–(d)) present unimodal size distributions. However, a bimodal size distribution can be observed for the sample in figure 4(a), with the smallest Pd cores prepared by applying only 50 cycles of Pd ALD. For the specific surface area imaged in figure 5(a), it can be extracted that 57% of the NPs present have a small diameter of $1.0 \pm 0.5 \text{ nm}$, whereas 38% have a larger diameter of $3.5 \pm 1.0 \text{ nm}$ (the other NPs have an intermediate size). The bimodal size distribution observed suggests that the NPs with a diameter of 1 nm are not covered by a Pt shell and thus do not form core/shell NPs. This hypothesis is supported by further interpretation of the bimodal size distribution. From earlier studies we know that the average diameter of Pd NPs prepared on an Al_2O_3 support is $1.3 \pm 0.7 \text{ nm}$ after 50 cycles of Pd ALD (see figure S11). From the linear increase in shell thickness ($0.03 \pm 0.01 \text{ nm/cycle}$) calculated earlier, the expected diameter of the core/shell NPs in this sample can be determined. Adding a shell thickness of $1.5 \pm 0.5 \text{ nm}$ after 50 cycles of Pt ALD to a Pd core diameter of $1.3 \pm 0.7 \text{ nm}$ results in a total diameter of $4.3 \pm 1.7 \text{ nm}$ for the core/shell NPs. This value is in agreement with the largest diameters obtained for the NPs in figure 4(a) ($3.5 \pm 1.0 \text{ nm}$). A possible explanation for the absence of a shell for a fraction of the Pd cores can be found in the fact that the smallest Pd cores (those at the lower side of the distribution) do not act as good nucleation centers for the Pt shell growth because of their reduced catalytic activity toward combustion processes. It can be hypothesized that Pt shell growth by the selective ALD process requires a critical Pd core diameter of 1 nm diameter in order to take place.

This hypothesis is corroborated by ALD and catalysis literature. ALD of Pt using MeCpPtMe_3 precursor dosing in combination with O_2 dosing involves surface reactions which are comparable to hydrocarbon combustion processes, i.e. the precursor ligands are removed through combustion-like processes with oxygen atoms created at the catalytic Pt surface. It is known that the combustion of hydrocarbons on oxide-supported Pd and Pt nanocatalysts is sensitive to the size of the NPs [53, 54]. In fact, the catalytic activity of Pd NPs smaller than 1 nm is drastically reduced in most chemical reactions, whereas a size between 1 and 10 nm is often optimal [54]. We therefore believe that the Pt shell does not grow on the smallest Pd NPs because of their reduced catalytic activity. As the highest catalytic activity of noble metal NPs is usually achieved for diameters between 2 and 10 nm [53–55], we note that the minimal Pd core diameter requirement is not a real drawback for the application of these core/shell NPs in catalysis. We demonstrated that our process allows for accurate tuning of the diameter in the 2–10 nm range. Consequently, even if the process may lead to the presence of a small fraction of smaller Pd NPs, these NPs will

Figure 4. HAADF-STEM images of Pd/Pt core/shell NPs with increasing core diameters. (a) 50, (b) 100, (c) 125 and (d) 175 ALD cycles were applied for the synthesis of the Pd cores. The number of cycles applied for the Pt shell deposition was kept constant at 50 cycles. The substrates were Si_3N_4 TEM windows covered by 3 nm Al_2O_3 prepared by ALD. The scale bar in (a) applies also for (b)–(d).

not significantly contribute to the catalytic reactions and thus do not have a major impact. Considering the specific case of oxygen reduction reactions, for example, the highest catalytic activity of Pd/Pt core/shell NPs is obtained when the diameter is between 2 and 6 nm [12, 55]. The ALD-based approach presented can therefore be considered promising for the synthesis of nanocatalysts for fuel cell applications, among others.

Closer inspection of the samples prepared with larger Pd cores (figures 4(b)–(d)) reveals that these also have actually a very small fraction (<5%) of NPs with a diameter of ~ 1 nm. This was not expected because the Pd process normally results in NPs with a unimodal and narrow size distribution (see figure S11), and the shell grows selectively on these Pd cores. One hypothesis is that surface diffusion could have taken place during the temperature increase applied between the deposition of the Pd cores at 100 °C and the deposition of Pt shells at 300 °C. This higher temperature enhances the diffusion and ripening mechanisms of Pd atoms and clusters and could have led to the formation of new Pd NPs. These small particles are probably not covered by a Pt shell due to

the low probability for precursor ligands decomposition and thus have kept their original size.

Figure 5(b) shows the average diameter of the NPs as a function of the number of Pd cycles. Concerning the particles synthesized by applying 50 cycles of Pd ALD for the cores, only the larger NPs (3.5 ± 1.0 nm) of the bimodal size distribution (the ones covered with a shell) were considered. The average diameter increases linearly, showing that for the Pd/Pt NPs the Pt shell growth is independent of the Pd core size once the Pd core diameter is larger than 1 nm. From the linear fit it can be deduced that the core/shell NPs grow with a rate of 0.02 nm per Pd ALD cycle. This implies that the diameter of the Pd core increases 0.02 nm per Pd ALD cycle. This agrees well with the data for ALD of Pd NPs, as shown in S11, highlighting the good reproducibility of the process.

Stability and high surface area compatibility

Due to their high catalytic activity, palladium and platinum belong to the most used materials in heterogeneous catalysis applications [56, 57]. On the basis of the sub-nanometer

Figure 5. (a) Size distribution and (b) average diameter of the NPs determined from the TEM images presented in figure 4 over a surface area of $100 \times 100 \text{ nm}^2$. The horizontal axis in (b) corresponds to the number of Pd ALD cycles for the synthesis of the Pd core. The error bars correspond to the standard deviations extracted from the NP size distributions. The dashed line is a linear fit of the data.

dimensions control shown in the previous sections, ALD of Pd/Pt and Pt/Pd core/shell NPs [36] or NPs of any other combination of Pt-group metals might be promising for the preparation of tuneable heterogeneous catalyst systems. However, when applied as a nanocatalyst, the synthesis process of the core/shell NPs should result in NPs that stay intact over time and under catalytically relevant conditions, as there is a direct correlation between the morphology and the catalytic performance of the catalyst. For this reason, initial studies on the stability of the core/shell NPs synthesized in this work have been carried out. Pd/Pt core/shell NPs have been imaged using HAADF-STEM directly and six months after their preparation. The core and shell structure remain visible and unchanged after six months in ambient conditions (room temperature, in air), as shown in figure 6(a).

A second stability study was performed by annealing a substrate with Pd/Pt core/shell NPs for one hour at 300°C , a temperature characteristic for the ignition of the Pt-catalyzed water gas shift reaction. This reaction plays an important role

Figure 6. (a) HAADF-STEM images of Pd/Pt core/shell NPs after six months in ambient conditions and (b) after one hour annealing at 300°C .

in many industrial processes such as methanol synthesis, hydrogen production and catalytic combustion [58, 59]. After this annealing treatment under vacuum, both the dimensions, as well as the morphology, remained unchanged, as can be observed in figure 6(b). No evidence of coalescence, Ostwald ripening or de-mixing has been observed. These initial studies reveal that the core/shell NPs show stability over time and at elevated temperatures.

Due to its ability to deposit thin films very conformally over high aspect ratio structures, ALD is also a promising method to prepare core/shell NPs on high-surface-area supported catalysts. To demonstrate the feasibility of the method in this respect, core-shell NPs were prepared on a high-density array of Al_2O_3 -covered GaP nanowires. Such nanowires are of interest for many heterogeneous catalysis applications such as fuel cells or sensors. With the strategy being general, i.e. both Pd/Pt and Pt/Pd core/shell NPs can be prepared by the method [36, 37], in this experiment Pt/Pd core/shell NPs were deposited as this allowed for a process based on thermal ALD only, which has virtually no limitations with respect to its ability to deposit materials at very

Figure 7. (a)–(c) HAADF-STEM images of Pt/Pd core/shell NPs supported on the tips of Al_2O_3 -coated GaP nanowires. The large particle at the top of the nanowire seen in (a) is a gold particle, which is used to grow the nanowires by the VLS process. (d)–(e) EDS mapping of Pt/Pd core/shell NPs on the nanowires corresponding to the STEM images in (b) and (c), respectively. The EDS mapping reveals that Pt (in blue) is confined to the centre of the NP, while a ~ 2 nm Pd shell (in red) is best visible at the NP edge. The Ga signal from the nanowire is shown in green. The scale bars in (b)–(d) are 20 nm.

high aspect ratio structures. Consequently, the Pt cores were deposited using MeCpPtMe_3 and O_2 gas, and the Pd shell process was based on $\text{Pd}(\text{hfac})_2$ and H_2 gas [36]. Figures 7(a)–(c) display STEM images of Pt/Pd core/shell NPs supported on the Al_2O_3 -coated GaP nanowires. The particle seen at the top of the nanowire in figure 7(a) is a gold particle used during the vapor-liquid-solid (VLS) process to grow the nanowires. As can be seen on the TEM images, the NPs are distributed over the whole nanowire.

Figures 7(d) and (e) show EDS mappings of Pt/Pd core/shell NPs of the same areas scanned in the TEM images shown in figures 7(b) and (c), respectively. The EDS mappings clearly show that Pt (in blue) is confined to the centre of the NP, while a Pd shell (in red) is visible at the NP edge. The Ga signal from the wire is shown in green. Overall, the EDS mappings reveal semi-spherical particles with clearly distinguishable core/shell nanostructures. This demonstrates the ability of ALD to cover high-surface-area supports with core/shell nanoparticle catalysts. It should be mentioned that this deposition of core/shell NPs on nanowires is a proof-of-concept, and we believe that the size distribution of the NPs can be narrowed by tuning the ALD deposition parameters, as has been shown for conformal deposition of Pt layers in high aspect ratio trenches [60].

Conclusion

The results presented clearly demonstrate that ALD enables the precise and independent control of the core and shell dimensions of bimetallic core/shell NPs. The stability and

high-surface-area compatibility of the NPs prepared in this work also show the viability of this versatile ALD approach as a new synthetic route for the production of nanocatalysts.

A detailed study of the preparation of Pd/Pt core/shell NPs using this novel ALD strategy has been presented. The controllable synthesis of core/shell NPs by ALD has been obtained using a robust Pd ALD process for the preparation of the core and a selective Pt ALD process for the shell. When supported on Al_2O_3 substrates, the Pd core diameters increase at a rate of 0.02 nm per Pd ALD cycle. The core size can therefore be precisely tuned by simply defining the number of ALD cycles to be applied. The shell growth study revealed that the Pt shell thickness can also easily be varied since Pt growth takes place at a rate of 0.03 nm per cycle on the Pd cores. This Pt growth is selective, which means that it only takes place on the Pd NPs and not on the support material. Furthermore, it has been found that the shell growth takes place only when the Pd core diameter is larger than 1 nm. As the highest catalytic activity of noble metal NPs is achieved for NP diameters between 2 and 10 nm, this ALD-based approach is a promising route for the preparation of efficient nanocatalysts.

From the results the following main general conditions for the synthesis of controllable core/shell NPs by ALD can be derived. First, a significant difference in surface energy between the deposited core metal and the support material is required to obtain island growth. The second requirement is an ALD process presenting a linear growth rate to deposit monodispersed NP cores with a narrow size distribution and a predefined diameter. Third, a selective ALD process

presenting a linear growth rate for the shell metal is required in order to obtain controllable shell growth on the cores only.

For a first evaluation of the results for potential applications of these core/shell NPs, preliminary stability studies have been carried out indicating that the core/shell NPs synthesized by this ALD approach show stability with time and at elevated temperatures. Also, the possibility to deposit a high density of core/shell NPs on high aspect ratio substrates, such as nanowire arrays, has been demonstrated in this work. The latter has been done for Pt/Pd core/shell NPs as the reported strategy is generic and can likely be employed for any combination of Pt-group metals (although the results will depend on the details of the ALD processes available). Furthermore, it is noted that ALD is a scalable technique which has an application to large-scale substrates that is relatively easy to implement due to the self-limiting nature of the ALD reactions.

This work therefore indicates that ALD and the strategy presented can be very promising for the preparation of core/shell NPs for applications such as nanocatalysts for which the ability to nanotailor their properties is becoming increasingly important.

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