

# An Alternative Phase-Transfer Method of Preparing Alkylamine-Stabilized Platinum Nanoparticles

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An alternative phase-transfer method has been developed to prepare alkylamine-stabilized Pt nanoparticles. This method involves preparing a Pt hydrosol and then mixing the Pt hydrosol with a toluene solution of dodecylamine. This is followed by the addition of 1 M NaOH or 1 × PBS buffer to adjust the pH of the hydrosol to suitable values. Dodecylamine-stabilized Pt nanoparticles prepared this way had a predominantly cubic appearance, uniform size distribution, and self-assembled on transmission electron microscopy copper grids with an interparticle spacing of 2.2 nm. These results were then used to derive a protocol for preparing oligonucleotide-stabilized Pt nanoparticles in the aqueous environment. The oligonucleotide-stabilized Pt nanoparticles formed this way were either of spherical or irregular cubic shape depending on whether H<sub>2</sub>-PtCl<sub>6</sub> or K<sub>2</sub>PtCl<sub>4</sub> was used as the starting metal salt.

## Introduction

The phase-transfer method was first used by Brust et al.<sup>1</sup> to prepare thiol-stabilized gold nanoparticles. Its application has since been extended to the preparation of other metal nanoparticles.<sup>2–6</sup> Initially, the common practice was to first extract the metal ions from an aqueous solution to a hydrocarbon (toluene) layer using a phase-transfer reagent such as tetraoctylammonium bromide and then carry out the NaBH<sub>4</sub> reduction in the presence of an alkanethiol. The nucleation and growth of the metal particles and the attachment of the thiol molecules therefore occur simultaneously in a single step. More recently, Sarathy<sup>3,4</sup> and Zhao<sup>6</sup> adopted a different approach in which preformed metal nanoparticles of gold, platinum, and silver, instead of metal ions, were directly transferred to the organic phase for thiolation. A metal hydrosol was prepared in advance using NaBH<sub>4</sub> as the reducing agent and mixed with a toluene solution of 1-dodecanethiol. Concentrated HCl was then added to the biphasic mixture under vigorous stirring to enable the transfer. The thiol-stabilized metal nanoparticles prepared this way were uniform in size and often formed self-assembled structures on a transmission electron microscopy (TEM) grid. The use of concentrated HCl makes this phase-transfer technique unsuitable for applications in the biological environment where the viability of biomolecules is lost at extreme pH values. We have previously developed a technique<sup>7</sup> to transfer Pt nanoparticles from an aqueous solution to a hydrocarbon environment using a small amount of NaBH<sub>4</sub> as the reducing agent, where concentrated HCl was not needed at all. The thiol-stabilized Pt nanoparticles so prepared were, however, polydisperse.

Here we report an alternative phase-transfer procedure for preparing alkylamine-stabilized Pt nanoparticles with improved results. In this process, the Pt hydrosols were prepared by the NaBH<sub>4</sub> reduction of a platinum precursor salt, and the nano-

particles were transferred directly to a toluene solution of dodecylamine by introducing a small amount of NaOH or PBS buffer. The pH change caused by the addition is very moderate, and hence the procedure is amenable to particle modifications carried out in a biological environment. A detailed description of an example application of this technique (amidst some small variations) in the biological environment is also provided.

## Experimental Section

Hydrogen hexachloroplatinate(IV) hydrate, potassium tetrachloroplatinate(II), and dodecylamine from Aldrich, sodium borohydride (98%) from Fluka, toluene from Baker, sodium hydroxide (pellets) from Merck, 1 × PBS buffer from Sigma, alkylamine-modified oligonucleotide, and poly A (5'-NH<sub>2</sub>-(CH<sub>2</sub>)<sub>6</sub>-AAA-AAA-AAA-AAA-AAA-AAA-AA, 333.6 μM) from Prologo were all used as received. Deionized water was distilled by a Milli-Q water purification system. All glassware and Teflon-coated magnetic stir bars were treated in aqua regia, followed by copious washing with distilled water before drying in an oven.

The Pt hydrosol was prepared according to the following procedure: 0.2 mL of 112 mM freshly prepared NaBH<sub>4</sub> solution was added dropwise to 10 mL of 2 mM H<sub>2</sub>PtCl<sub>6</sub> solution under vigorous stirring at room temperature. The Pt hydrosol thus obtained was brown in color. Toluene (10 mL) containing 400 μL of dodecylamine was added to this Pt hydrosol, turning it into a turbid, grayish-white mixture. NaOH (120 μL, 1 M) solution was introduced next, and the mixture separated into two clear layers in the container. The color of the toluene layer was brown, showing that the Pt nanoparticles had been successfully transferred from the aqueous to the hydrocarbon phase.

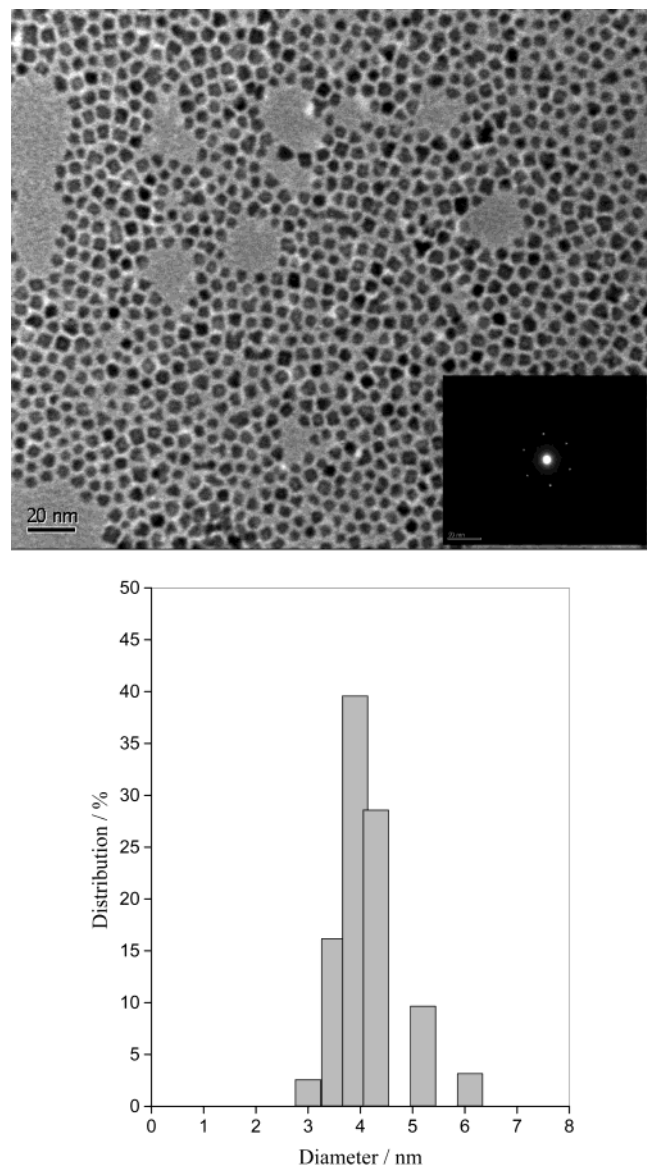
The transfer of Pt nanoparticles from aqueous to toluene could also occur with 10 mL of 1 × PBS buffer (pH = 7) substituting for the 120 μL of 1 M NaOH solution. The experimental results were however significantly different if K<sub>2</sub>PtCl<sub>4</sub> was used to replace H<sub>2</sub>PtCl<sub>6</sub> as the metal precursor salt, as will be described later in this article.

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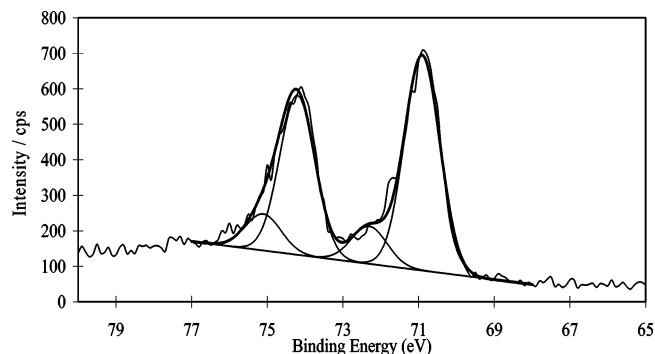
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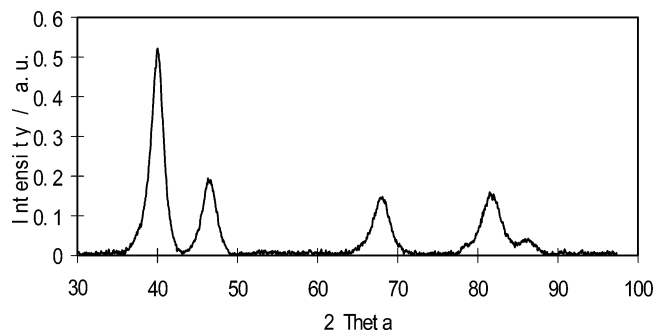
**Figure 1.** TEM image of dodecylamine-stabilized Pt nanoparticles transferred from the aqueous solution to toluene by NaOH. The inset is the electronic diffraction pattern of the transferred Pt nanoparticles.  $d = 4.12$  nm,  $\sigma = 0.60$  nm.

For the preparation of oligonucleotide-stabilized Pt nanoparticles, 50  $\mu$ L of the Pt hydrosol prepared above was diluted with 50  $\mu$ L of distilled water and 15  $\mu$ L of 333.6  $\mu$ M 5'-modified poly A was introduced. After thorough mixing, 100  $\mu$ L of 1  $\times$  PBS buffer (pH = 7) was added. A brown-colored Pt nano-system in which the particles were stabilized by poly A was obtained, which could be stored for several weeks without changes.

A JEOL JEM2010 instrument was used to obtain all TEM images of the nanoparticles. For TEM measurements, a drop of the metal nanoparticle solution was placed on a 3-mm copper grid coated with a continuous carbon film. Excess solution was removed by an absorbent paper. The mean particle size and particle size distribution were obtained from a few randomly chosen areas in the TEM image containing approximately 200 nanoparticles each. X-ray photoelectron spectroscopic analysis (XPS) was carried out on a VG ESCALAB MKII spectrometer using samples centrifuged from the Pt hydrosol. Samples for XPS were copiously washed with distilled water before the analysis. Narrow scan photoelectron spectra were recorded in the Pt 4f region. X-ray diffraction (XRD) patterns of the Pt



**Figure 2.** X-ray photoelectron spectra of Pt nanoparticles precipitated from the metal hydrosol.

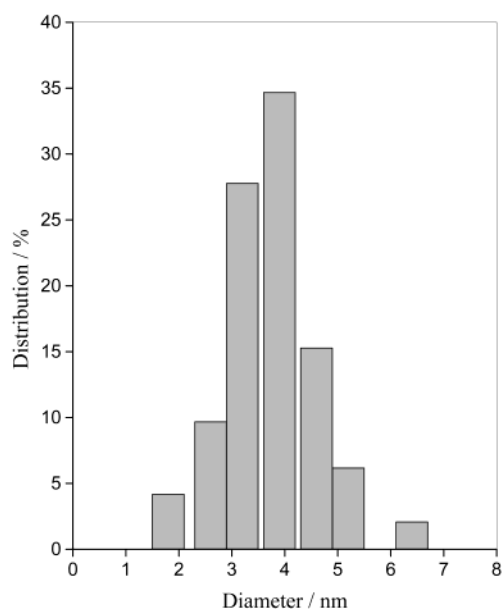
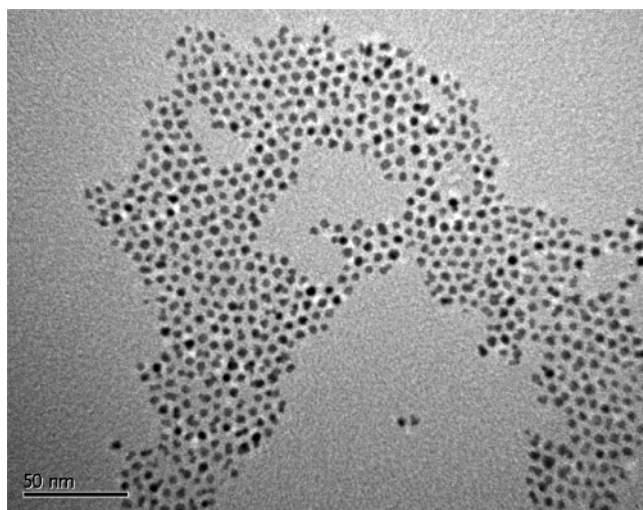


**Figure 3.** XRD patterns of Pt nanoparticles precipitated from the Pt hydrosol.

hydrosol precipitates were obtained on a Rigaku D/Max-3B diffractometer using Cu K $\alpha$  radiation. All samples were vacuum-dried before the measurements.

## Results and Discussions

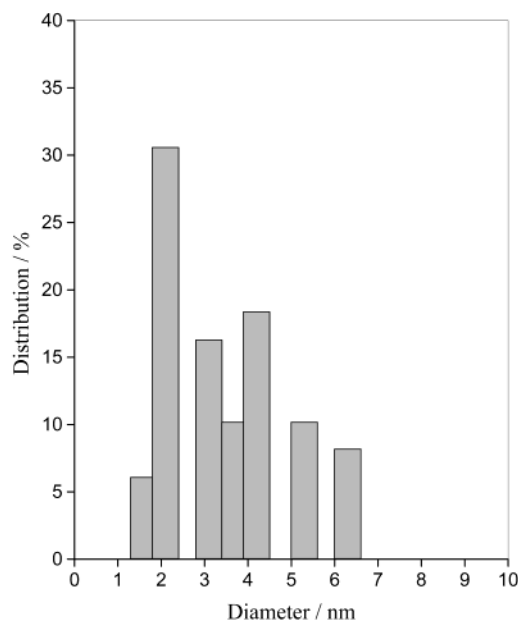
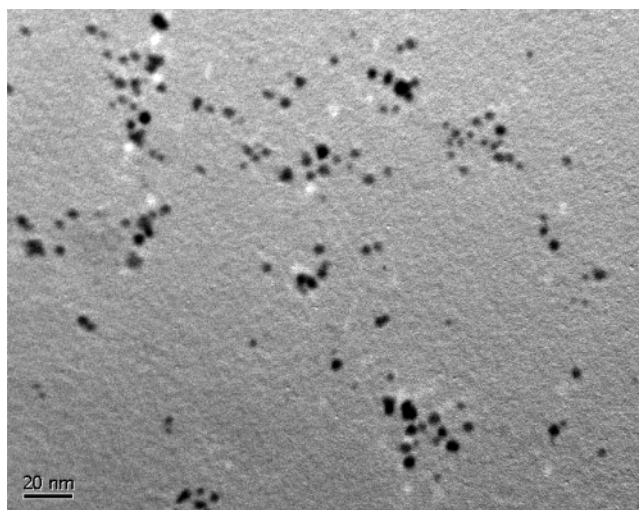
Even without external stabilizers, Pt hydrosols with an average particle size of 2.5 nm and a standard deviation of 0.45 nm could still be obtained from the NaBH<sub>4</sub> reduction of H<sub>2</sub>-PtCl<sub>6</sub>, which were stable for a few hours without precipitation.<sup>7</sup> The complete reduction of H<sub>2</sub>PtCl<sub>6</sub> was confirmed by inductively coupled plasma atomic emission spectrometry analysis of the aqueous supernatant solution after centrifugation and by UV-vis spectroscopy of the hydrosol.<sup>7</sup> When a toluene solution of dodecylamine was introduced to the Pt hydrosol, a turbid and grayish-white emulsion was obtained. This turbid mixture could be stored for several days without changes if NaOH was not added to it. The transfer of Pt nanoparticles from the aqueous phase to toluene occurred and was completed within minutes after the addition of a 1 M NaOH solution. The reason for the NaOH-facilitated transfer of Pt nanoparticles from water to toluene is not clear at present, although the following speculations may be made: Dodecylamine is expected to be protonated by the slightly acidic (pH = 3) Pt hydrosol. Protonation could diminish the affinity of dodecylamine for the Pt surface. The increase in pH caused by NaOH addition restored the amine to its natural form, re-enabling the attachment of amine to the nanoparticle surface, and the dodecylamine-protected Pt nanoparticles were stabilized in toluene. The dodecylamine-stabilized Pt nanoparticles were highly stable and could be stored for several months without sedimentation. A TEM image of the dodecylamine-stabilized Pt nanoparticles is shown in Figure 1. The histogram from counting 200 well-separated particles shows a narrow particle size distribution with a mean particle diameter of 4.12 nm and a standard derivation of 0.60 nm. The slight increase in the particle size is an indication of particle ag-



**Figure 4.** TEM image of dodecylamine-stabilized Pt nanoparticles transferred to toluene with  $1 \times$  PBS buffer.  $d = 3.72$  nm,  $\sigma = 0.86$  nm.

glomeration that occurred during the transfer process. Except for a small number of spherically and triangularly shaped particles, the predominant shape for the particles was cubic. The observation is quite different from the results of Sarathy et al.<sup>3–4</sup> who obtained mostly spherical Pt nanoparticles.

The assembly of nanoparticles into well-defined two- or three-dimensional spatial configurations may produce some interesting properties, and self-assembly is a simple but effective means to form ordered structures without external forces. Two-dimensional (2D) ordered structures of Au nanoparticles and Ag nanoparticles are easily formed by nanoparticles prepared by the phase-transfer method and stabilized by alkanethiol.<sup>8–9</sup> However, reports on the 2D-ordered structures of Pt nanoparticles, particularly cubic-shaped Pt nanoparticles, are less common.<sup>4,6</sup> Zhao and co-workers<sup>6</sup> reported the assembly of alkanethiol-stabilized cubic Pt nanoparticles prepared by the phase-transfer method only with the help of concentrated HCl. The self-assembly of the nanoparticles prepared in this work should also be a possibility, since a close-packed monolayer of nanoparticles might form after solvent evaporation due to amine stabilization. The arrangement of Pt nanoparticles in Figure 1 is well ordered, as shown by a constant center-to-center nearest-



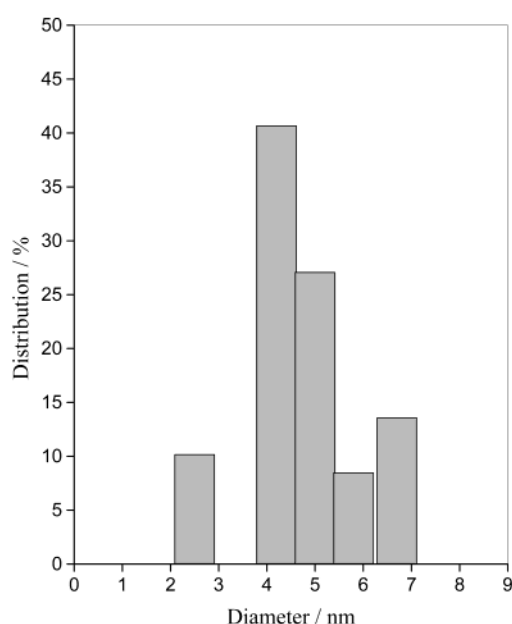
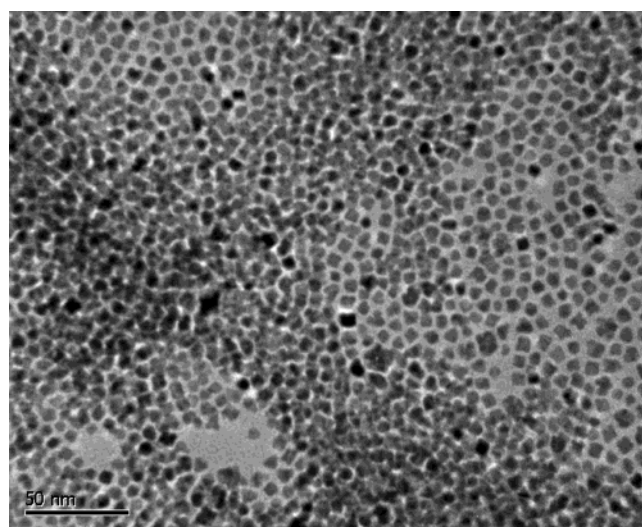
**Figure 5.** TEM images of amine-modified poly-A-stabilized 3.8-nm Pt nanoparticles prepared from  $\text{H}_2\text{PtCl}_6$ .

neighbor distance of ca. 6.3 nm throughout the self-assembled region. From an enlarged image of Figure 1, calculations showed that the average interparticle spacing edge on edge was 2.2 nm, which is much shorter than twice the hydrocarbon length of dodecylamine (1.77 nm) adsorbed on the surface of the Pt nanoparticles. The hydrocarbon length was calculated according to Bain's empirical formula,<sup>10</sup>  $l = (0.25 + 0.127n)$  nm, where  $n$  is the number of  $\text{CH}_2$  groups and 0.25 nm is used to account for the presence of amine and methyl terminating groups in the molecule. The calculation suggests that (1) either the dodecylamine molecules were interdigitated<sup>11</sup> or (2) they were not extended outward normal to the Pt nanoparticle surface but were inclined at an angle of  $38^\circ$  with the surface.

The composition of the nanoparticles from the Pt hydrosol was analyzed by XPS. Figure 2 shows that the Pt 4f region of the spectrum could be deconvoluted into two pairs of doublets. The more intense doublet (at 70.9 and 74.2 eV) is a signature of Pt in the zerovalent state. The second and weaker doublet (at 72.3 and 75.1 eV), with binding energies of 1.4 eV higher than Pt(0), could be assigned to the Pt(II) oxidation state as in PtO and  $\text{Pt}(\text{OH})_2$ .<sup>12–13</sup>

In addition, XRD measurements were also carried out on the same Pt sample used in the XPS analysis (Figure 3). The lines



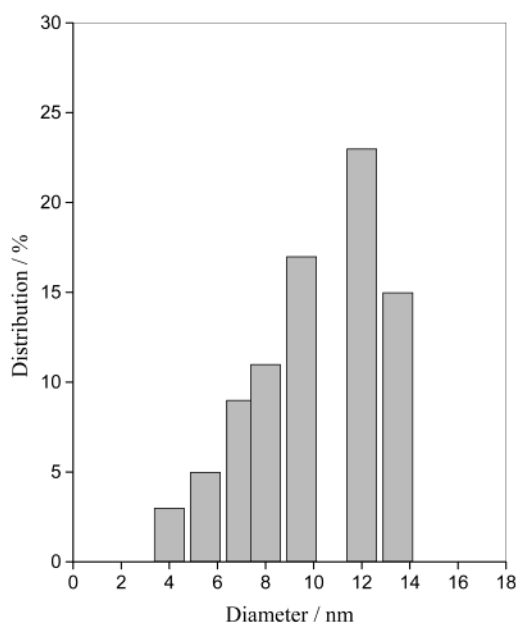
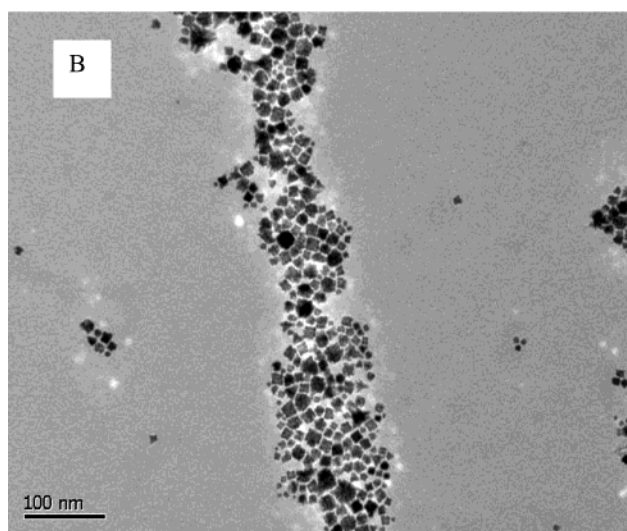
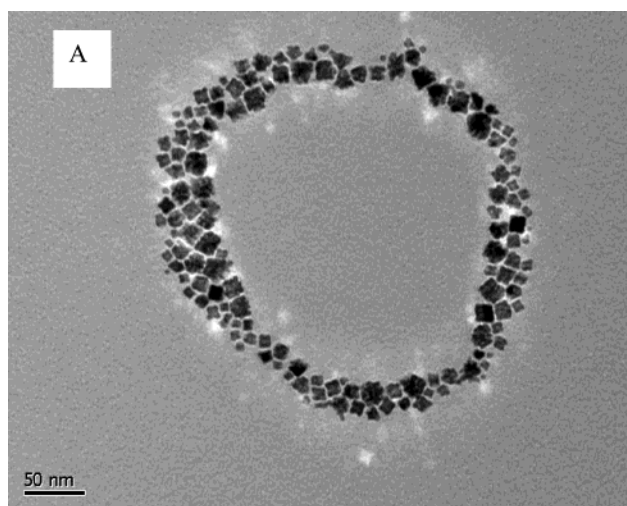


**Figure 6.** TEM images of alkylamine-stabilized 6-nm Pt nanoparticles prepared by the phase-transfer technique using  $K_2PtCl_4$  as the starting metal salt.

of (111) ( $d = 0.2255$  nm), (200) ( $d = 0.1955$  nm), (220) ( $d = 0.1380$  nm), (311) ( $d = 0.1179$  nm), and (222) ( $d = 0.1129$  nm) diffractions of metallic Pt are clearly identifiable, indicating that the Pt nanoparticles had a fcc lattice structure.<sup>14</sup>

If a  $1 \times$  PBS buffer (pH = 7) was used instead of 1 M NaOH, the phase transfer of Pt nanoparticles was equally rapid and complete. The TEM image of alkylamine-stabilized Pt nanoparticles obtained in this way is shown in Figure 4. The size and the size distribution of the Pt nanoparticles were similar to the Pt nanoparticles obtained by using NaOH to increase the pH of the Pt hydrosol.

The result that PBS buffer was equally adept at promoting the attachment of amine to the Pt nanoparticles is a welcome feature and suggests the following method of preparing oligonucleotide-stabilized Pt nanoparticles: The ends of the oligonucleotides are first amine modified and then mixed with a Pt hydrosol. A PBS buffer designed for a pH that keeps most biomolecules active and viable is then introduced to facilitate the attachment of the amine-modified oligonucleotides to the Pt nanoparticles, resulting in the formation of oligonucleotide-stabilized nanoparticles. A TEM image of amine-modified poly-



**Figure 7.** TEM images of poly-A-stabilized 12-nm Pt nanoparticles prepared from  $K_2PtCl_4$ .

A-stabilized Pt nanoparticles is shown in Figure 5 as an example. Different from the TEM images of Figures 1 and 4, most of the Pt particles stabilized by poly A were spherical with an average particle diameter of 3.8 nm.

The oligonucleotide-stabilized Pt nanoparticles were stable in 1 M aqueous NaCl solutions (the “unprotected” or citrate-protected nanoparticles were not). There was no precipitation from the nanoparticle dispersion even after several days of storage in 1 M aqueous NaCl. This shows that amine-modified oligonucleotides are superior to simple chelating agents such as citrate ions in inhibiting particle agglomeration. The added protection could come from the long sugar–phosphate backbone that prohibits the particles getting close enough to undergo particle aggregation. The work on amine-modified oligonucleotide-stabilized Pt nanoparticles is still ongoing, and additional information will be reported later.

If  $\text{K}_2\text{PtCl}_4$  was substituted for  $\text{H}_2\text{PtCl}_6$  as the starting metal salt, the Pt nanoparticles were cubic with an average diameter of 5.5 nm (data not shown). The morphological and size difference between Pt nanoparticles prepared from the  $\text{NaBH}_4$  reduction of  $\text{K}_2\text{PtCl}_4$  and from the  $\text{NaBH}_4$  reduction of  $\text{H}_2\text{PtCl}_6$  may be traced to a precursor or counterion effect.<sup>15</sup> The dodecylamine-stabilized Pt nanoparticles in toluene obtained similarly were much larger with a mean equivalent diameter of 6 nm (Figure 6). The particles were also predominantly cubic, but their self-assembly into ordered structures was not as easy as those prepared from  $\text{H}_2\text{PtCl}_6$ . Another startling difference between  $\text{K}_2\text{PtCl}_4$ - and  $\text{H}_2\text{PtCl}_6$ -derived nanoparticles lies with the oligonucleotide modification. Most of the poly-A-stabilized Pt nanoparticles from  $\text{K}_2\text{PtCl}_4$  exhibited a highly irregular cubic structure with an average particle size of 12 nm. More importantly, these Pt nanoparticles would self-assemble into some rather intriguing geometries on the TEM copper grid, as shown in parts A and B of Figure 7. Whether these interesting structures (which were highly reproducible) were chance encounters or indicative of some specific properties of poly-A-stabilized Pt nanoparticles remains unclear at present.

## Conclusions

By treatment of Pt hydrosols prepared from the  $\text{NaBH}_4$  reduction of  $\text{H}_2\text{PtCl}_6$  or  $\text{K}_2\text{PtCl}_4$  with NaOH or a PBS buffer, an alternative phase-transfer method of preparing dodecylamine-stabilized Pt nanoparticles was developed in this work. The dodecylamine-stabilized Pt nanoparticles prepared in this way had a predominantly cubic structure. The particle size was strongly influenced by the choice of the metal precursor salt. The average particle size of dodecylamine-stabilized Pt nanoparticles from  $\text{H}_2\text{PtCl}_6$  was 4.12 nm (NaOH treatment) or 3.72 nm (PBS treatment), whereas the corresponding average particle

size from  $\text{K}_2\text{PtCl}_4$  was 6 nm (NaOH treatment). The dodecylamine-stabilized Pt nanoparticles could easily self-assemble into ordered structures with average interparticle spacing of 2.2 nm on a TEM copper grid. A simple calculation suggests that either the dodecylamine molecules were interdigitated or they were not extended outward normal to the Pt nanoparticle surface but were inclined at an angle of  $38^\circ$  with the surface.

The PBS buffer facilitated attachment of amine to Pt nanoparticles was extended to prepare oligonucleotide-stabilized Pt nanoparticles. The preparation of poly-A-stabilized Pt nanoparticles took place entirely in the aqueous phase. Poly-A-stabilized Pt nanoparticles prepared from the  $\text{H}_2\text{PtCl}_6$  precursor were spherical, with an average particle size of 3.8 nm. However, similar particles prepared from the  $\text{K}_2\text{PtCl}_4$  precursor were much larger, at 12 nm on the average, and exhibited an irregular cubic morphology. Most importantly, the latter Pt nanoparticles could order into some rather intriguing patterns on the TEM copper grid, which should be of interest to further studies.

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