

Preparation of Alkanethiolate-Protected Palladium Nanoparticles and Their Size Dependence on Synthetic Conditions

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Palladium nanoparticles protected by alkanethiolates with a core diameter 1.3–3.9 nm were synthesized by the treatment of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with tetraalkylammonium bromide and LiBET_3H in THF, followed by the addition of alkanethiols. The mean size and its deviation as observed by transmission electron microscopy varied in relation to changes in the reaction conditions involving variables such as the ammonium salt, the molar ratio of the reactants, the reaction time, and the alkanethiol. Smaller particles were obtained when the ratio of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ to other reagents was decreased, the reaction time was increased, and a long alkanethiol was used.

Introduction

Throughout the past decade, the number of reports published on nanometer-sized materials indicates that this relatively recent science is attracting increasing interest. This increasing interest is largely due to the wide range of applications of these materials in several fields, including advanced electronics,¹ nonlinear optics,² catalysis,³ and hydrogen absorption, especially concerned with palladium nanoparticles.⁴ These applications derive from some particular features of these materials such as the quantum size effect,⁵ which means that the electronic bands of the bulk material become discrete states when nanometer size is reached. These discrete levels induce the nanoparticles to present a molecule-like behavior, and their physical and chemical properties are directly related to the core size. Consequently, prior to investigating these properties and their derived applications, it is essential to develop a rational synthetic method that can provide us with the ability to control the size of the particles and to obtain a narrow dispersion of diameter.

Stable nanoparticles free from agglomeration are obtained by protecting them with polymers⁶ or surfactants.⁷ For the synthesis of gold nanoparticles, Brust et al.⁸

developed a convenient method using an alkanethiol as a protective agent. Covered by a thiolate shell, the particles become stable in both organic solvents and dry states. The use of this type of ligand also provides the prospect of further functionalization of the particles, because plain alkanethiolates can be easily substituted for other thiols having functional moieties.^{9–13} In the present article, a newly developed method for the preparation of alkanethiolate-protected palladium nanoparticles is reported, and the size dependency of these nanoparticles on several reaction conditions is also described. Application of this method to construct biferrocene-modified palladium nanoparticles, which have the ability to form a film by electrodeposition, has been reported elsewhere.¹⁴

Experimental Procedure

Materials. The starting material, $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$, was synthesized as reported in the literature.¹⁵ All other reagents were purchased from Kanto Chemicals, Aldrich, or TCI and used as received. Octanethiol and dodecanethiol were degassed by the freeze–pump–thaw method before use. The plates used for preparative thin-layer chromatography (PTLC) were purchased from Merck (silica gel 60 F₂₅₄, 2 mm).

Physical Measurements. UV–vis absorption spectra were recorded on a JASCO V-570 spectrometer. Transmission electron microscopy (TEM) images were obtained with a Hitachi HF-

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2000 microscope, and the analysis of the particle size was performed by the image processing and analysis program Scion Image.¹⁶ Powder X-ray diffraction (XRD) analysis of the Pd particles was carried out with a Rigaku Miniflex spectrometer.

Preparation of Alkanethiolate-Protected Palladium Nanoparticles. The synthetic procedure has many parameters (reagents, molar ratios, and so on) that can be varied. A particular set of conditions were established as the basis for all of the experiments. Subsequently, specific changes in the respective parameters were carried out relative to the established set of conditions. This set, designated the standard condition, is described first, and the qualitative or quantitative changes for each parameter will be stated later herein.

Standard Condition. Under a nitrogen atmosphere, 0.130 g (0.50 mmol) of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ and 0.924 g (2.0 mmol) of $[\text{N}(\text{CH}_3)_2(\text{C}_{12}\text{H}_{25})_2]\text{Br}$ (a surfactant) were dissolved in 80 mL of dehydrated THF and stirred until an orange-yellow solution was formed. To the solution, 1.5 mL (1.5 mmol) of Super-Hydride (1.0 M solution of lithium triethylborohydride in THF) was subsequently added, and almost immediately the solution turned dark brown, which is indicative of the presence of Pd particles. The mixture was vigorously stirred for 30 min. Then a THF solution of 5.720 g (20 mmol) of octadecanethiol was added. The sample was continuously stirred for another 15 min, and the solvent was removed by vacuum evaporation until only a small volume (2–3 mL) remained. An excess amount (100 mL) of ethanol was added by pouring, and the mixture was stored in a freezer overnight. The precipitate was collected on a membrane filter (0.45 μm pore size), and washed with ethanol and acetone. The washing continued until the filtrated solution was completely colorless.

Further purification was carried out to remove the possible presence of remaining surfactant or thiol, and the procedure is as follows. The precipitates were dissolved in toluene, and the remaining reagents were separated off by a PTLC plate and use of hexane as the eluent. After the brown band had been collected, the Pd particles were extracted with THF (100 mL) with the aid of sonication. Then the silica gel was removed by glass filtration and the filtrate was concentrated by rotary evaporation. An excess amount (100 mL) of ethanol was subsequently added by pouring, and the mixture was stored overnight. This allowed the remaining precipitates to settle, after which they were collected on a membrane filter and washed with ethanol and acetone. Although this purification process decreased the yield dramatically, largely due to the great affinity of the particles for the silica gel, it did not affect the final size of the particles.

This condition is entry 16 in Table 1. Variations on this condition employed in our experiments included changes in the alkyl groups of the surfactant, in the starting material/surfactant molar ratio, in the starting material/reducing agent molar ratio, in the starting complex/thiol molar ratio, in the stirring time between the addition of the reducing agent and the thiol, and in the alkyl group of the thiol. Experiments using an anionic surfactant and without surfactant, respectively, were also carried out. Octanethiol and dodecanethiol were added without dissolving them first in THF because they were used in liquid form.

Results and Discussion

Synthesis of Palladium Nanoparticles. In the present study, we employed a single organic phase system for the synthesis of palladium nanoparticles rather than the commonly employed two-phase system.^{8,17–19} The absence of an aqueous phase makes the manipulation easier because the extractions are eliminated and, as Yee et al. pointed out,²⁰ provides the possibility of using many different types of thiols. In this system, a palladium

complex and a reducing agent soluble in organic solvents should be used as the starting material. For this purpose, we chose $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$, because it can be easily synthesized in a stable form,¹⁵ and Super-Hydride (LiBET_3H), because it does not decompose unless exposed to air, which made it possible to set the amount to a specific value.

Yee et al. stated that more work needed to be done before control of size and dispersion of palladium nanoparticles could be achieved.²⁰ The explanation for the lack of control found in their study might lie in the fact that in their process the thiol was added first, and therefore the size was fixed from the outset of the experiment. We overcame this problem by introducing the use of a surfactant, which allowed us to investigate a wide range of possibilities to control mean size. This step, in conjunction with the simplicity of using only one phase, resulted in a convenient way to synthesize palladium nanoparticles and simultaneously control their size.

Another way to form a protective layer for the palladium nanoparticles is to use polymers. Nevertheless, according to the results reported by Toshima et al.,²¹ the use of polymers can lead to aggregates, whereas the use of surfactants as protective agents in their research gave particles of smaller size, with a value between 1.7 and 2.1 nm. The last values are similar to those obtained in our research, although we achieved a wider range of possibilities (between 1.3 and 3.9 nm).

Addition of the palladium complex and a tetraalkylammonium salt to THF gave a homogeneous solution of micelles. Super-Hydride was used to reduce the palladium complex, the stirring time was meant to enhance the growth process, alkanethiol was added to form a final protective layer around the particles, and the excess amount of ethanol was added in order to induce the particles to precipitate. The resulting samples were stable in air and could be kept for months without decomposing. In addition, they could be easily dissolved without decomposing in organic solvents such as toluene, THF, or hexane, though they were insoluble in ethanol or acetone. The UV–vis spectra of the samples in toluene exhibited only Mie scattering. No surface plasmon band was observed. These findings were in good agreement with the observations reported by Chen et al.¹⁷ Thus, the size of the particles was not able to be evaluated using UV–vis measurements.

In contrast, TEM provided clear and specific information about size and size distribution for every sample, and these data allowed us to compare and classify the results obtained from different reaction conditions and then to develop a rational method by which to vary the size of the particles. Representative TEM photographs and the diameter distribution of the palladium nanoparticles are shown in Figure 1.

To confirm the existence of the particles, we carried out XRD measurements on several samples. For particles with a size of 2.4 nm, a broad signal containing two peaks appeared at around 40° , which correspond to the (111) and (200) planes of a face-centered cubic (fcc) lattice. Comparing it with the XRD measurements of palladium nanoparticles taken by Teranishi et al.,²² the half-width of the peak that they detected for particles of 2.4 nm is almost the same as in our case. For particles of bigger size (3.9 nm), the half-width of the peak at 40° did not decrease

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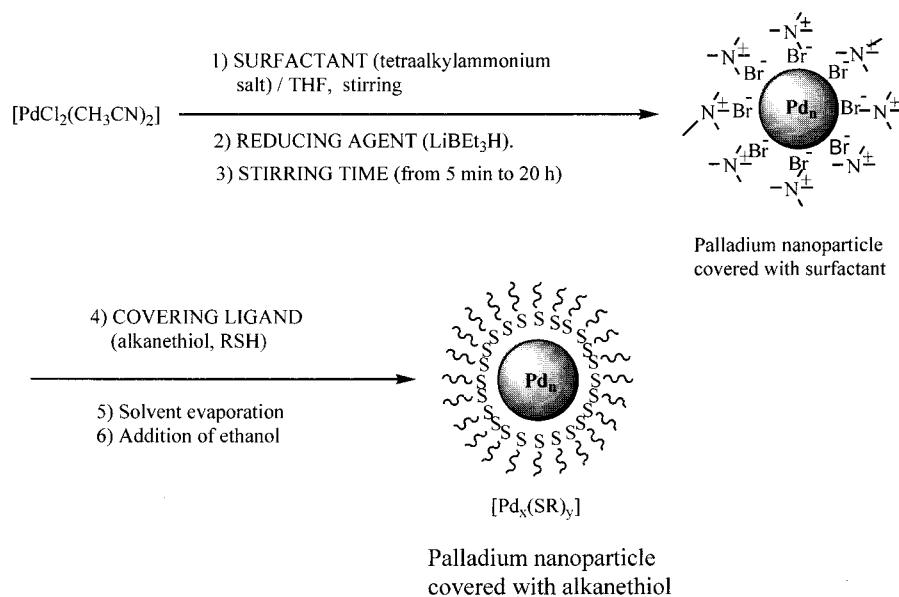
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Scheme 1^a

^a The steps that have been used as parameters are written in capital letters.

as expected but showed the same value as in the case of particles of 2.4 nm, which indicates that using our synthetic method the particles become more amorphous when size increases. According to a recent report on the geometry of palladium nanoparticles,²³ there are times in which the geometry could not be established in any sense. Although the issue of amorphous particles has been the subject of big controversy, they stated that amorphous structures were found theoretically for the case of gold particles. Only in the case of bigger particles (3.9 nm) was it also possible to detect two peaks at 68° and 82° , although the half-width is similar to that of the particles of 2.4 nm. They correspond to the (220) and (311) planes of a fcc lattice. All these data indicate that the palladium particles obtained in this method have a fcc structure, although some of them are amorphous.

One of our initial targets was to diminish the size dispersion increased by the use of an additional aqueous phase for the synthesis of Pd nanoparticles, as described in several previous reports.^{17,18} The two-phase system is a suitable method in the case of gold particles,^{8,19} but the growth dynamics of palladium counterparts have been reported to show great sensitivity to the surrounding conditions.^{17,24} Accordingly, we supposed that if those conditions were not homogeneous, as is the case in the two-phase system, there would not be uniform growth for all of the particles, resulting in a wider size distribution. Nevertheless, even though we used more homogeneous surrounding conditions (single organic phase), the values of size distribution did not differ significantly from those obtained by the two-phase system. For instance, the results on size dispersion obtained by Chen et al.¹⁷ (3.0 ± 0.9 nm, 2.8 ± 0.8 nm) were quite similar to findings in this study (3.0 ± 0.9 nm, 2.8 ± 0.6 nm). These results indicate, using the terminology of full-shell clusters, that particles with different numbers of shells are present in one sample.

Size-Dependency on the Synthetic Conditions: (1) Alkyl Groups of the Surfactant. As can be expected, the alkyl groups of the surfactant seem to have a major influence on the resulting size of the nanoparticles. This

synthetic condition has been studied using three different surfactants: $[\text{N}(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2]\text{Br}$, $[\text{N}(\text{C}_8\text{H}_{17})_4]\text{Br}$, and $[\text{N}(\text{C}_{10}\text{H}_{21})_4]\text{Br}$. With $[\text{N}(\text{C}_{10}\text{H}_{21})_4]\text{Br}$, instead of a black precipitate of nanoparticles, a fine green powder was obtained. TEM gave evidence that in the experiment with $[\text{N}(\text{C}_{10}\text{H}_{21})_4]\text{Br}$, no nanoparticle was formed. The results of the other two surfactants are shown in Table 1.

For the experiments with $[\text{N}(\text{C}_{12}\text{H}_{25})_2(\text{CH}_3)_2]\text{Br}$ as surfactant (entries 3, 8, and 16), the mean particle size was between 2.2 and 3.0 nm. In contrast, the use of $[\text{N}(\text{C}_8\text{H}_{17})_4]\text{Br}$ resulted in smaller particles, and the mean size for the three experiments with this surfactant was under 2.2 nm (entries 6, 10, and 22). For the combination of this surfactant and octadecanethiol, the resulting size was 1.3 ± 0.3 nm, which was the smallest value in the present study.

In other research about palladium nanoparticles, it has been reported that the particle size depended on the alkyl chain lengths of the stabilizer molecules, although they used ammonium alkylisocyanides for that purpose.²⁵ In addition, for the synthesis of gold particles, it has been demonstrated that the type of surfactant was important in influencing the size and morphology of the growing particles.²⁶ This influence on the resulting size can be explained as follows: before the reduction, the surfactant formed a micelle structure confining the starting complex, and this structure mainly determined the size of the particles. Thus, variations in the alkyl groups of the surfactant allow variations in the nature of this micelle structure, which, in turn, would lead to changes in the size of the particle formed after the reduction. In the case of the experiment with $[\text{N}(\text{C}_{10}\text{H}_{21})_4]\text{Br}$, instead of the black precipitate of nanoparticles, a fine green powder was obtained, and it gave no evidence of nanoparticles in the TEM measurement. This phenomenon may be related to a difference in the micelle structure.

(2) Starting Material/Surfactant Molar Ratio. The three ratios of surfactant investigated, 1/1, 1/4, and 1/10, led to changes in the mean size of the particles, whose values are shown in Table 1. Larger variations were

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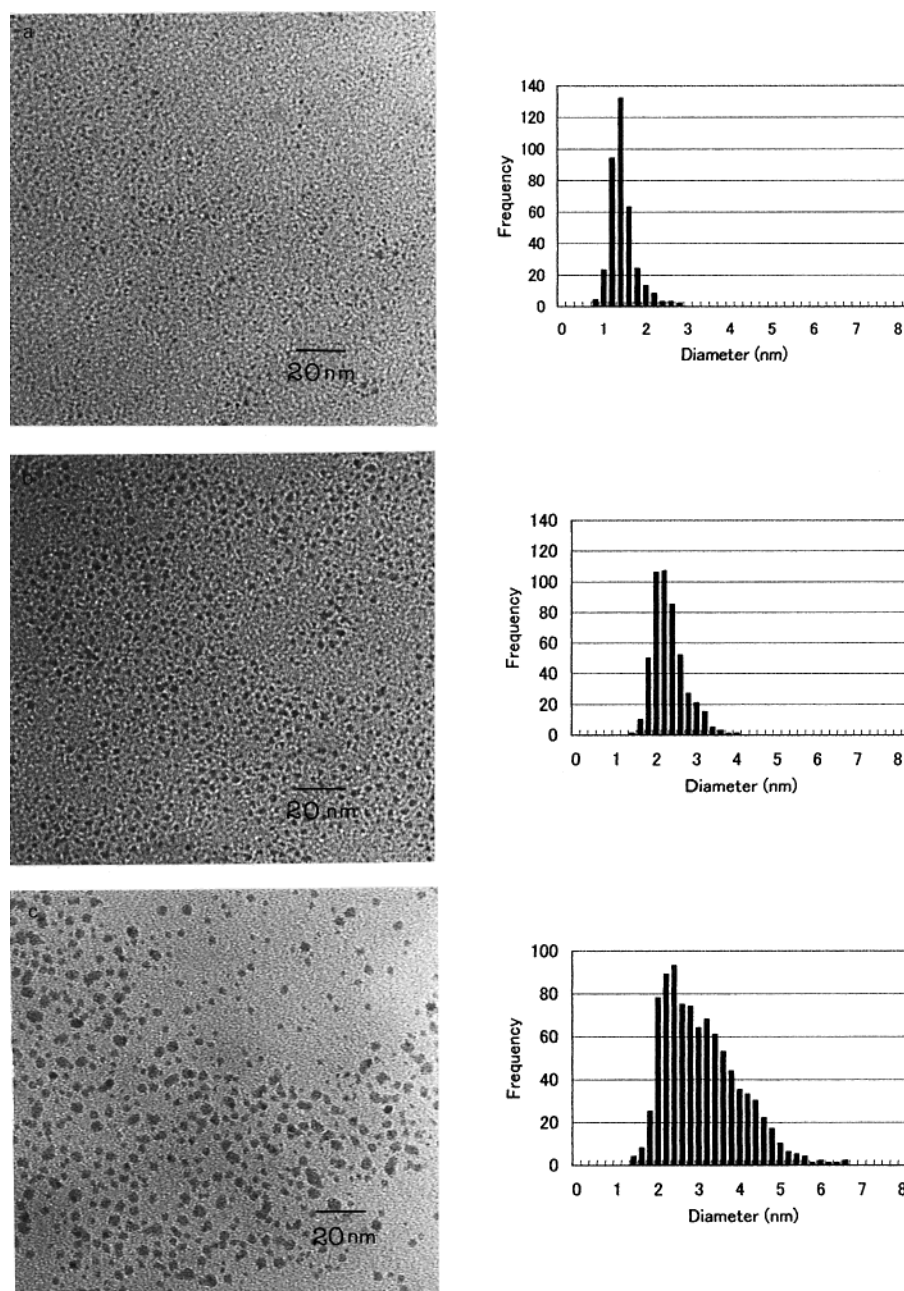


Figure 1. Representative TEM photographs and the size distribution histograms of palladium clusters with a mean size of 1.3 ± 0.3 nm, 2.2 ± 0.4 nm, and 3.0 ± 0.9 nm. The reaction conditions are those described as entries 22, 16, and 3 in Table 1.

obtained in the experiments using a molar ratio of 1/1, e.g., 2.3 ± 0.6 for octadecanethiol (entry 11), which reached a mean particle size of 3.9 ± 1.9 nm in the case of octanethiol (entry 1). On the other hand, when an excess amount of surfactant was used, smaller particles were formed. For example, a mean size of 1.7 ± 0.5 nm was obtained with the 1/10 ratio (entry 21). Even with octanethiol, a ligand that usually produces large particles, the result for a ratio of 1/10 was relatively small, only 2.2 ± 0.5 nm (entry 5).

This parameter also seems to be important in determining the final particle size. In fact, the biggest particles in this study (3.9 nm) were obtained by applying this variation. As explained above, changes in the micelle structure formed by the surfactant lead to variations in the size of the particles. The experiment with a 1/10 molar ratio demonstrated a fair decrease in size compared with the results of other ratios of surfactant. This finding is in good agreement with results reported for gold particles.^{27,28}

Those previous reports found that an increase in the concentration of the surfactant resulted in the formation of smaller particles.

It has been suggested that in the chemical formation of gold particles in the presence of surfactants, particle growth is inhibited by surfactant adsorption onto the particles.^{29,30} Supposing the same tendency for palladium particles, an increase in the concentration of surfactant would inhibit particle growth, presumably by inducing changes in the three-dimensional array of the micelle structure. As previously mentioned, for a ratio of 1/1 a sharp increase in size was obtained. In that case, the

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Table 1. Diameters and Standard Deviations (nm) of Pd Clusters Obtained with Varied Synthetic Conditions

entry	n^a	molar ratio			stirring time ^e /min	diameter ^f /nm
		b	c	d		
1	8	1/1	1/3	1/40	30	3.9 ± 1.9
2	8	1/4	1/3	1/40	5	2.7 ± 0.8
3	8	1/4	1/3	1/40	30	3.0 ± 0.9
4	8	1/4	1/3	1/40	1200	3.7 ± 1.6
5	8	1/10	1/3	1/40	30	2.2 ± 0.8
6	8 ^g	1/4	1/3	1/40	30	2.2 ± 0.8
7	12	1/4	1/3	1/40	5	2.1 ± 0.5
8	12	1/4	1/3	1/40	30	2.3 ± 0.5
9	12	1/4	1/3	1/40	1200	3.5 ± 1.4
10	12 ^g	1/4	1/3	1/40	30	1.6 ± 0.4
11	18	1/1	1/3	1/40	30	2.3 ± 0.6
12	18	1/4	1/3	1/40	5	2.0 ± 0.6
13	18	1/4	1/2	1/40	30	2.4 ± 0.7
14	18	1/4	1/3	1/1	30	2.2 ± 0.7
15	18	1/4	1/3	1/10	30	2.2 ± 0.6
16	18	1/4	1/3	1/40	30	2.2 ± 0.4
17	18	1/4	1/6	1/40	30	1.8 ± 0.9
18	18	1/4	1/10	1/40	30	1.7 ± 0.5
19	18	1/4	1/20	1/40	30	1.6 ± 0.5
20	18	1/4	1/3	1/40	1200	2.4 ± 0.6
21	18	1/10	1/3	1/40	30	1.7 ± 0.5
22	18 ^g	1/4	1/3	1/40	30	1.3 ± 0.3

^a In $C_nH_{2n+1}SH$. ^b $PdCl_2(CH_3CN)_2/[N(C_{12}H_{25})_2(CH_3)_2]Br$. ^c Starting material/reducing agent. ^d Starting material/thiol. ^e Between the addition of $LiBET_3H$ and the thiol. ^f Average and deviation for Pd clusters. ^g $[N(C_8H_{17})_4]Br$ was used instead of $[N(C_{12}H_{25})_2(CH_3)_2]Br$ as the surfactant.

inhibition in growth caused by the surfactant would be lower. This ratio not only induced an increase in the mean particle size but also widened size distribution.

(3) Starting Material/Reducing Agent Molar Ratio. Five molar ratios from 1/2 to 1/20 were investigated, and the results indicated that larger amounts of reducing agent led to a decrease in size (entries 13, 16–19). The explanation for such tendency can be found in the research carried out by Teranishi et al.²² They studied intensively the influence of the reducing agent on the size of Pd nanoparticles, and they stated that, in general, an increase in the concentration of the reducing agent increases the reduction rate of metal ions, leading to smaller metal nanoparticles.

(4) Starting Material/Thiol Molar Ratio. We used octadecanethiol to study this dependence for ratios of 1/1, 1/10, and 1/40, and the results were 2.2 ± 0.7 , 2.2 ± 0.6 , and 2.2 ± 0.4 nm, respectively (entries 14–16). The final mean size turned out to be the same for the three molar ratios, which indicates that variations in this molar ratio do not influence the growth of the particles.

(5) The Stirring Time between the Addition of the Reducing Agent and the Thiol. After the addition of the reducing agent, the growth of the particles commenced, and it was found that the induction time before the addition of the thiol had an influence on this growth, as can be deduced from the comparison among entries 2–4, entries 7–9, and entries 12, 16, and 20, all of which are shown in Table 1.

It is clear then that at longer reaction times, the particle size increases. The change from 5 to 30 min did not give a large variation in size, showing an increase of only 0.2–0.3 nm depending on the thiol used. However, increasing the time to 20 h (1200 min) led to the formation of much larger particles. The sharpest change was shown by dodecanethiol, for which an increase from 30 min to 20 h led to a size variation from 2.3 to 3.5 nm (entries 7–9). Given that the thiol is the ligand that will finally cover the clusters, its addition marked the end of the growth.

Thus, in the case of a longer time (20 h) before this addition, it is possible that the surfactant had sufficient time to rearrange itself in a way that allowed the particle to grow more freely, whereas in the case of a shorter time (5 min), the faster addition of the thiol might stop the growth at a rather early stage.

(6) The Alkyl Group of the Thiol. This dependency was investigated under many combinations of conditions, and the results of its application have already been shown in the tables along with the other parameters investigated. Nevertheless, further investigation is necessary to detect the general trends. The choice of alkanethiol affected the extent of variation in size upon changing other conditions.

When the parameter related to the alkyl groups of the surfactant was investigated (vide supra), a relationship between the final size and the length of the alkyl group of the thiol was found. For both surfactants, as the number of carbons in the alkyl chain of the thiol decreases, the mean size increases (e.g., compare entries 3, 8, and 16). Octanethiol proved to be effective to induce an increase in size, but it widened the size distribution considerably compared to that with the other thiols.

The same trend was also found when the starting material/surfactant molar ratio was taken as a parameter, as noted above. As previously mentioned, if this ratio changes, the result will be a great size variation. Nevertheless, this size variation also depends strongly on the thiol used, because the values obtained for octadecanethiol differed only in a range of 0.8 nm when $[N(C_{12}H_{25})_2(CH_3)_2]Br$ was used as the surfactant (entries 11, 16, and 21), whereas in the case of octanethiol, the range was wider, reaching 1.7 nm (entries 1, 3, and 5).

Similarly, when the stirring time was taken as a parameter, there were different results depending on the thiol used (entries 2–4 for octanethiol; entries 7–9 for dodecanethiol; and entries 12, 16, and 20 for octadecanethiol). With octadecanethiol, there is no noticeable change in size comparing the results obtained for a stirring time of 30 min and for a stirring time of 20 h (2.2 and 2.4 nm, respectively). On the other hand, for dodecanethiol, a remarkable increase in size was obtained when the stirring time was prolonged from 30 min to 20 h. For 30 min, the mean size was 2.3 nm, but in the case of a 20 h time, the particles reached a mean size of 3.5 nm.

The trend for the dependency on the alkyl group of the thiol was that the longer the alkyl group, the smaller the size of the particles. Although the results proved that the surfactant and its related parameters were the main determiners of the final particle size in this method, the number of carbons in the alkyl group of the thiol also proved to have influence on the resulting size. According to the literature,³¹ the variation in size upon addition of the thiol could result from an adjustment in the number of thiolate ligands on the surface that depends on the length of the thiol.

(7) Use of an Anionic Surfactant and without Surfactant. The use of an anionic surfactant such as $CH_3(CH_2)_{11}OSO_3Na$ led to aggregation of the particles, resulting in larger agglomerates with a diameter of ca. 100 nm. This is in good agreement with the experimental results reported for gold particles, because it has been demonstrated that both cationic and nonionic surfactants can be utilized as substrates with which to control the growth of the gold particles and that an anionic surfactant does not guarantee well-controlled particle growth.²⁹

(31) Dassenoy, F.; Philippot, K.; Ely, T. O.; Amiens, C.; Lecante, P.; Snoeck, E.; Mosset, A.; Casanove, M.-J.; Chaudret, B. *New J. Chem.* **1998**, 703–711.

The result of the absence of surfactant was that after the addition of the reducing agent, the organic solution became completely transparent and a black precipitate was readily formed. This finding indicated that bulk palladium metal was formed on reduction, which confirms that a surfactant is needed to control the growth of the particles.

Conclusions

Palladium nanoparticles in a range of 1.3–3.9 nm were prepared by using a one-phase system. This method provided a novel and expedient way to synthesize alkanethiol-protected palladium nanoparticles. Moreover, by controlling several reaction parameters, it was possible to predetermine particle size. TEM photographs not only proved that the particles were formed but also allowed us to compare the different results so that a rational classification could be established. On the basis of the

various experiments described above and their respective results, suitable conditions to synthesize clusters with any size desired between 1.3 and 3.9 nm can be determined. According to the trends that were discovered, the general rules required to obtain small clusters were as follows: use long thiols; increase the amount of the surfactant and that of the reducing agent; increase the stirring time after the addition of the reducing agent; and use $[\text{N}(\text{C}_8\text{H}_{17})_4]\text{Br}$ as the surfactant. As can be expected, the bigger the particles, the larger the size distribution.

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