Synthesis of nearly monodisperse palladium (Pd) nanoparticles by using oleylamine and trioctylphosphine mixed ligands

Zhiqiang Yang, Kenneth J. Klabunde [*]

Departments of Chemistry, Kansas State University, 111 Willard Hall, Manhattan, KS 66506, United States

ABSTRACT

In this paper, we report a facile method to prepare nearly monodisperse Pd nanoparticles by heating Pd(II) ions in 4-*tert*-butyltoluene solvent, in the presence of oleylamine and trioctylphosphine (TOP) ligands. It has been found the concentration of TOP ligand was highly pivotal for the formation of Pd nanoparticles. Without TOP, only aggregated Pd particles were obtained due to the reduction of Pd(II) by oleylamine. When the molar ratio of TOP to Pd(II) was less than two, well-protected Pd nanoparticles were obtained. However, when the molar ratio reached to two, only Pd(II)–TOP coordination complexes were obtained as the final product. Also, the addition of excess oleylamine as a supplementary protecting ligand has proven to be very important. By controlling the experimental conditions, Pd nanoparticles were obtained by this simple synthetic process, and the average size controllable in the range of 9.5–14.9 nm, with standard deviation in the range of 8–13%.

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1. Introduction

In recent years, considerable efforts have been made to synthesize metal nanoparticles. When the particle size is in the nanorange, different physical/chemical properties compared with the bulk counterparts may occur, which is extremely attractive for both academic studies and practical applications [1]. In order to prepare high quality metal nanoparticles that are soluble in organic solvents, organic ligands with long C-chains such as alkylthiols, alkylamines, alkyl carboxyl acids, and phosphines are extensively applied. The ligands can chemically adsorb on the particle surface and then protect them from aggregation. Furthermore, to realize the finest control over the particle's shape, size, and size distribution, mixed ligands are normally engaged. In these cases, it is very important to understand the function of each ligand, but unfortunately, this is not usually possible.

Pd nanoparticles have proven to be highly active catalysts. For example, polyvinylpyrrolidone (PVP)-protected Pd nanoparticles were applied to catalyze the Suzuki reaction between phenylboronic acid and iodobenzene [2]; non-supported Pd nanoparticles were used for the selective hydrogenation of 1-hexyne [3]. A number of preparation methods have been developed to prepare Pd nanoparticles. The reactions may be carried out in aqueous solutions [4–7], inverse micelle systems [8,9], or high-boiling-point organic solvents [10,11]. Reducing agents such as lithium

triethylborohydride (superhydride) [12], lithium borohydride [8], sodium borohydride [5,13], hydrazine [4], sodium hypophosphite [9] are normally used to reduce Pd(II) ions to Pd metal. The reduction can also be realized by heating Pd(II) species in ethylene glycol [14,15] or ethanol/water solutions [16,17]. In order to control the particle size and size distribution, a variety of protecting agents have been investigated, including surfactants [4,7,9], polymers [15,16,18], dendrimers [5,6,19], alkanethiols [12,13,17], phosphines [10,11], thioethers [20], and alkanecyanides [21].

Alkylamines have been employed as mild reducing agents to synthesize gold and silver nanoparticles [22,23]. In our early studies, octylamine and dodecanethiol were used to synthesize highly monodisperse sulfurized Pd nanoparticles [24]. To the best of our knowledge, no other amine-induced reduction of Pd(II) has been reported. In this paper, the reduction of Pd(II) by oleylamine and the influence of trioctylphosphine on this reaction, is presented. This approach provides a facile method to synthesize nearly monodisperse Pd nanoparticles with controllable size. In addition, it is a good example to show how different ligands may play special roles in a ligand-mixed system.

2. Experimental

2.1. Materials

Sodium tetrachloropalladate(II) (Na_2PdCl_4, 99%), trioctylphosphine ($[CH_3(CH_2)_7]_3P$, 90%) were purchased from Aldrich Chem. Co. Oleylamine ($CH_3(CH_2)_7CH=CH(CH_2)_7CH_2NH_2$, 97%) and 4-*tert*-

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butyltoluene ((CH$_3$)$_3$CC$_6$H$_4$CH$_3$, 96%) were bought from ACROS Organics. Other chemicals were bought and used as received.

2.2. Thermolysis without TOP

In a glass tube, 0.029 g of Na$_2$PdCl$_4$ (1.0 × 10^{-4} mol), 10 ml of 4-*tert*-butyltoluene, and 0.50 ml of oleylamine (1.5 × 10^{-3} mol) were added in sequence. The mixture was sonicated for 20 min. The tube was then connected to a vacuum/argon system via a rubber septum equipped with needles. The mixture was degassed and then flushed with argon several times. After that, it was heated (about 192 °C) in a preheated sand-bath for 1 h under the protection of argon. During that time, black precipitates were produced. After 1 h, the tube was removed from the sand-bath and left to cool. Finally, the black precipitates were collected by centrifugation and washed with acetone several times.

2.3. Thermolysis with different amounts of TOP

In a glass tube, 0.029 g of Na$_2$PdCl$_4$, 10 ml of 4-*tert*-butyltoluene, 0.50 ml of oleylamine, and certain amounts of TOP were added sequentially. The molar ratios of TOP to Pd(II) were altered systematically from 0.4, 0.6, 1.0, 1.4, to 2.0. After sonication for 20 min, the thermal reaction and the product collection were carried out in the same way as described above. For convenience, the obtained products are labeled as Sample (*n*×) in this paper (*n* = the molar ratio of TOP to Pd(II) ions).

2.4. Equipment and analysis

Transmission electron microscopy (TEM) was performed on a Philips CM100 microscope operated at 100 kV. To prepare a TEM sample, the washed products were redispersed into toluene and then a drop of solution was dropped onto a carbon/Formvar co-coated copper grid, which was then allowed to dry in air. UV–Vis absorption analysis was carried out on a Cary 500 UV–VIS–NIR spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded by a Bruker D8 X-ray diffractometer with Cu Kα radiation.

3. Results and discussion

3.1. Reduction of Pd(II) ions by oleylamine

In the reaction system, oleylamine was applied in an excess amount (the molar ratio of amine to Pd(II) was 15) to facilitate the completion of the reduction. 4-*tert*-Butyltoluene was used as a high-boiling-point (192 °C), non-coordinating solvent. After sonication for 20 min at room temperature, the reddish-brown-colored Na$_2$PdCl$_4$ powder was mostly dissolved and a colorless solution was formed, which was attributed to the generation of certain Pd(II)–oleylamine complexes. When boiled at ca.192 °C under the protection of argon, the system turned to black in ten minutes, indicating the formation of small particles. After one hour, black-colored precipitates were collected as Sample (0×). The powder XRD pattern of this sample shows the features of pure face-centred cubic palladium crystallites (Fig. 1).

The formation of Pd(0) is attributed to the reduction of Pd(II) ions by oleylamine at high temperature, in which the amine ligands are oxidized to nitriles [25]. The formation of soluble Pd(II)–oleylamine coordination complexes occurs before the heat treatment, and the amine-induced reduction occurs during the heating step. The overall reaction is assumed to happen according to the following equation via Pd(II)–amine intermediates:

$$2Na_2PdCl_4 + C_{18}H_{35}NH_2 \rightarrow [Pd(II) - amine\ complexes]$$
$$\rightarrow 2Pd^0 + C_{17}H_{33}CN + 4NaCl + 4HCl$$
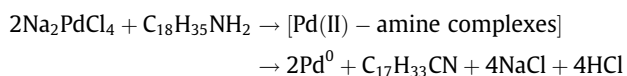
A typical TEM image (Fig. 2) of Sample (0×) shows large, irregular aggregates in the dimension of tens of micrometers. They are composed of numerous stacked small Pd(0) nanoparticles with diameter in the range of 10–20 nm, which can be observed at the edge of the aggregates. Although oleylamine has been applied successfully as the protecting ligand for the synthesis of a variety of metal nanoparticles, our results indicate it may not be the best capping ligand for Pd nanoparticles. To further confirm that, another experiment was carried out under the same conditions except that the molar ratio of oleylamine to Pd(II) was increased to 150. The obtained particles were still not stable in the solution and ready to settle down as black precipitates as seen in Sample (0×).

3.2. Reduction of Pd(II) ions in the presence of oleylamine and TOP

When other experimental conditions were fixed, different amounts of TOP were added before heating. The molar ratio of TOP to Pd(II) were set as 0.4, 0.6, 1.0, 1.4, and 2.0. After heating, stable black colloidal solutions were obtained for Sample (0.4×) to Sample (1.4×), while Sample (2.0×) remained as a clear lightly yel-

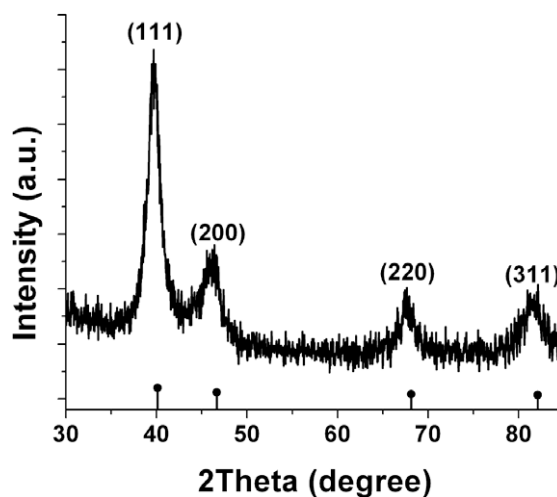**Fig. 1.** Powder XRD pattern of Sample (0×) indicating the formation of Pd(0) crystallites. The standard pattern (the vertical lines) is based on JCPDS file 46-1043. (*Notice*: a small amount of water was added during wash in order to remove NaCl that was generated in the reaction.)

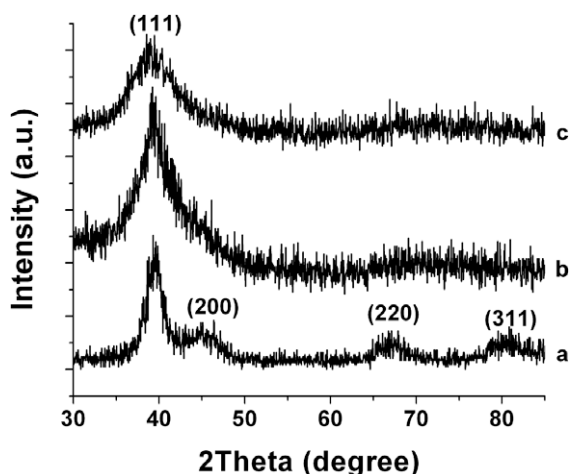**Fig. 2.** TEM image of Sample (0×) shows aggregated particles.

Fig. 3. Powder XRD patterns of Sample (0.4×) (a), Sample (0.6×) (b) and Sample (1.0×) (c).

low solution. While the optical densities for Sample (0.4×), Sample (0.6×), and Sample (1.0×) were indistinguishable to the naked eye, the decrease of the darkness for Sample (1.4×) was obvious (see Supplementary material, Fig. S1 for the different appearance of the as-synthesized samples).

The powder XRD patterns of the obtained samples still show the features of pure face-centred-cubic Pd(0) nanocrystallites (Fig. 3). When increasing the molar ratio of TOP to Pd(II), the broadening of the (1 1 1) peak and the disappearance of other peaks are noticeable, which may result from the changes in the particle's size or crystallinity.

The typical TEM images of the obtained samples are shown in Fig. 4 (also see Supplementary material, Fig. S2 for the histogram patterns). Generally speaking, when increasing the molar ratio of TOP to Pd(II), the particles become smaller in size and rounder in shape. Sample (0.4×) shows irregular faceted particles with an average diameter of 10.7 ± 2.9 nm. The standard deviation (SD) is 27%. For Sample (0.6×), the average diameter is 10.8 ± 2.0 nm (SD = 19%). While the average particle size remains almost the same compared with Sample (0.4×), the narrowing in particle size distribution is noticeable. Sample (1.0×) shows smaller and more spherical particles with an average diameter of 9.5 ± 1.2 nm (SD = 13%). These particles could assemble into hexagonal close-packing supperlattices on the TEM grid. For Sample (1.4×), the particles become further smaller, but the monodispersity becomes poorer (average particle size: 7.6 ± 1.9 nm; SD: 25%).

Due to the damping effect of the d–d transitions, Pd nanoparticles usually do not show a surface plasmatic (SP) absorbance in UV–Vis spectra [26]. Consistent with this observation, an UV–Vis measurement of Sample (1.0×), which was washed and then redis-
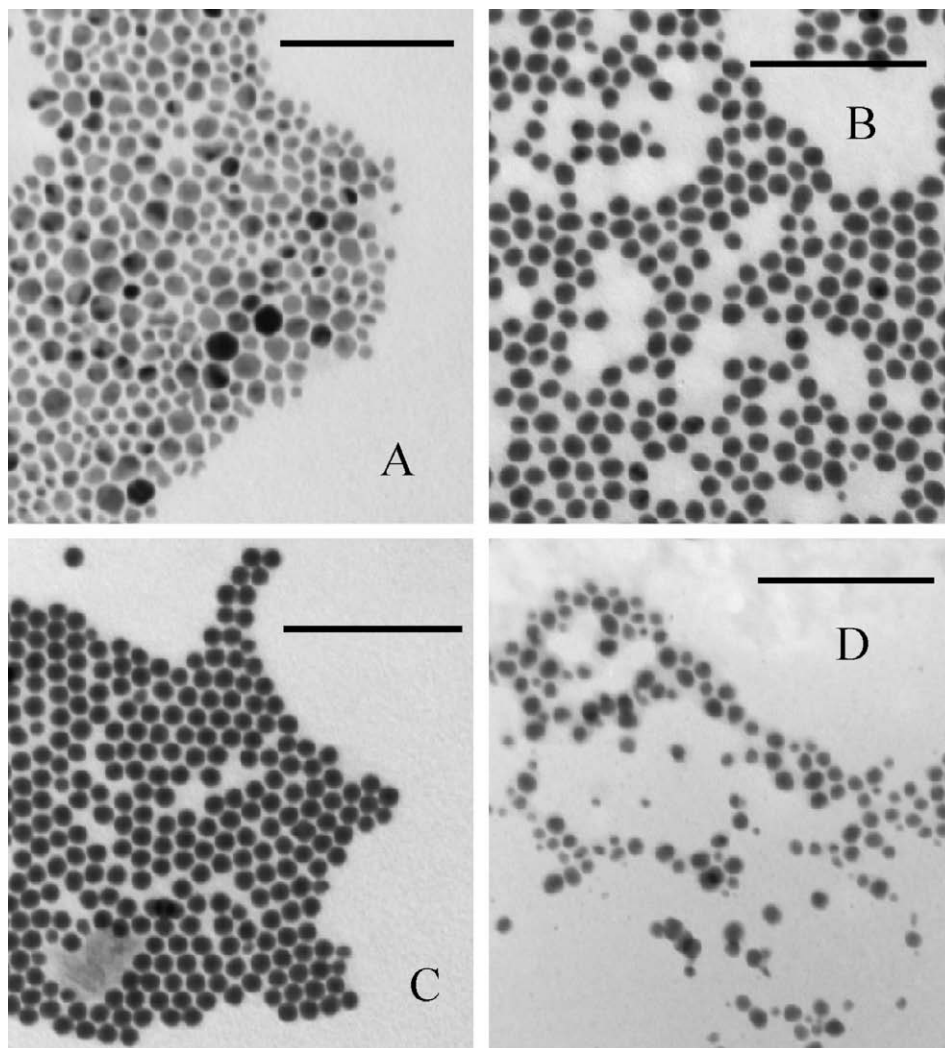

Fig. 4. TEM images of (A) Sample (0.4×), (B) Sample (0.6×), (C) Sample (1.0×) and (D) Sample (1.4×). Scale bar = 100 nm.

solved in hexane, presents no SP band (see Supplementary material, Fig. S3).

3.3. The function of TOP

As mentioned above, when the source Pd(II) salt was dissolved in 4-*tert*-butyltoluene with oleylamine at room temperature, certain Pd(II)–amine complexes were formed. When TOP was added into such a system, the Pd(II)–amine complexes were converted to Pd(II)–TOP complexes due to the stronger coordinating potence to Pd(II) ions of phosphine ligands over amine ligands. To prove this, the change of the UV–Vis absorbance for Sample (1.0×) before and after adding TOP was measured. When TOP was added to the Pd(II)–oleylamine system, a new peak at ca. 318 nm was generated (Fig. 5). To indicate such a peak was not due to the pure TOP ligands, the UV–Vis absorbance of TOP in hexane was measured and no peak was found at this position. Furthermore, when adding Na$_2$PdCl$_4$ to this TOP/hexane mixture, a peak came out at 318 nm (see Supplementary material, Fig. S4). All of these results confirm that the absorbance at 318 nm for Sample (1.0×) after adding

TOP was really due to the generation of certain Pd(II)–TOP complexes.

After heat treatment, different final products were generated, highly depending on the concentration of TOP. A preliminary explanation for this phenomenon is as follows: When no TOP was applied, only aggregated Pd(0) particles were obtained due to the amine-induced reduction and the poor protecting ability of amine ligands for the as-synthesized Pd(0) particles. However, for Sample (2.0×), only certain Pd(II)–TOP complexes were produced, which were quite stable in the reaction system. For Sample (0.4×) to Sample (1.4×), since the amounts of TOP ligands were

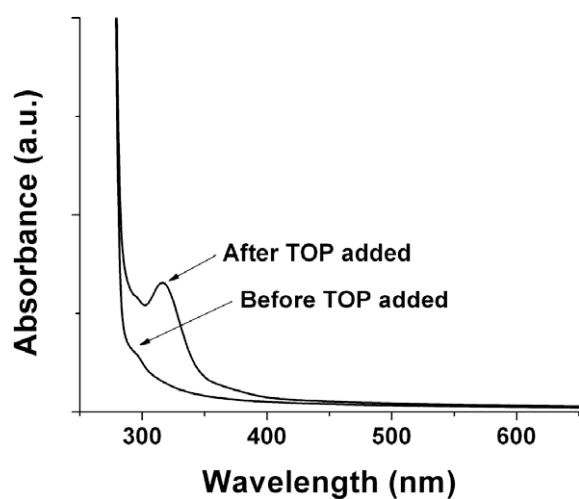Scheme 1. Influence of TOP on the final products. (*Note*: all the ratios are molar ratios.)

Fig. 5. UV–Vis absorbance for Sample (1.0×) before and after adding TOP at room temperature to show the generation of Pd(II)–TOP complexes. For each measurement, 30 ul of the solution was taken and then mixed with 3 ml of hexane, which was also used as the reference.
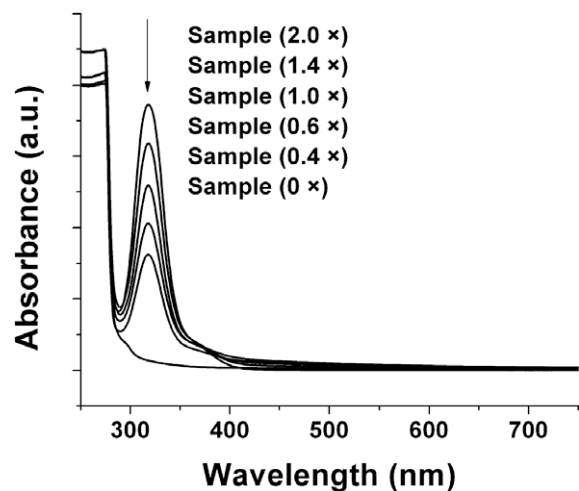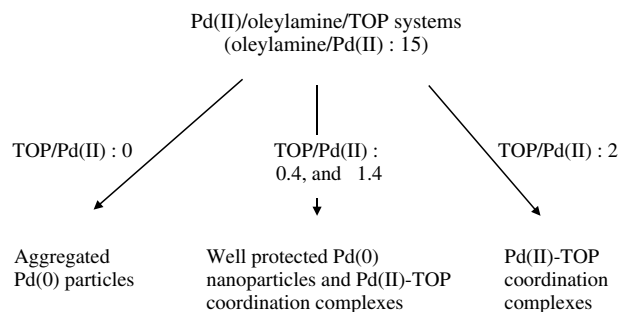
Fig. 6. UV–Vis patterns of the sample solutions after heating. For each measurement, an aliquot of 30 ul was taken and then mixed with 3 ml of hexane. Reference: hexane.
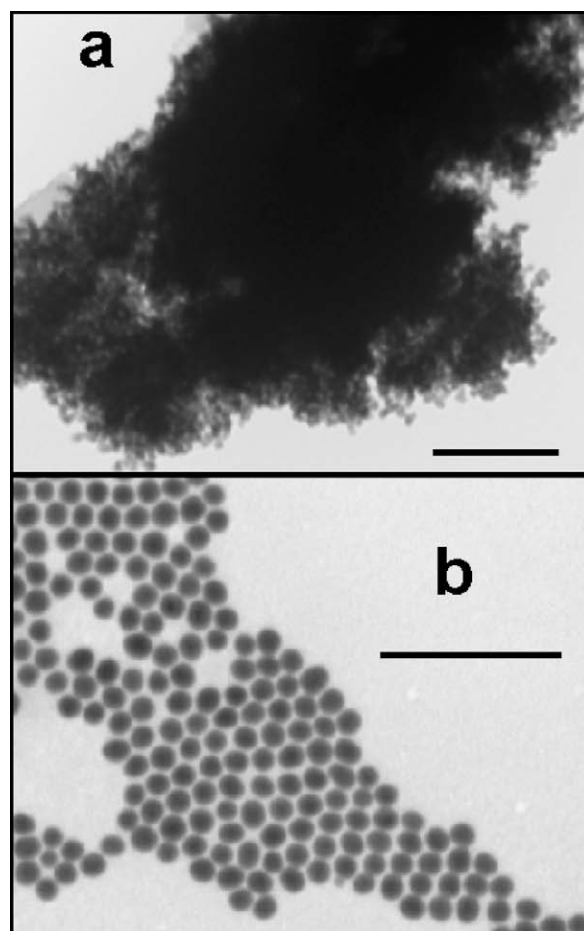
Fig. 7. TEM images of the particles prepared according to Sample (0.6×) except changing the molar ratio of oleylamine to Pd(II). (a) Decreasing the ratio to 3, (b) increasing the ratio to 60. Scale bar = 100 nm. Also see the TEM image of Sample (0.6×) in Fig. 4b for comparison.
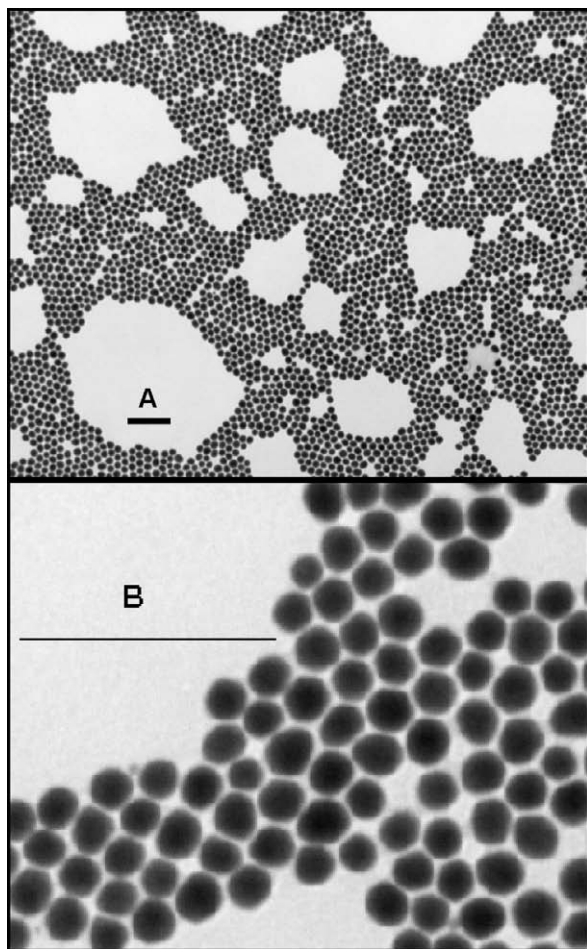
Fig. 8. TEM images of the sample prepared according to Sample (0.6×) except increasing the molar ratio of oleylamine to Pd(II) to 60 and heating for 17 h. (A) Small magnification to show the hexagonal close-packing pattern in short range. (B) Large magnification to show the faceted quasi-spherical shape. Scale bar = 100 nm.

3.4. The cooperative protecting effects of oleylamine

As mentioned previously, the main function of oleylamine in this system was to reduce Pd(II) ions. Without TOP added, only aggregated Pd nanoparticles were obtained even when the molar ratio of oleylamine to Pd(II) reached to 150. But further studies indicated that, addition of an appropriate amount of oleylamine as a supplementary capping ligand was very important and necessary even when TOP was added. The experiments were carried out according to Sample (0.6×) except changing the concentration of oleylamine. In Sample (0.6×), the molar ratio of oleylamine to Pd(II) was set as 15 arbitrarily. When the molar ratio was decreased to 3, only aggregated Pd(0) particles were generated (Fig. 7a). However, when the molar ratio was increased to 60, well-protected Pd(0) nanoparticles were obtained with a little bigger size but narrower distribution (size: 11.6 ± 1.4 nm, SD = 12%) compared with Sample (0.6×) (Fig. 7b. Also see Supplementary material, Fig. S5 for the histogram of the size distribution). Furthermore, this sample has been found to be quite stable toward long-term digestive ripening. After boiling for 17 h, a typical TEM picture shows Pd nanoparticles with an average diameter of 14.9 ± 1.2 nm (SD = 8%). A close-up TEM picture indicates that, when the size increases, it is more likely to form quasi-spherical particles with certain crystal facets (Fig. 8. Also see Supplementary material, Fig. S5 for the histogram of the size distribution).

4. Conclusions

In this paper, we report the influence of TOP ligand on the synthesis of Pd nanoparticles by oleylamine-induced reduction of Pd(II) ions. Without TOP, only aggregated Pd particles were generated. When an appropriate amount of TOP was added, nearly monodisperse Pd nanoparticles could be obtained. But further increasing the molar ratio of TOP/Pd(II) to 2 resulted in the formation of Pd(II)–TOP coordination complexes. Also, the function of oleylamine as a supplementary ligand was discussed, which will be helpful for understanding the cooperation of mixed protecting ligands in certain systems.

Acknowledgements

Appendix A. Supplementary material

The different appearance of the as-synthesized samples; the histograms indicating the size distribution; the UV–Vis absorbance of Sample (1.0×) after wash; the UV–Vis absorbance to show the generation of Pd(II)–TOP complexes at room temperature. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.030.

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inadequate, some Pd(II) ions were consumed to form Pd(II)–TOP complexes, while the remaining Pd(II) ions would still be reduced by oleylamine. Since well-protected particles were generated in these cases, the chemical binding of TOP (from the free Pd(II)–TOP complexes in solution) on the as-synthesized Pd(0) particles is assumed. So, some TOP ligands were consumed to protect the Pd nanoparticles, while the others still remained in solution as Pd(II)–TOP complexes. Fig. 6 shows the UV–Vis absorbance of the solutions after heating. A peak at 318 nm was found for all the samples except Sample (0×).

According to the above discussion, the influence of different amounts of TOP on the final products is systematically shown in Scheme 1. It should be pointed out, for collecting Pd(0) nanoparticles, the Pd(II)–TOP complexes could be removed by washing with acetone.

A similar influence of thiol ligands on a Pd(II)/octylamine system was reported previously [24]. With increasing thiol concentration, the final products changed from sulfur-rich Pd nanoparticles to a tiara-like Pd(II)–thiolate complex. Another similar example was reported regarding the influence of oleic acid on the preparation of Co(0) nanocrystals [27]. Increasing the concentration of oleic acid also resulted in the transformation of Co(0) nanoparticles to Co(II) cluster compounds. The results described herein add to our understanding of these sensitive chemical processes that are ligand-controlled.

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