Nanoparticles

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Self-Organization of Spherical, Core–Shell Palladium Aggregates by Laser-Induced and Thermal Decomposition of [Pd(PPh$_3$)$_4$]**

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Metallic nanoparticles serve many functions. For example, palladium and platinum metal nanoparticles stabilized by surfactants and solvents can act as catalysts for hydrogenation[1,2] and Heck, Suzuki, and Stille cross-coupling reactions.[3–5] Nanoparticles are also potential building blocks for designing larger organized structures for chemical sensing applications and magnetic and electronic devices.[6] This is fundamentally important because these structures display properties that are distinct from those of the individual constituent particles.[7] Several methods have been applied to obtain 3D aggregates of metal nanoparticles,[8–11] one of the more efficient being the "brick-and-mortar" ("BM") strategy, which involves the use of multifunctional organic ligands, polymers, or biomolecules as the cohesion "mortar".[12,13] Naka et al. have also used cubic silsesquioxanes as the cross-linker for generating spherical palladium aggregates.[14]

Recently we have embarked on a project to assemble metal nanoparticles by the laser decomposition of transition metal carbonyls or phosphanes, with particular interest in understanding the reaction pathways that lead to nanoparticle formation. We chose the photolysis of organometallic species in which the metal is already present in the zero oxidation state, thereby eliminating the need for reducing agents and possibly high temperatures. Herein a facile method for assembling palladium nanoparticles into spherical, core–shell aggregates by visible laser decomposition of commercially available tetrakis(triphenylphosphane)palladium is presented. In this two-step procedure, palladium nanocores (15–25 nm) are first generated by laser decomposition and then smaller palladium nanocrystals (< 5 nm) are formed by the thermal decomposition of the remaining [Pd(PPh$_3$)$_4$] aggregated around the Pd core.

In a typical experiment, [Pd(PPh$_3$)$_4$] (11.5 mg, 0.01 mmol; 99% Sigma-Aldrich) was dissolved in 5 mL of DMF (HPLC grade, Aldrich) and 5 mL of ethanol (AR grade, Aldrich) to form an orange solution. The UV/Vis absorption spectrum of the solution was recorded with a Shimadzu UV-2550 spectrometer to check its absorptivity around 532 nm, which is the pulsed-laser wavelength available in our laboratory (Figure 1). The broad absorption spectrum (from < 300 to 650 nm) obtained showed that it should be possible to induce changes in [Pd(PPh$_3$)$_4$] by irradiation with the laser. The solution was then irradiated with a 532-nm pulsed YAG laser (Continuum Surelite III-10, 80–100 mJ per 10-ns pulse), with vigorous stirring, for 30 min. A change of color from orange to black occurred in around 10 minutes, thereby indicating the decomposition of the precursor and formation of palladium nanoparticles. This could also be seen from the changes in the UV/Vis spectrum (Figure 1). An aliquot of this solution (labeled as product **A**) was removed immediately for characterization, while the remainder (labeled as product **B**) was kept in the dark and maintained under ambient conditions for 24 h without shaking or stirring. This allowed the precursor to decompose thermally in the dark and generate more Pd particles. Both **A** and **B** were centrifuged and rinsed with DMF and ethanol several times to remove the free PPh$_3$. The remaining black solids were then collected and redispersed in ethanol for further investigation. The UV/Vis absorption spectrum of **B** dispersed in ethanol is essentially the same as that of **A**.

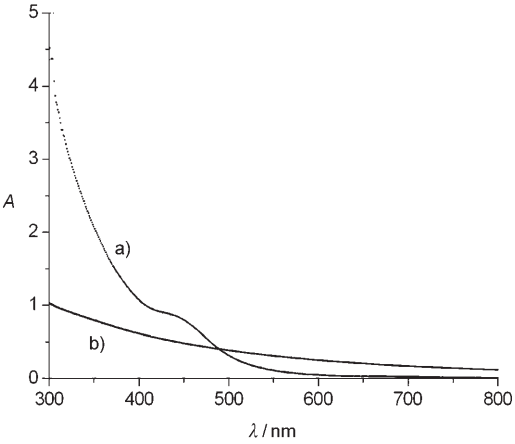

Figure 1. The absorption spectrum of the precursor [Pd(PPh$_3$)$_4$] (a) and the as-prepared core and core–shell palladium nanoparticles (b).

Figure 2 shows a scheme for the formation of our core–shell palladium spheres. The first step requires the laser photodecomposition of [Pd(PPh$_3$)$_4$] into Pd atoms and free PPh$_3$. We monitored the progress of the photodecomposition by ^{31}P NMR spectroscopy and, indeed, the signals of the precursor ($\delta = 29.8$ ppm) decrease in intensity with a concomitant increase of the signal for free PPh$_3$ ($\delta = -4.75$ ppm).

A TEM image taken of the Pd nanocores (**A**) with a JEOL TEM-2010F instrument (field emission, 200 keV) is shown in Figure 3. A narrow distribution of core sizes, with diameters ranging from 15 to 25 nm, is achieved upon laser photodecomposition of [Pd(PPh$_3$)$_4$]. The selective area electron diffraction (SAED) pattern obtained during the acquisition of the TEM image shows the cores to be polycrystalline palladium corresponding to a face-centered cubic (fcc)

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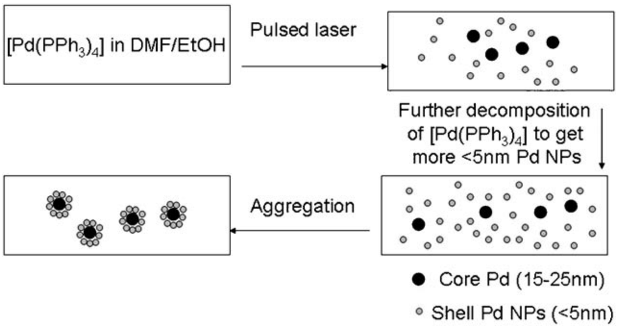

Figure 2. Formation of the core–shell palladium nanostructures. NP = nanoparticle.

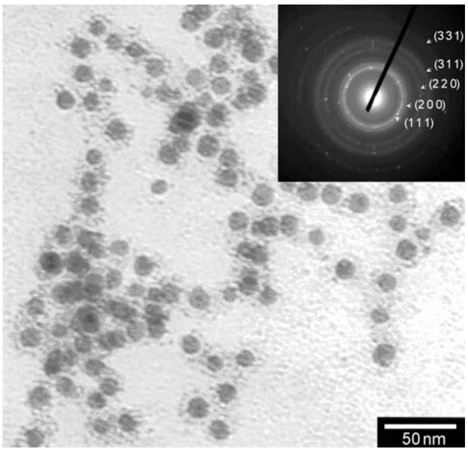

Figure 3. TEM image showing the cores formed during the laser-induced decomposition of [Pd(PPh$_3$)$_4$]; the insert shows the SAED pattern of these core Pd particles.

structure. Smaller palladium nanoparticles of the order of 5 nm can also be seen individually or as aggregates on the surface of the larger core particles upon closer inspection.

Further thermal decomposition of the remaining [Pd(PPh$_3$)$_4$], in the absence of irradiation, produces many more of these small Pd nanoparticles (< 5 nm) and, in turn, induces even more aggregation on the surface of the core Pd nanoparticles. This results in the formation of spherical core–shell palladium structures (**B**; Figure 4 a). These TEM images of product **B** show that the overall core–shell spheres are larger but maintain a fairly narrow size distribution of 100 ± 20 nm. Incidentally, the core diameters remain unchanged at about 20 nm. With the higher magnification provided by a JEOL TEM-3010 (300 keV) instrument, the shells were seen to be composed of dark spots (Figure 4 b,c). These dark spots were determined to be individual Pd nanocrystals whose lattice spacing of 0.23 nm corresponds to the (111) distance of fcc Pd (Figure 4 d). Almost every nanoparticle smaller than about 5 nm appears to be a discrete entity in the nanoshell of the core–shell structure, although some merging of the particles could also be observed upon closer inspection.

An X-ray diffraction (XRD) analysis with a Siemens Powder XRD D5005 diffractometer also confirmed the formation of the Pd nanoparticles by revealing the characteristic diffraction peaks of the palladium fcc phase (Figure 5).[15]

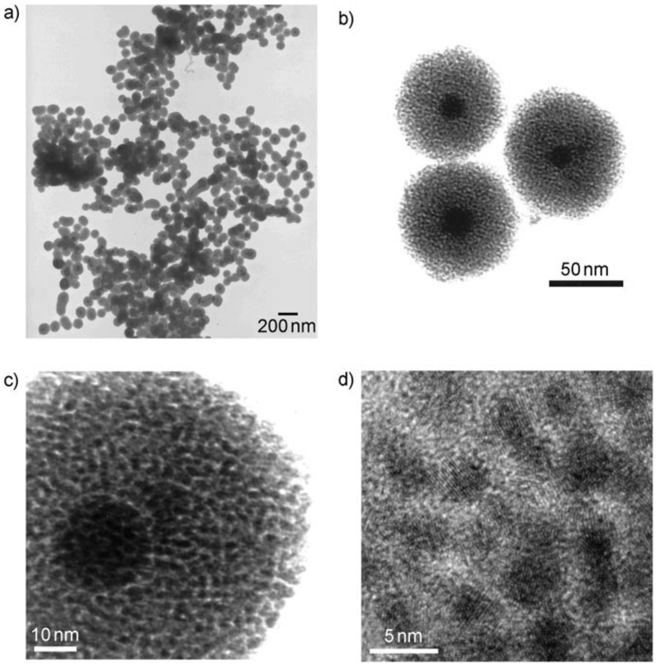

Figure 4. a) TEM image of the core–shell structure; b) and c) high-magnification TEM images showing the core–shell structure clearly; d) an HRTEM image of the shell showing that it is composed of palladium nanoparticles.

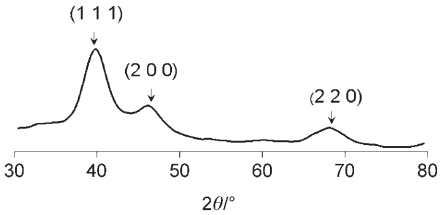

Figure 5. The XRD pattern of the core–shell palladium spheres (product **B**).

An energy-dispersive X-ray (EDX) analysis of the core–shell structure revealed the presence of phosphorus within the shell with a P/Pd ratio of around 0.06. Therefore, the shell most likely consists of at least two types of PPh$_3$, namely free PPh$_3$ in the space surrounding the small Pd nanoparticles and PPh$_3$ adsorbed on the nanoparticle surface. Both these types of PPh$_3$ play a key role in the aggregation process during formation of the core–shell structure. Unfortunately we did not obtain an NMR signal for the adsorbed PPh$_3$ because of the low concentration of the core–shell nanoparticles. Although it is likely that [Pd(PPh$_3$)$_4$] would also be trapped upon Pd nanoparticle formation, this species would decompose within the nanoparticle in a manner similar to the thermal decomposition in solution. Hence, [Pd(PPh$_3$)$_4$] represents, at most, a minor contribution to the composition of the core–shell Pd structure, especially if the nanoparticles have been left in the dark for a few days.

When the EDX beam was directed towards the center of the core–shell structure, the P/Pd ratio was found to decrease to 0.02. We believe that the detected phosphorus, albeit in lower amounts, originates from the shell, since the beam still has to sample this region around the core. A simple calculation shows that for a core thickness of about 20% of the whole structure (as estimated from Figure 4b), the P/Pd ratio should decrease slightly to about 0.05 assuming that the core consists of only Pd atoms of the same density as the shell. However, a larger decrease is seen, which strongly suggests that the packing of Pd atoms within the core is denser, closely resembling that of the pure metal, and that phosphorus species are absent. Hence, EDX analysis supports the formation of an almost pure Pd core, or at least one with a much higher Pd density, surrounded by aggregates of smaller Pd nanoparticles interspersed with phosphanes.

We also found that when the solution of $[Pd(PPh_3)_4]$ was irradiated with the pulsed laser for a longer time (>2 h), no core–shell structures could be obtained even after the solution had been stored in the dark for a few days. During such a prolonged irradiation period the precursor would have decomposed completely to give only the core palladium nanoparticles. If the duration of the photolysis is shortened not all of the precursor decomposes, thus allowing the remainder to undergo gradual thermal decomposition to form the smaller palladium nanoparticles, which then aggregate on the core surface. In another experiment, $[Pd(PPh_3)_4]$ was allowed to decompose slowly in the absence of any laser or light irradiation under ambient conditions and without any heating, shaking, or stirring. The solution gradually became turbid and within 24 to 40 h turned from orange to black. After performing the required workup to isolate the nanoparticles, we found that they were spherical aggregates with no Pd core. These spherical aggregates are larger, with diameters of up to 400 nm.

The formation of larger aggregates of Pd nanoparticles in the absence of irradiation is due to the smaller number of "seed" nuclei in the solution. The precursor can only decompose slowly in the dark to form smaller Pd nanoparticles (<5 nm), which, in turn, are adsorbed by the free PPh_3 released during the decomposition process. These individual nanoparticles aggregate, perhaps through intermolecular π–π interactions, and their growth may be diffusion-controlled.[16] Laser photolysis greatly influences the size of the Pd aggregates formed. In the initial step, efficient decomposition of $[Pd(PPh_3)_4]$ accelerated by the intense laser pulse releases more palladium atoms during each pulse and causes the aggregation into larger palladium nanoparticles (20 ± 5 nm). Since no further triphenylphosphane is added, there is insufficient adsorbate to prevent the formation of these large nanocores. However, once the irradiation is stopped, and providing some Pd precursors remain, slower thermal decomposition can take place instead to form much smaller nanoparticles. Interestingly, these smaller particles tend to move towards the larger, laser-generated Pd cores to form core–shell assemblies. We are not aware of any previous work that reports the formation of such a core–shell structure for palladium, although aggregates resembling the shell structure have been observed previously.[14]

It is worth pointing out that the outer-shell aggregates of palladium nanoparticles are formed spontaneously without the influence of any external forces. As seen in Figure 4b, the core–shell structures are spherical. According to the diffusion-controlled-growth theory, every nucleus gathers the neighboring primary particles within its individual field of attraction, which extends as a circular arc around a spherical particle to a defined distance from the center of the particle. It is therefore not surprising that the nanostructures obtained here are spherical when this formation process is considered[17] as the particles tend to grow into a spherical shape in order to minimize their surface energy.[18] In the present case, the shape of the spontaneously formed core–shell aggregates also becomes spherical in order to minimize their surface energy.

In summary, stable core–shell palladium nanoparticles (100 ± 20 nm) are formed by laser decomposition followed by thermal decomposition of a solution containing $[Pd(PPh_3)_4]$. The core (20 ± 5 nm) consists of pure, metallic palladium while the shell is an aggregate of smaller Pd particles (<5 nm) interspersed with phosphanes. If the palladium precursor is allowed to decompose thermally only the shell structure is formed, whereas if the laser irradiation is prolonged only the core structure is observed. This provides a convenient method for tuning the structure of palladium nanoparticles by making use of both photochemical and thermal decomposition pathways.

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