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Precise Seed-Mediated Growth and Size-Controlled Synthesis of Palladium Nanoparticles Using a Green Chemistry Approach

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In this paper, we present a “green” and size-controlled seed-mediated growth method by which differently sized palladium (Pd) nanoparticles, spanning from 3.4 to 7.6 nm, with an increment of 1.4 nm, were synthesized. Monodisperse Pd nanoparticles (ca. 3.4 nm, standard deviation = 0.7 nm) were first synthesized and stabilized in an aqueous solution at 95 °C using nontoxic ascorbic acid and sodium carboxymethyl cellulose (CMC) as reducing agent and capping agent, respectively. These Pd nanoparticles were subsequently employed as seeds on the surface of which fresh Pd^{2+} ions were reduced by the weak reducing agent ascorbic acid. Optimal conditions were determined that favored the homogeneous and sequential accumulation of Pd atoms on the surface of the Pd seeds, rather than the formation of new nucleation sites in the bulk growth solution, thereby achieving atomic-level control over particle sizes. The adsorbed CMC molecules did not inhibit the addition of Pd atoms onto the seeds during the growth but provided stabilization of the Pd nanoparticles in aqueous solution after the growth. Potential mechanisms that underpin this seed-mediated growth process are provided and discussed. One advantage of this seed growth process is that it provides stoichiometric control over the size of the Pd nanoparticles by simply varying Pd^{2+} added during the growth stage. Furthermore, the use of ecologically friendly reagents, such as water (solvent), CMC (capping agent), and ascorbic acid (reducing agent), in both the seed synthesis and subsequent seed-mediated growth provides both “green” and economic attributes to this process.

Introduction

The ability to precisely control the synthesis of nanoparticles is of significant importance not only for fundamental scientific interests but also for emerging technology applications,^{1–4} since the electrical, optical, and magnetic properties as well as the catalytic activity of these nanoparticles strongly depend on their size.^{5–8} Nanoparticles of narrow size distribution can further function as building blocks for the construction of highly ordered arrays that exhibit the collective properties of the individual nanoparticles.^{5,9–14}

The most common method employed for the synthesis of metal nanoparticles involves the reduction of metal ions in solution, usually in the presence of a stabilizing material known as a capping agent.¹⁵ The whole synthesis process

has long been believed to occur in two stages, nucleation (from supersaturated solution) followed by a diffusive, agglomerative growth.^{15,16} Initially, a part of the metal ions in solution are chemically reduced to yield metal atoms which subsequently agglomerate to form small metal clusters.¹⁵ Finally, these metal clusters act as the nucleation centers/catalyst for the reduction of remaining metal ions present in the adsorbed state (on the surface of metal clusters), thereby leading to further growth.¹⁷ However, growth and formation of new metal clusters/nucleation sites occur simultaneously. As such, a broad size distribution is the consequence, and the particle size cannot be predicted *a priori*.^{18–20} The stronger the reducing agent used during the particle synthesis, the more difficult it is to avoid the formation of new nucleation sites during the growth stage. Capping agents function to passivate the surface and suppress the growth of the metal clusters/seeds that would otherwise aggregate due to the high surface energy of the system. To date, many studies have focused on improving methods for size-controlled synthesis of metal nanoparticles, including changing the nature^{13,15} and concentration⁸ of the capping agent, reducing agent,¹⁵ and system temperature.^{21,22} However, there is still a significant challenge in obtaining a targeted nanoparticle size from a given set of synthetic conditions due to difficulties in avoiding formation of new nucleation sites during the growth stage. To conquer this obstacle, seed-mediated growth methods, where

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the nucleation and growth stages are controllably separated, and the new nucleation is technically avoided during the growth, have been developed for the synthesis of larger metallic nanoparticles onto smaller seeds.^{23–29} For example, Brown and Natan reported a growth route to synthesize Au nanoparticles spanning from 30 to 100 nm based on 12 nm seeds via surface-catalyzed reduction of Au^{3+} with hydroxylamine.²⁴ Jana et al. reported a seed-based synthesis of Au nanoparticles via gradual addition of ascorbic acid during the growth stage.^{26,27} Pal and co-workers have reported a seed-mediated growth method for the synthesis of Au nanoparticles using photochemically prepared seed particles.^{18,28} Cubic copper nanoparticles were also synthesized following a similar seed-mediated process from the same group.²⁹ However, one limitation of the seed-mediated growth method involves the lack of availability of small seeds ($< 5 \text{ nm}$) with a narrow size distribution, and hence, size-controlled synthesis of nanoparticles with a size spectrum of less than 10 nm is difficult via sequential seed-mediated growth. Another formidable challenge is to precisely control the sequential growth on the seeds in narrow size increments ($< 1.5 \text{ nm}$) through metal salt addition/reduction during the growth stage. Moreover, a detailed understanding of the underpinning phenomena that control these seed-mediated processes is needed.

Integration of green chemistry principles into nanotechnology is of contemporary interest in the emerging areas of nanoscience and technology.^{30–34} This requires not only the generation of favorable functional nanomaterials but also the elimination of the chemical hazards to human health and the environment during the creation and use of these materials. Utilization of inexpensive and nontoxic chemicals, environmentally friendly solvents, and renewable/biodegradable materials is a central tenant in materials synthesis and processing when considering green chemistry strategies. The reaction medium, reducing agent, and capping agent are three key factors in the synthesis and stabilization of metal nanoparticles. The choice of these needs to be seriously considered from both an economic and green chemistry perspective. In most nanoparticle synthesis strategies, environmentally persistent/toxic reagents and chemicals are employed, thus spoiling the “green” virtue of these syntheses.^{30,32} Therefore, it is important to develop alternative nanoparticle synthesis strategies, wherein green chemistry principles³³ are soundly implemented.

Our research group has successfully developed new approaches for the synthesis and stabilization of Fe/Pd, Pt, and Pd nanoparticles in aqueous solution using sodium carboxymethyl cellulose (CMC) as a capping agent and sodium

borohydride (NaBH_4) as a reducing agent.^{8,13,35} CMC is a water-soluble polysaccharide possessing both carboxylate and hydroxyl groups that allow this “green” and inexpensive polysugar to exert strong interactions with metal particles.¹³ NaBH_4 is a highly reactive chemical, posing potential environmental and biological risks. As such, it would be desirable to identify a more ecologically friendly alternative. Ascorbic acid, known as vitamin C, is a mild reducing agent which is commonly used as an antioxidant food additive. It has been previously used as a reducing agent for aqueous phase synthesis of other metal nanoparticles.^{36,37} Its use as the reducing agent, along with the use of CMC as the capping agent, in the aqueous phase synthesis of Pd nanoparticles would provide green attributes to this process.

The objective of this work is to implement green chemistry principles³³ and techniques in both the synthesis of Pd seeds and a subsequent seed-mediated growth process with the aim to yield differently sized Pd nanoparticles, spanning from 3.4 to 7.6 nm, with an increment of 1.4 nm. Our ultimate goal is to optimize processing conditions that favor controlled growth of Pd atoms on the surface of Pd seeds rather than the formation of new nucleation sites in the bulk growth solution, thereby achieving atomic-level size-controlled synthesis of monodisperse Pd nanoparticles with no need for further size selection processing.

Experimental Section

Materials. $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ was purchased from Strem Chemicals. Carboxymethylcellulose sodium salt (average $M_w \sim 90\,000$), sodium borohydride (purity = 99.99%), and dodecanethiol were obtained from Sigma-Aldrich. L-Ascorbic acid, deionized ultrafiltered water with specific conductance of 2.0 $\mu\text{S}/\text{cm}$, hydrochloric acid (37.4%), and hexane were all supplied from Fisher Scientific.

Synthesis of Pd Nanoparticle Seeds. The Pd nanoparticle seeds were synthesized by reducing Pd^{2+} in a CMC aqueous solution at 95 °C using L-ascorbic acid as reducing agent. First, 250 mL of a 0.15 wt % CMC aqueous solution was introduced into a 500 mL volumetric flask and gradually heated to 95 °C using a stirred/hot plate followed by the addition of 1000 μL of a 0.05 M $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution under stirring (700 rpm). Subsequently, 3000 μL of a 0.05 M L-ascorbic acid aqueous solution was added under constant stirring (700 rpm) and allowed to proceed for a reduction reaction at 95 °C for 5 min. Finally, the reaction system (i.e., volumetric flask) was moved from the hot stir plate to a room temperature (~23 °C) stir plate and then aged for about 24 h under stirring (300 rpm) prior to transmission electron microscopy characterization of these Pd nanoparticle seeds. As will be shown later in this paper, the average size of the Pd nanoparticle seeds is 3.4 nm.

Seed-Mediated Growth Processes. After the Pd nanoparticle seeds were aged for 24 h, a seed-mediated growth process was performed. The Pd seeds were first mixed with a certain amount of Pd salt followed by a gradual addition of ascorbic acid solution. Using the 3.4 nm Pd nanoparticles as seeds, it was desired to further control the sequential growth of Pd atoms on the surfaces of the seeds through Pd^{2+} salt addition/reduction, thereby achieving differently sized Pd nanoparticles depending on the amount of Pd^{2+} salt added into the system during the growth stage. The amount of Pd^{2+} salt added in the system for a

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desired degree of growth was estimated per the following mass balance equation:

$$R_{\text{Pd}^{2+}} = \frac{\frac{4}{3}\pi(R_d \times 10^{-9})^3 - \frac{4}{3}\pi(R_s \times 10^{-9})^3}{\frac{4}{3}\pi(R_s \times 10^{-9})^3} \quad (1)$$

where $R_{\text{Pd}^{2+}}$ is the molar ratio of the Pd^{2+} added in the growth stage relative to the Pd^{2+} used for seed synthesis, R_s is the radius of the seeds, and R_d is the radius of the desired particle obtained upon growth. This equation applies provided that (i) the Pd^{2+} salt added during the growth was completely reduced, (ii) the growth occurs homogeneously on the surface of the Pd nanoparticle seeds, and (iii) the reduction occurs in such a manner that no new nucleation sites are formed in the bulk solution during the growth stage (i.e., a weak reducing agent is needed for avoiding formation of new particles).

In this study, it was desired to grow Pd nanoparticles in 1.4 nm increments from the 3.4 nm seeds. The mass balance expression (eq 1) was used to determine the amount of the Pd^{2+} salt addition required to grow Pd nanoparticles to the sizes 4.8, 6.2, and 7.6 nm. Three sets of 250 mL flasks were labeled I, II, and III, respectively. For the growth of 4.8 nm Pd nanoparticles, 360 μL of a 0.05 M $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution was added to 50 mL of the aqueous Pd nanoparticle seed dispersion in flask (I) and then stirred (700 rpm) for 3 h to allow a complete mixing of the Pd^{2+} with the Pd nanoparticle seeds at room temperature. Next, 1800 μL of a 0.03 M L-ascorbic acid aqueous solution was slowly added (dropwise) under stirring (700 rpm). In flask (II), for the growth of 6.2 nm Pd nanoparticles, 50 mL of the aqueous Pd nanoparticle seed dispersion was initially mixed with 1000 μL of a 0.05 M $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution and stirred (700 rpm) for 3 h. This was followed by slow addition (dropwise) of 5000 μL of a 0.03 M L-ascorbic acid aqueous solution under stirring (700 rpm) at room temperature. In flask (III), for the growth of 7.6 nm Pd nanoparticles, 50 mL of the aqueous Pd nanoparticle seed dispersion was mixed with 2040 μL of a 0.05 M $\text{Na}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$ aqueous solution and stirred (700 rpm) for 3 h at room temperature. Subsequently, 10 200 μL of a 0.03 M L-ascorbic acid aqueous solution was slowly added (dropwise) under stirring (700 rpm). After the addition of the ascorbic acid solutions, the stirring speed was changed to 300 rpm where the growth systems were aged for 7 h. The resulting Pd nanoparticles dispersions were then characterized and employed in phase transfer/extraction experiments. In the experiments where the NaBH_4 (0.03 M) was used as reducing agent, the procedures are same as those described above.

Extraction of Pd Nanoparticles. Once the Pd nanoparticles were formed using the seed-mediated growth process, 20 mL of the CMC stabilized Pd (CMC-Pd) nanoparticle dispersion in aqueous solution was contacted with 10 mL of hexane followed by the addition of 100 μL of dodecanethiol and 10 μL of concentrated HCl (37.4%). The two phase system was then vigorously shaken to facilitate phase transfer/extraction of the Pd nanoparticles from the aqueous solution into the hexane phase with the aid of a vortex mixer (Fisher Scientific). The Pd nanoparticle dispersion in hexane was repeatedly washed with deionized water to completely remove the acid from the system. All the extractions were performed at room temperature. Notably, in order to ensure a complete extraction, the dispersions of Pd nanoparticles with sizes larger than 6 nm were diluted three times before contacting with hexane for the extraction. The residual Pd

content in the aqueous phase obtained after extraction was detected using an inductively coupled plasma-optical emission spectrometer (ICP-OES).

Preparation of Fourier Transform Infrared (FT-IR) Samples. The CMC-Pd nanoparticles were separated from the aqueous solution by centrifugation (Labnet International Inc., Hermle Z 200A) using ethanol as an antisolvent at a speed of 6000 rpm/4185g. This process was repeated three times to ensure the complete removal of the excess/isolated CMC in the system. The FT-IR samples were prepared by forming a thin pellet of KBr (95 mg) and the solid Pd nanoparticles (5 mg). A pure 100 mg KBr pellet was used as background and was subtracted from the FT-IR spectra of the Pd nanoparticle samples. In order to make a comparison between the FT-IR spectra of the CMC-Pd nanoparticle samples and neat CMC as well as CMC that had been heated to 95 °C and cooled to room temperature, FT-IR samples were prepared by forming a thin pallet of KBr and the CMC (both heated and unheated). In the case of the CMC that had been heated to 95 °C, 250 mL of a 0.15 wt % CMC aqueous solution was introduced into a 500 mL volumetric flask and gradually heated to 95 °C using a stir/hot plate. After aging 5 min at 95 °C, the CMC solution in water was allowed to cool to room temperature. The CMC molecules were finally separated from the water using a vacuum freeze-dryer prior to preparation of this KBr/CMC sample for FT-IR characterization. FT-IR spectra were obtained using a Nicolet AVATAR 360 E.S.P spectrometer.

Transmission Electron Microscopy (TEM). TEM samples were prepared by placing three droplets of the aqueous CMC-Pd nanoparticle dispersions, or three drops of the dodecanethiol-Pd nanoparticle dispersions in hexane, onto a carbon coated nickel TEM grid and evaporating the solvent naturally at ambient conditions overnight. TEM images of the Pd nanoparticles were obtained using a Zeiss EM 10 transmission electron microscope at an operating voltage of 60 kV. The film negatives from TEM were scanned using a Professional scanner (Epson Perfection 4990 PHOTO). The color TEM images presented were produced by selecting “color negative film” as the film type and “24-bit color” as the image type in the scanner software. The TEM images of the Pd nanoparticles obtained in this work were analyzed using the Image J software package to create average particle size and size distribution histogram.³⁸

Powder X-ray Diffraction (XRD). XRD patterns were collected with a Rigaku Miniflex powder X-ray diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) radiation. CMC-Pd nanoparticles were precipitated by centrifugation using ethanol as an antisolvent at a speed of 6000 rpm/4185g. After precipitation, a little amount (~0.5 mL) of water was used to redisperse the Pd nanoparticles, yielding highly concentrated Pd nanoparticles in water. Subsequently, the concentrated Pd nanoparticle dispersion was evenly placed on the surface of a glass slide followed by removal of the water with a gentle stream of N_2 . The Pd nanoparticle samples attached on the surface of the glass slide were then used for XRD measurement.

Results and Discussion

1. “Green” Synthesis of Pd Nanoparticle Seeds. *1.1. Synthesis of Pd Nanoparticle Seeds.* Synthesis of the CMC stabilized Pd (CMC-Pd) nanoparticles in aqueous solution using ascorbic

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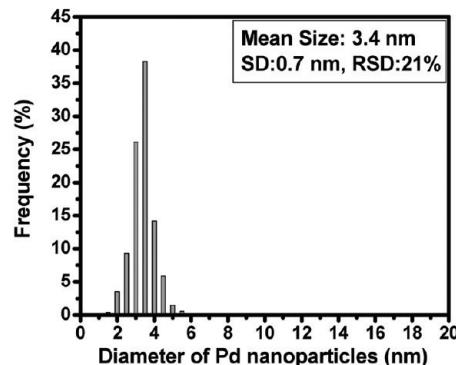
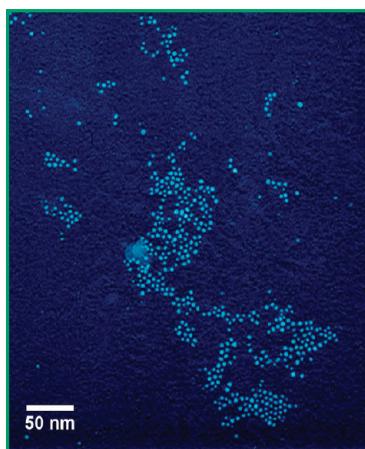


Figure 1. TEM image of CMC-Pd nanoparticle seeds synthesized in aqueous solution at 95 °C using ascorbic acid as reducing agent along with the size distribution histogram of these particles. Total number of particles counted for the histogram is 537.

acid as the reducing agent at room temperature was investigated. While ascorbic acid (standard electrode potential, $E^0 = 0.058$ V for dehydroascorbic acid/ascorbic acid redox system)³⁹ is capable of reducing Pd^{2+} into $\text{Pd}^{(0)}$ ground-state at room temperature ($E^0 = 0.915$ V for Pd^{2+}/Pd redox system),⁴⁰ the CMC-Pd nanoparticles synthesized at room temperature are large, which is reflected by the formation of a cloudy yellow-brown Pd particle suspension (digital image is given on the left of Figure S1 in the Supporting Information). The existence of an induction period (i.e., several minutes before there is a noticeable change in color of the solution) of the reaction indicates that the reduction of the Pd^{2+} is slow and inefficient due to the weak reducing ability of the ascorbic acid at room temperature. TEM analysis further confirmed the formation of large Pd nanoparticles with a wide size distribution (average size = 56 nm, and standard deviation SD = 31 nm) as shown in Figure S2 in the Supporting Information. Previously, our group has synthesized small CMC-Pd nanoparticles with narrow size distribution (approximately 2.4 nm, SD = 0.5 nm) under the same synthesis conditions while using the strong reducing agent, NaBH_4 ⁸ ($E^0 = -0.481$ V for $\text{B(OH)}_3/\text{NaBH}_4$ redox system).¹⁵ Clearly, the formation of larger Pd nanoparticle size with wider size distribution in the current system is primarily due to the use of the weak reducing agent, ascorbic acid. TEM analysis was used to study the effect of temperature during synthesis on the Pd nanoparticle size and size distribution. The average CMC-Pd nanoparticle size and size distribution is plotted as a function of system temperature in Figure S3 in the Supporting Information. Interestingly, an increase of the system temperature results in a significant decrease in both the size and size distribution of the CMC-Pd nanoparticles. An increase of the system temperature to 95 °C results in small Pd nanoparticles (average size = 3.4 nm) with narrow size distribution (SD = 0.7 nm, relative standard deviation RSD = 21%) as shown in Figure 1. Given their small size and narrow size distribution, these CMC-Pd nanoparticles were used as seeds for subsequent growth of larger nanoparticles. The dispersion of the CMC-Pd nanoparticle seeds synthesized at 95 °C appears as a transparent dark brown solution as shown on the right of

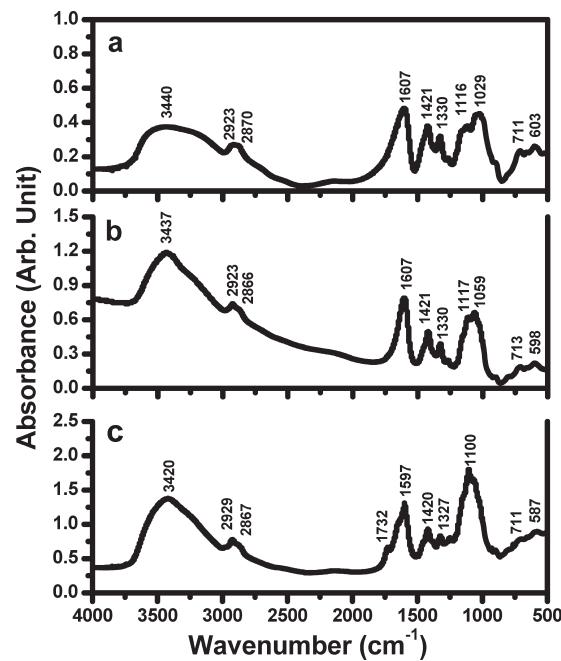


Figure 2. FT-IR spectra of (a) neat CMC recorded at room temperature (with no heat processing), (b) neat CMC recorded at room temperature after the CMC had been heated to 95 °C for 5 min and then cooled to room temperature, and (c) CMC-Pd nanoparticles that were synthesized in aqueous solution at 95 °C and cooled to room temperature.

Figure S1 in the Supporting Information. The higher synthesis temperature of 95 °C was used for a short period of time (5 min) to dramatically boost the reduction reaction rate, thereby resulting in fast nucleation and growth. As a result, small Pd nanoparticles with narrow size distribution were obtained. A more detailed study involving the effect of temperature on the size and size distribution of CMC-Pd nanoparticles synthesized via ascorbic acid reduction is reported elsewhere.⁴¹ Given that the synthesis of the Pd nanoparticle seeds was effectively accomplished using only the low-cost and ecologically friendly reagents of water (solvent), CMC (capping agent), and ascorbic acid (reducing agent), this method constitutes a “green” nanoparticle synthesis.

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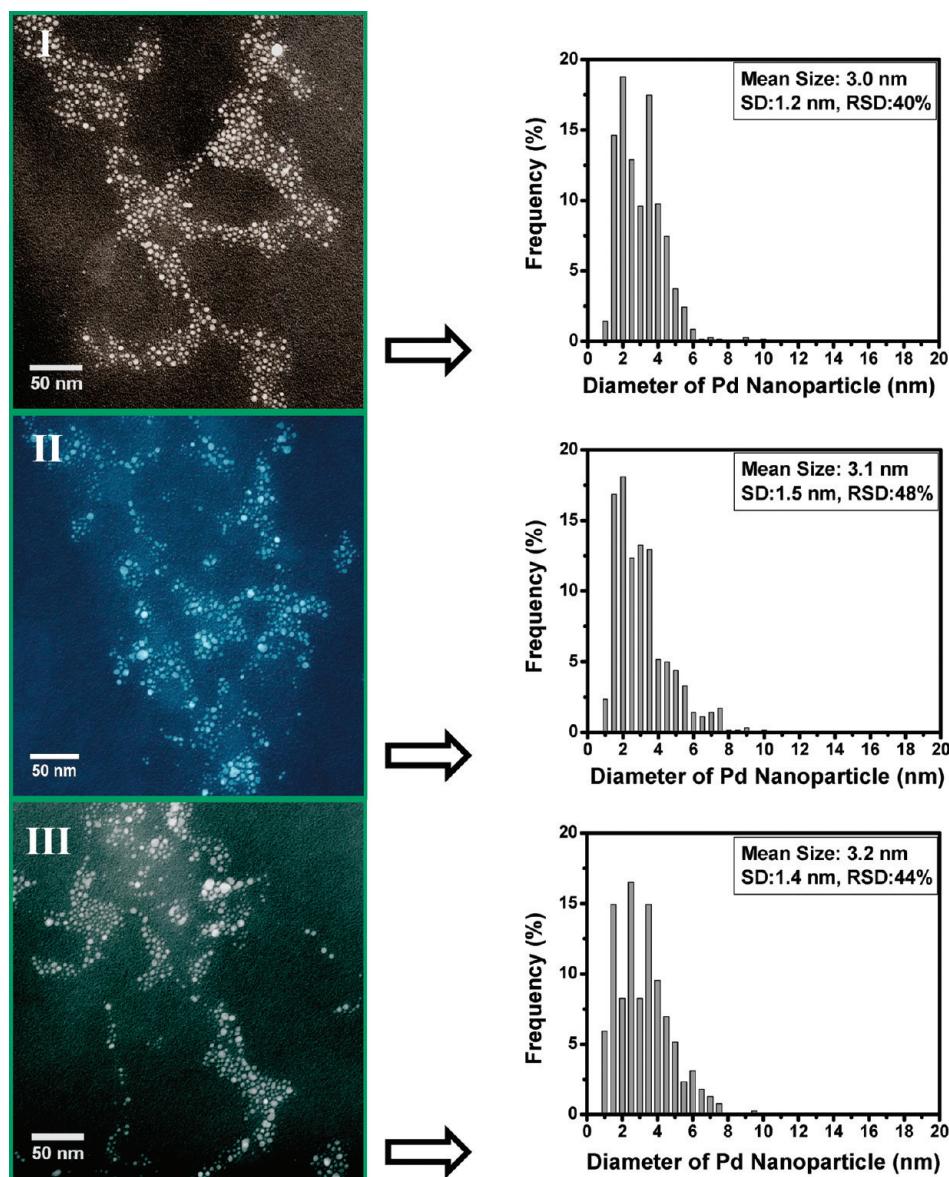


Figure 3. TEM images of Pd nanoparticles obtained from the seed-mediated growth process where the strong reducing agent of NaBH_4 was used, along with the size distribution histogram. The mean size of the Pd nanoparticles obtained in these seed-mediated growth experiments are 3.0 nm (I), 3.1 nm (II), and 3.2 nm (III) compared to the theoretical mean sizes of 4.8 nm (I), 6.2 nm (II), and 7.6 nm (III) based on the amount of Pd^{2+} added to the seed solution in each experiment. The use of NaBH_4 reducing agent results in new nucleation sites and hence smaller particle sizes than these theoretical sizes.

1.2. Interaction of CMC with Pd Nanoparticle Seeds. Our previous FT-IR studies have demonstrated that CMC molecules interact with Pd particles via both the COO^- and $-\text{OH}$ functional groups at room temperature.⁸ These interactions facilitate the CMC molecule assembly into a protective monolayer on the surface of Pd nanoparticles, which results in both passivation of the surface and steric stabilization of the Pd nanoparticles. In order to better understand the impact of the higher temperature (95 °C) processing on the interaction/capping function of the CMC with the Pd nanoparticles (considering the possibility of CMC degradation during synthesis at high temperature), FT-IR was used in this work to investigate the interaction between the CMC and Pd nanoparticles. The FT-IR spectrum of the neat CMC with no heat processing is shown in Figure 2a. Figure 2b presents the FT-IR spectrum of CMC (recorded at room temperature) after the CMC had been processed at 95 °C for 5 min. Figure 2c presents the FT-IR

spectrum of CMC-Pd nanoparticles synthesized using ascorbic acid as reducing agent at 95 °C and cooled to room temperature. As evidenced by similar FT-IR bands in Figure 2a and b, the CMC was not significantly affected by the heat processing at 95 °C. In Figure 2c, the wavenumber separation, Δ , between the asymmetric $\nu_{\text{as}}(\text{COO}^-)$ and symmetric $\nu_s(\text{COO}^-)$ stretches is 177 cm^{-1} ($1597 \text{ cm}^{-1} - 1420 \text{ cm}^{-1}$) corresponding to the bidentate bridging interaction of COO^- group with Pd nanoparticle surfaces.^{8,42} A new peak is observed at 1732 cm^{-1} in Figure 2c (not observed in Figure 2a and b), which is ascribed to the presence of a small fraction of unassociated carboxylic acid⁴³ on the surface of the Pd nanoparticles, perhaps due to the addition of the excess weak ascorbic acid during the synthesis. In addition, the two peaks

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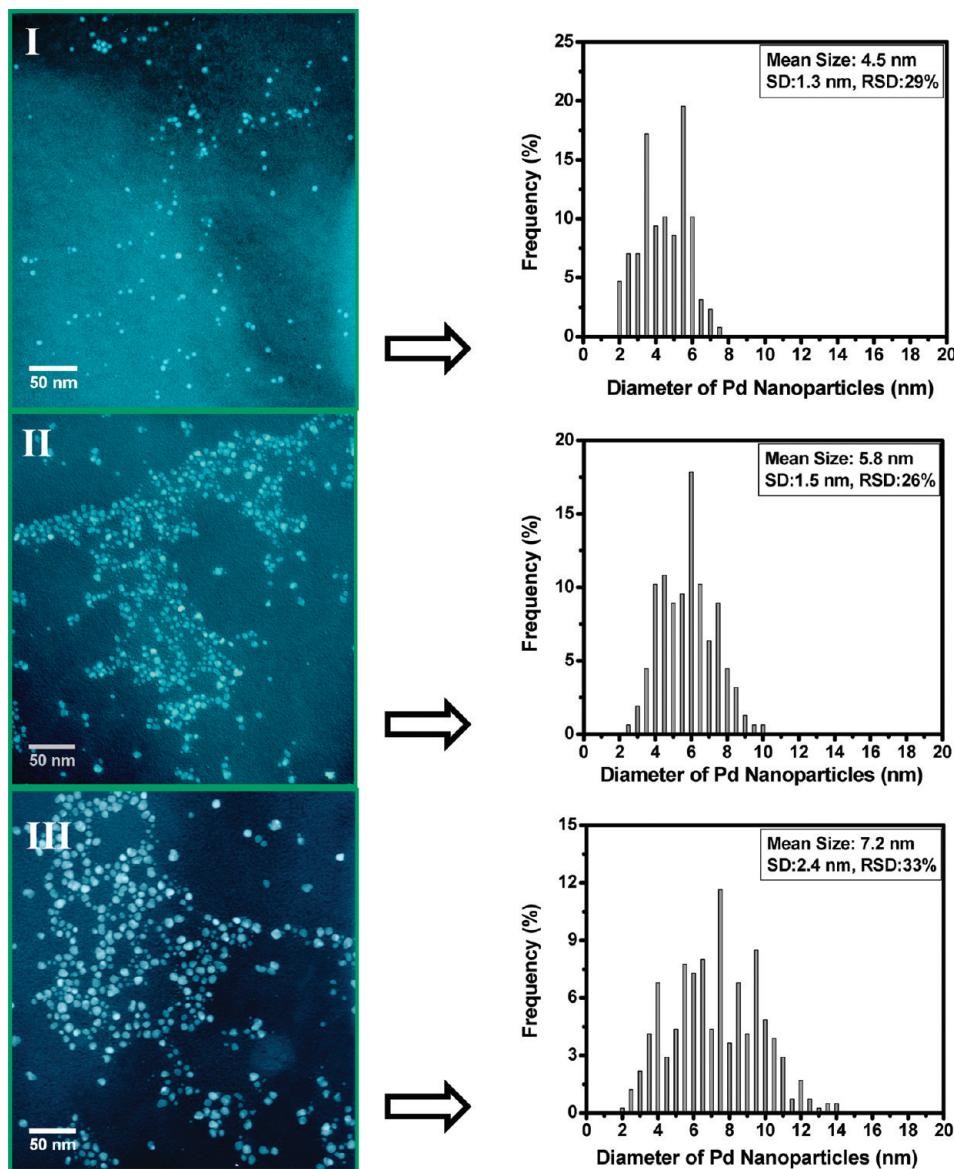


Figure 4. TEM images of Pd nanoparticles obtained from the seed-mediated growth process where concentrated aqueous ascorbic acid solution (0.3 M) was employed during the growth stage, along with the size distribution histogram. The mean size of the Pd nanoparticles obtained in these seed-mediated growth experiments are 4.5 nm (I), 5.8 nm (II), and 7.2 nm (III) compared to the theoretical mean sizes of 4.8 nm (I), 6.2 nm (II), and 7.6 nm (III) based on the amount of Pd^{2+} added to the seed solution in each experiment. The high concentration ascorbic acid solution resulted in uneven growth on the nanoparticle surfaces as evidenced by polydispersity and nonspherical particles.

at 1117 and 1059 cm^{-1} from CMC in Figure 2b vanished upon the interaction with the Pd nanoparticles and were replaced by a new peak at 1100 cm^{-1} (Figure 2c), further indicating the presence of the CMC as an integral component of the Pd nanoparticles.¹³ It is also noted that the $-\text{OH}$ stretching peak of the CMC molecules experiences a shift from 3437 to 3420 cm^{-1} in the presence of the Pd nanoparticles (Figure 2b and c), suggesting an existence of hydrogen bonding between the CMC molecules and Pd nanoparticle surface.⁸ The formation of the small Pd nanoparticles (3.4 nm) with narrow size distribution ($\text{SD} = 0.7 \text{ nm}$) as shown in Figure 1, on the other hand, further demonstrates the ability of CMC to suppress the growth of Pd nanoparticles at the temperature of 95 °C. Evidently, CMC molecules can serve as an effective capping agent to stabilize Pd nanoparticles in aqueous solution even at high temperature (95 °C).

2. Seed-Mediated Growth Process. *2.1. NaBH_4 Involved Seed-Mediated Growth.* Seed-mediated seed growth

on the 3.4 nm CMC-Pd nanoparticles was initially studied using NaBH_4 (0.03 M) as the reducing agent. Three room temperature seed-mediated growth experiments were performed where the amount of Pd^{2+} salt added (according to eq 1) would yield nanoparticles of 4.8, 6.2, and 7.6 nm from growth on the 3.4 nm seeds provided that the (i) Pd^{2+} salt added during the growth was completely reduced, (ii) growth occurs homogeneously on the surface of the Pd nanoparticle seeds, and (iii) reduction occurs in such a manner that no new nucleation sites are formed in the bulk solution during the growth stage. Therefore, the theoretical mean sizes of the Pd nanoparticles obtained in these three experiments should be 4.8, 6.2, and 7.6 nm, respectively. However, in experiments where the strong reducing agent of NaBH_4 was employed, mean nanoparticle diameters of 3.0 nm ($\text{SD} = 1.2 \text{ nm}$, $\text{RSD} = 40\%$), 3.1 nm ($\text{SD} = 1.5 \text{ nm}$, $\text{RSD} = 48\%$), and 3.2 nm ($\text{SD} = 1.4 \text{ nm}$, $\text{RSD} = 44\%$) were obtained, respectively (Figure 3). Apparently, the use of

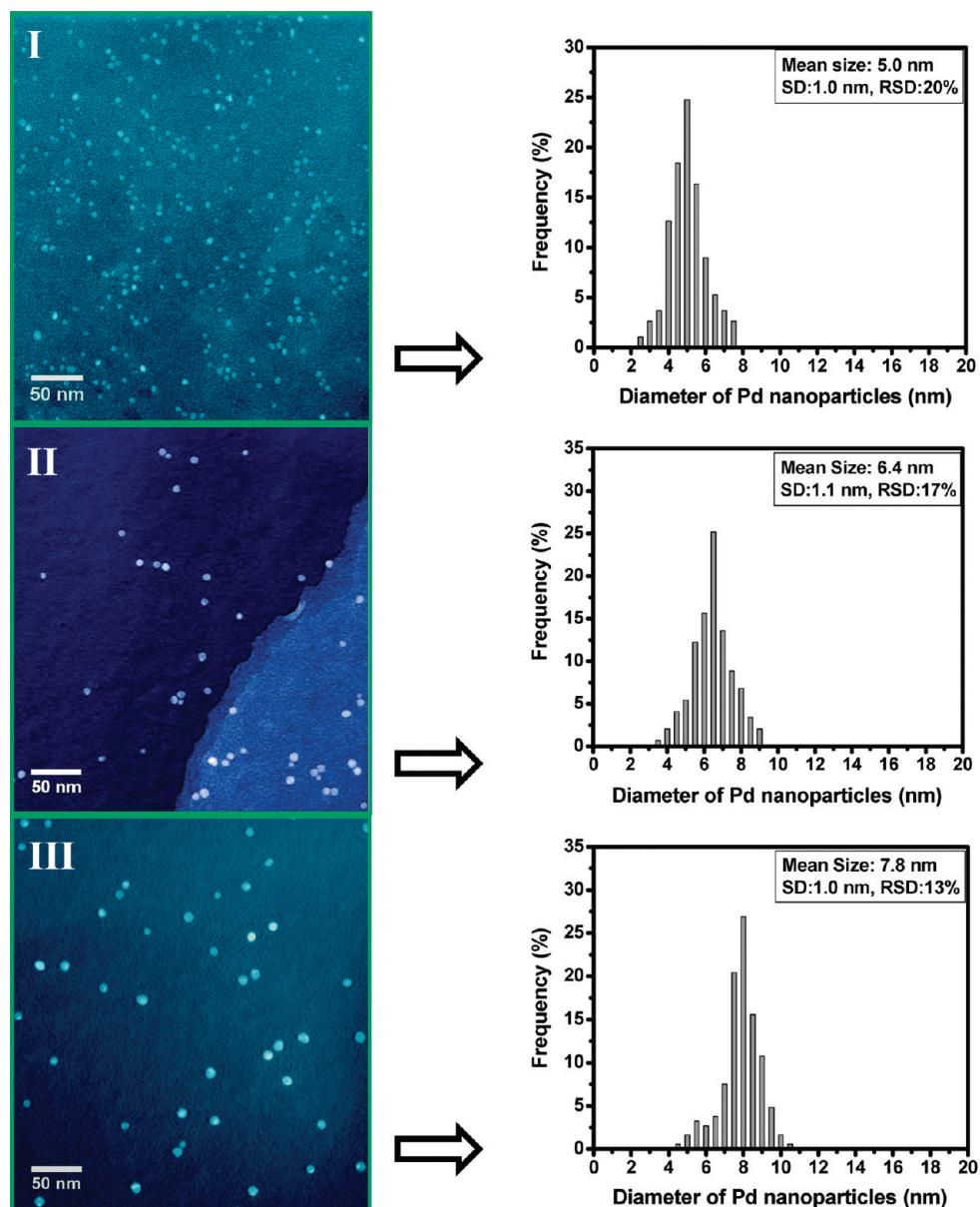


Figure 5. TEM images of Pd nanoparticles obtained from the seed-mediated growth process where low concentration ascorbic acid solution (0.03 M) was employed during the growth stage, along with the size distribution histogram. The mean sizes of the Pd nanoparticles obtained in these seed-mediated growth experiments are 5.0 nm (I), 6.4 nm (II), and 7.8 nm (III) compared to the theoretical mean sizes of 4.8 nm (I), 6.2 nm (II), and 7.6 nm (III) based on the amount of Pd^{2+} added to the seed solution in each experiment. The lower concentration ascorbic acid is favorable to a homogeneous accumulation/distribution of Pd atoms among the surfaces of the Pd seeds during the growth stage.

NaBH_4 results in a significant amount of Pd nanoparticles which are even smaller than the original Pd seeds in each of these three growth systems, as shown in Figure 3. This indicates the occurrence of new nucleation sites during growth stage. Since NaBH_4 is a strong reducing agent at room temperature, it enables rapid reduction of Pd^{2+} into $\text{Pd}^{(0)}$ without the aid of the Pd nanoparticle seeds as catalysts during the growth stage. As such, a large number of new nucleation sites were generated in the bulk growth solution. This new nucleation process competes with the growth occurring on the surface of Pd nanoparticle seeds in consuming the Pd^{2+} added in the growth stage. As a result, the mean Pd nanoparticle sizes obtained using NaBH_4 as the reducing agent during the growth are much smaller than the theoretical mean particle sizes of 4.8, 6.2, and 7.6 nm, as shown in Figure 3. In addition, broad size distributions were obtained in each case (Figure 3).

2.2. Ascorbic Acid Involved Seed-Mediated Growth. The studies using NaBH_4 in the previous section illustrate that the strong reducing agent produced new nucleation that competes with the seed-mediated growth during reduction. The same three experiments that should theoretically yield 4.8, 6.2, and 7.6 nm particles were performed using a weaker reducing agent in order to avoid the occurrence of new nucleation during the growth stage as was observed with NaBH_4 . Ascorbic acid was selected as a weak reducing agent in this work due to its relatively weak reduction potential.³⁹ As described previously in this paper, the addition of ascorbic acid into an aqueous Pd^{2+} solution produced large Pd nanoparticles (approximately 55 nm, as shown in Figure S2 in the Supporting Information) with a wide size distribution per a slow induction period due to the weak reducing ability of the ascorbic acid. However, the presence of Pd nanoparticle seeds drastically accelerated the reduction of the Pd^{2+}

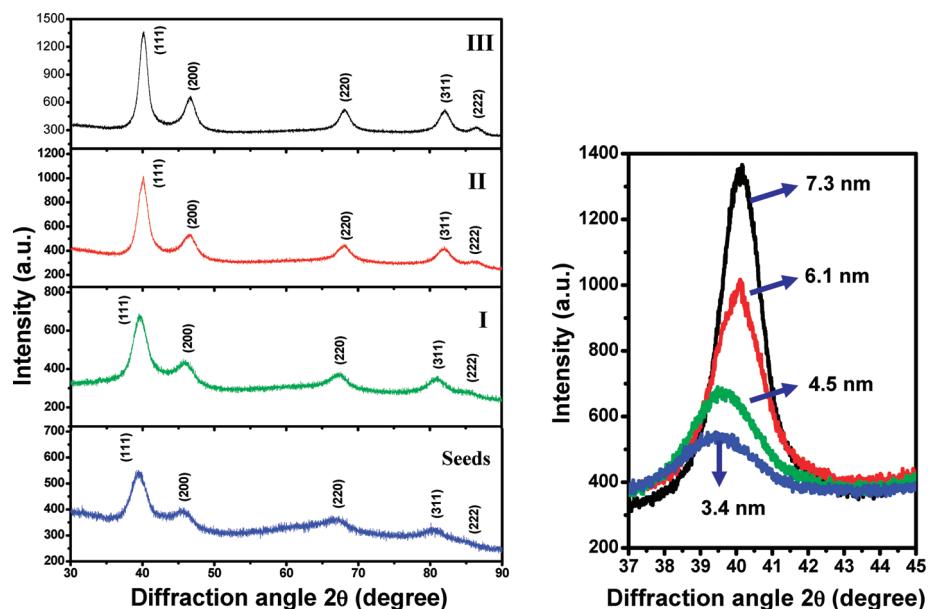


Figure 6. XRD patterns of Pd nanoparticle seeds and Pd nanoparticles obtained from the seed-mediated growth process using low concentration ascorbic acid (0.03 M). The mean sizes of the Pd nanoparticles obtained from the XRD data are 3.4 nm (seeds), 4.5 nm (I), 6.1 nm (II), and 7.3 nm (III) compared to the theoretical mean sizes of 4.8 nm (I), 6.2 nm (II), and 7.6 nm (III). The (111) peaks of these Pd nanoparticles used for the determination of particle sizes are also presented (on the right) for a comparison of particle size.

during the growth stage, which is reflected by the appearance of a completely transparent Pd nanoparticle dispersion rather than a cloudy one. The effect of the ascorbic acid concentration on the seed-mediated growth was investigated, where the 3.4 nm CMC-Pd nanoparticles were used as seeds. Initially, a concentrated aqueous ascorbic acid solution (0.3 M) was employed during the growth stage, where the actual sizes of the Pd nanoparticles obtained from the three different experiments were 4.5 nm ($SD = 1.3$ nm, RSD = 29%), 5.8 nm ($SD = 1.5$ nm, RSD = 26%), and 7.2 nm ($SD = 2.4$ nm, RSD = 33%), respectively (Figure 4). Evidently, this high concentration ascorbic acid solution resulted in broad size distributions of the Pd nanoparticles, where there is uneven growth of Pd atoms on the nanoparticle surfaces evidenced by polydispersity and nonspherical particles. On the other hand, when a low concentration (0.03 M) ascorbic acid solution was employed during the growth stage, the mean diameters of the Pd nanoparticles obtained from the three experiments were 5.0 nm ($SD = 1.0$ nm, RSD = 20%), 6.4 nm ($SD = 1.1$ nm, RSD = 17%), and 7.8 nm ($SD = 1.0$ nm, RSD = 13%), respectively (Figure 5). The mean diameters of the Pd nanoparticles obtained using the low concentration ascorbic acid solution are similar to the theoretical mean sizes of 4.8, 6.2, and 7.6 nm. The narrower size distribution of these Pd nanoparticles compared with those shown in Figure 4 suggests that the lower ascorbic acid concentration is favorable to a homogeneous accumulation/distribution of Pd atoms among the surfaces of the Pd seeds during the growth stage.

XRD characterization was used to determine both the size and crystalline structure of the Pd nanoparticle seeds (shown in Figure 1) and Pd nanoparticles obtained via the ascorbic acid (0.03 M) induced growth process (shown in Figure 5). The XRD patterns of these Pd nanoparticles are presented in Figure 6 (on the left). Several peaks are observed in each XRD pattern at around 40°, 46°, 68°, 82°, and 86°. These peaks correspond to the {111}, {200}, {220}, {311},

and {222} planes of a face-centered-cubic (fcc) lattice, respectively, indicating fcc structure of the Pd nanoparticles. Using the Scherrer equation⁴⁴ and the XRD data in Figure 6, the mean size of the Pd seeds is 3.4 nm and the mean sizes of the Pd nanoparticles obtained after each growth experiment are 4.5, 6.1, and 7.3 nm, respectively. These sizes are quite consistent with the TEM observations. The (111) peaks of these Pd nanoparticles are specifically presented in Figure 6 (on the right) for a comparison of their sizes. The significant high scattering angle shifts indicate sequential increase of the particle size, which is possibly due to the contraction in Pd–Pd interatomic distance with an increase in particle size.⁴⁵

Evidently, the gradual addition of low concentration ascorbic acid during the growth can effectively induce a homogeneous sequential growth of Pd atoms through the reduction of Pd^{2+} on the surfaces of the Pd seeds while effectively avoiding the formation of new nucleation sites in the bulk growth solution. As such, the stoichiometrically size-controlled synthesis of Pd nanoparticles was effectively achieved. Importantly, green chemistry principles³³ were soundly implemented in this size-controlled seed-mediated growth process through the use of ascorbic acid as reducing agent, CMC as capping agent, and water as growth solvent.

3. Extraction of Pd Nanoparticles into Organic Phase and Their Self-Assembly. *3.1. Extraction of Pd Nanoparticles.* Many applications of monodisperse nanoparticles require stable organic dispersions including the formation of self-assembled ordered arrays and thin films.^{9–13} To obtain an organic phase dispersions of the Pd nanoparticles in this study, extraction of the Pd nanoparticle seeds and the larger sized Pd nanoparticles obtained in each growth experiment (shown in Figure 5 as I, II, and III) was attempted using dodecanethiol as an extractant in an effort to transfer the

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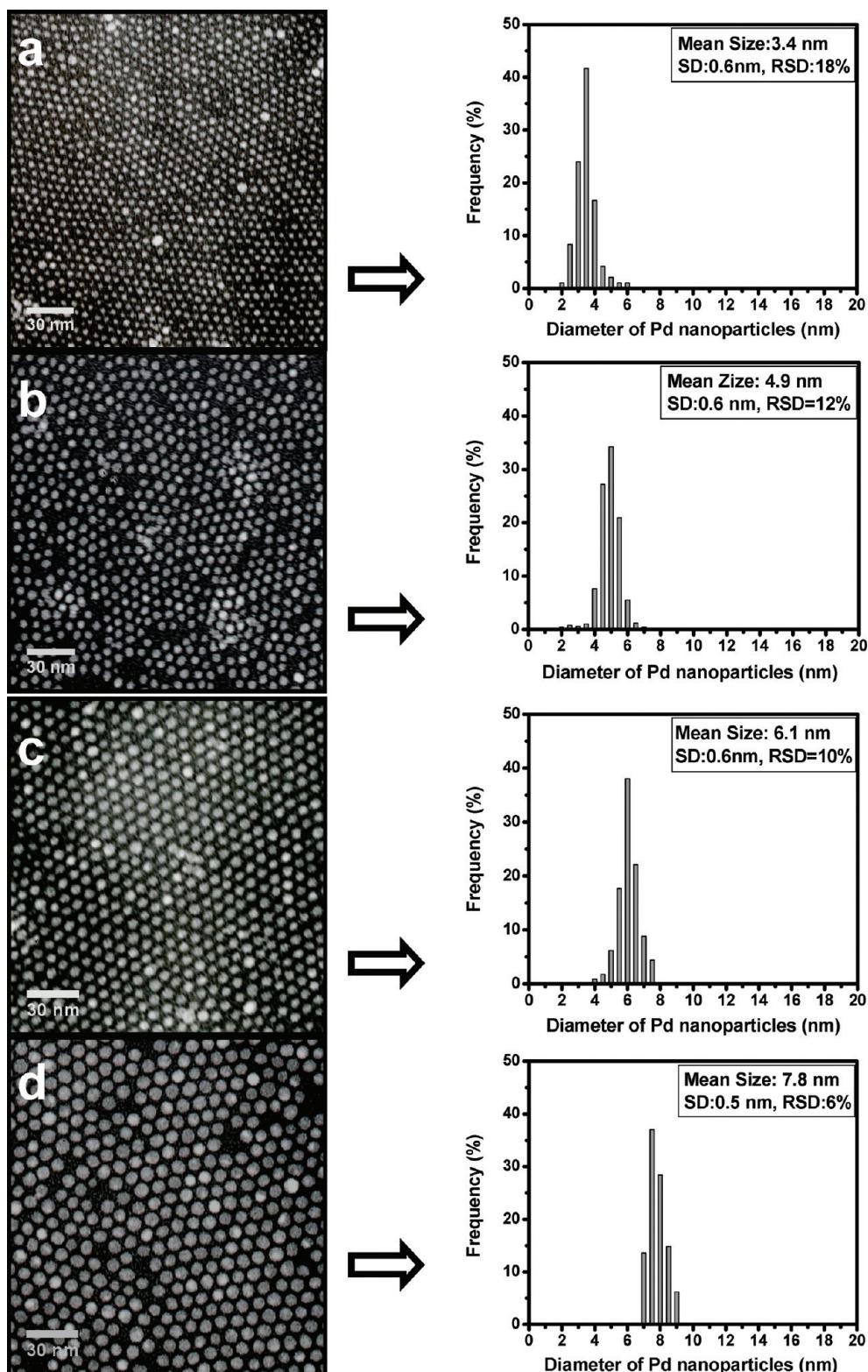


Figure 7. High magnification TEM images and size distribution histograms of the dodecanethiol-Pd nanoparticles obtained after extraction into the hexane phase and solvent evaporation on a TEM grid. The mean sizes of these dodecanethiol-Pd nanoparticles are (a) 3.4 nm, (b) 4.9 nm, (c) 6.1 nm, (d) and 7.8 nm, where these postextracted nanoparticles correspond to the pre-extracted aqueous phase CMC-Pd nanoparticles shown in Figure 1 and Figure 5I, II, and III, respectively.

Pd nanoparticles from the aqueous phase into an organic phase. Unfortunately, these Pd nanoparticles could not be extracted directly from aqueous phase into hexane phase using only dodecanethiol as an extractant. The inability to transfer these Pd particles into the hexane phase is attributed

to the strong interaction between CMC and the Pd particles within the aqueous phase.¹³ However, the addition of a small amount of concentrated HCl does allow for a complete extraction of these Pd nanoparticles from the aqueous phase into a hexane phase upon vigorous shaking of the mixture

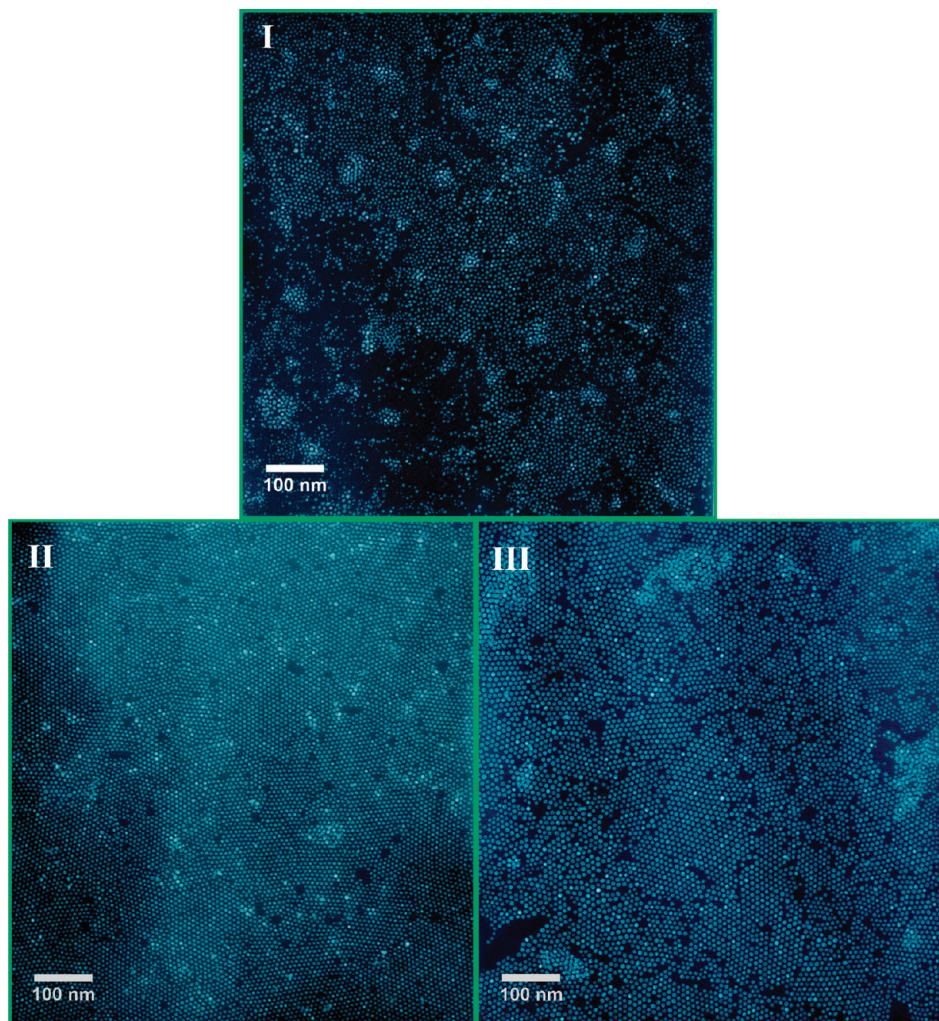


Figure 8. Low magnification TEM images of dodecanethiol-Pd nanoparticle arrays obtained after extraction into the hexane and solvent evaporation on a TEM grid. The particles shown here in (I), (II), and (III) correspond to the particles shown in Figure 7b, c, and d, respectively. Notably, narrow size distribution of these dodecanethiol-Pd nanoparticles contributes to the formation of ordered arrays after solvent evaporation.

system. The addition of highly concentrated hydrochloric acid (37.4%) significantly lowers the pH value of the aqueous phase, thereby dramatically affecting the equilibrium between $-COO$ and $COOH$ on the CMC capping ligands, rendering the $COOH$ dominant in the system and thus significantly weakening the interaction between the CMC and the Pd nanoparticles. This provides an opportunity for the dodecanethiol to conveniently interact with the Pd nanoparticle surface without the strong competition from the $-COO$ moieties of the CMC. The well-established chemical bonding between the $-SH$ and metallic nanoparticle surface enables the dodecanethiol to anchor/self-assemble in an oleophilic monolayer on the surfaces of Pd particles, thereby providing for good solvation of the Pd nanoparticles by the hexane solvent. It should be noted that the aqueous dispersions of the Pd nanoparticles with sizes larger than 6 nm could not be extracted completely from the aqueous phase into the organic phase. However, three times dilution of the aqueous particle dispersion enabled a complete extraction of these Pd nanoparticles into the hexane phase. The dilution of the Pd nanoparticle dispersions provides more chances for the dodecanethiol to approach the surface of the Pd nanoparticles without suffering from serious steric hindrance from adjacent Pd nanoparticles.

3.2. Self-Assembly of Pd Nanoparticles. After extraction into hexane, three drops of the dodecanethiol-capped Pd (dodecanethiol-Pd) nanoparticle dispersions were placed on the surface of TEM grids (carbon coated copper TEM grids), where the Pd nanoparticles were self-assembled on the surface via evaporation of the hexane solvent. Figure 7a presents a typical TEM image of the dodecanethiol-Pd nanoparticles obtained by extracting CMC-Pd nanoparticle seeds from the aqueous solution into the hexane phase. These dodecanethiol-Pd nanoparticles were shown to have the same average size of 3.4 nm and a similar size distribution ($SD = 0.6$ nm, $RSD = 18\%$), as compared to the CMC-Pd seeds originally synthesized in the aqueous phase. As known above, in this paper, the gradual addition of ascorbic acid with low concentration (0.03 M) during the growth resulted in the formation of Pd nanoparticles with precisely controlled sizes. The extraction of the particles obtained from the three seed-mediated growth experiments and shown in Figure 5 I, II, and III into hexane phase yielded dodecanethiol-Pd nanoparticle dispersions with average sizes of 4.9 nm ($SD = 0.6$ nm, $RSD = 12\%$), 6.1 nm ($SD = 0.6$ nm, $RSD = 10\%$), and 7.8 nm ($SD = 0.5$ nm, $RSD = 6\%$), respectively, as shown in Figure 7b–d. These dodecanethiol-Pd nanoparticles are somewhat narrower in size

Table 1. Summary of the Mean Sizes and Size Distributions of Both the CMC-Pd Nanoparticles Obtained upon 0.03 M Ascorbic Acid Induced Sequential Growth and the Corresponding Dodecanethiol-Pd Nanoparticles Obtained after Extraction^a

experiment	theoretical mean diameter (nm)	measured diameter (nm)		
		before extraction		after extraction
		XRD analysis	TEM analysis	
Pd particle seeds	3.4	3.4	3.4 ± 0.7, RSD = 21%	3.4 ± 0.6, RSD = 18%
seed growth sample I	4.8	4.5	5.0 ± 1.0, RSD = 20%	4.9 ± 0.6, RSD = 12%
seed growth sample II	6.2	6.1	6.4 ± 1.1, RSD = 17%	6.1 ± 0.6, RSD = 10%
seed growth sample III	7.6	7.3	7.8 ± 1.0, RSD = 13%	7.8 ± 0.5, RSD = 6%

^a For comparison, the theoretical mean sizes of the Pd particles based on stoichiometric calculations are also provided.

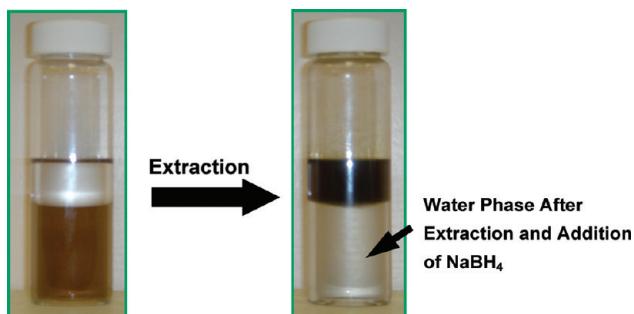


Figure 9. Digital images of the extraction of 7.8 nm Pd nanoparticles (as determined by TEM and shown in Figure 5III) from the aqueous phase into the organic phase. After extraction, 1 mL of a 1.0 M NaBH_4 aqueous solution was added to the aqueous phase where no noticeable color change occurred, indicating a complete reduction of Pd^{2+} during the growth stage.

distribution than those originally obtained via the seed-mediated growth process in aqueous solution before extraction. Similar results were also observed for Au and Pt nanoparticle extraction experiments reported before.^{12,13} Interestingly, the RSD of these dodecanethiol-Pd nanoparticles appears to decrease with increasing particle size. The dodecanethiol-Pd nanoparticles obtained after extraction correspond very well to the theoretical mean sizes that were targeted during the seed-mediated growth experiments, illustrating the effectiveness of both the seed-mediated growth process presented in this paper as well as the ability of this extraction process to provide high quality organic nanoparticle dispersions of a priori predicted sizes. It is worth noting that the TEM images of the dodecanethiol-Pd nanoparticles shown in Figure 7 (high magnification) and Figure 8 (low magnification) illustrate significant regions of ordered arrays of the Pd nanoparticles on the surface of the TEM grids after simple evaporation of the hexane solvent. The alkyl tails of the dodecanethiol ligands extending from adjacent particles interdigitate each other, causing these uniform Pd nanoparticle building blocks to be assembled into ordered arrays.

4. Requirements for Effective Seed-Mediated Growth of Pd Nanoparticles. There are several requirements that must be met in order to ensure the success of the stoichiometric size-controlled synthesis of Pd nanoparticles using this seed-mediated growth process. These include (i) avoidance of new nucleation during the growth stages, (ii) complete consumption/reduction of the Pd^{2+} during seed synthesis and subsequent growth stages, (iii) homogeneous growth of Pd atoms onto the Pd nanoparticle seeds, and (iv) ability to maintain the stabilization of the Pd nanoparticles using CMC during the growth steps. The following sections briefly illustrate that these criteria have been met in this seed-mediated growth process.

4.1. Absence of New Nucleation during Growth. The use of a strong reducing agent such as NaBH_4 during the growth stages led to the formation of new nucleation sites as was demonstrated above (see section 2.1). In order to avoid new nucleation, the weak reducing agent ascorbic acid was employed to reduce Pd^{2+} into $\text{Pd}^{(0)}$ during the growth. Table 1 summarizes the experimental results on the size and size distribution of both CMC-Pd nanoparticles obtained via 0.03 M ascorbic acid induced growth and dodecanethiol-Pd nanoparticles obtained from their extraction. For comparison, the size and size distribution of the Pd nanoparticle seeds and the theoretically/stoichiometrically predicted Pd particle sizes are also presented in Table 1. The results in Table 1 indicate that the Pd^{2+} added during the growth stage predominantly contributes to the addition of Pd atoms onto the surface of the Pd seeds rather than creating new nucleation sites in the bulk growth solution, since almost all of the Pd nanoparticles obtained after the growth stages are larger than the Pd seeds (3.4 nm) with narrow size distributions.

4.2. Complete Consumption/Reduction of Pd^{2+} during Both Seed Synthesis and Subsequent Growth. The complete consumption/reduction of Pd^{2+} is required after both the synthesis of the Pd seeds and subsequent seed-mediated growth stages. To meet with this requirement, ascorbic acid was added at three times the stoichiometrically required amount necessary for the complete reduction of the Pd^{2+} (i.e., 200% excess ascorbic acid was used) during both the synthesis of the Pd seeds and each growth stage. Upon extraction of the Pd nanoparticles into the hexane phase, a clear aqueous phase was obtained. In order to determine if any unreduced Pd^{2+} still existed in this aqueous phase, 1 mL of a 1.0 M NaBH_4 aqueous solution was injected into the transparent aqueous phase. No noticeable color change occurred (Figure 9) upon the addition of NaBH_4 , indicating a complete reduction of Pd^{2+} after both the synthesis of Pd seeds and in each subsequent growth step. Moreover, the Pd content in the aqueous solution after extraction was determined to be less than the Pd detection limit (0.01 mg/L) of the ICP-OES. Evidently, Pd^{2+} was completely converted into $\text{Pd}^{(0)}$ after both the seed synthesis and subsequent growth stages.

4.3. Homogeneous Growth of Pd Atoms onto the Pd Nanoparticle Seeds. The homogeneous growth of Pd atoms onto the surfaces of the Pd seeds is reflected in the narrow size distribution of the products and the fact that the mean size from each growth stage was similar to the theoretical size for a given Pd^{2+} salt addition. It was determined that the concentration of the ascorbic acid plays an important role in affecting the size distribution of the Pd nanoparticles obtained upon growth. Concentrated ascorbic acid addition, even at a slow rate, results in unequal growth of Pd atoms

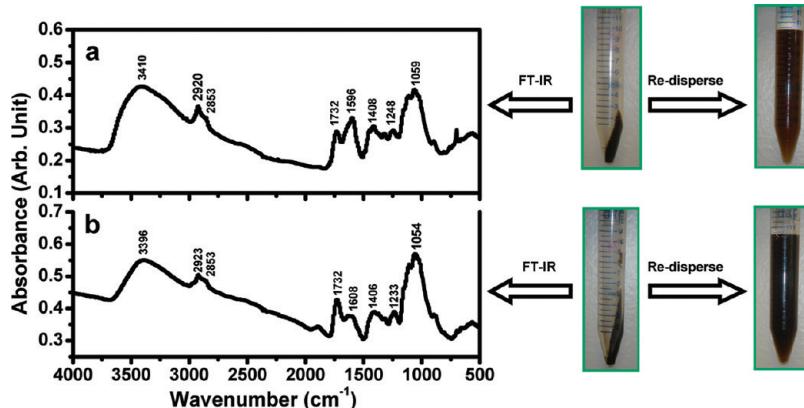
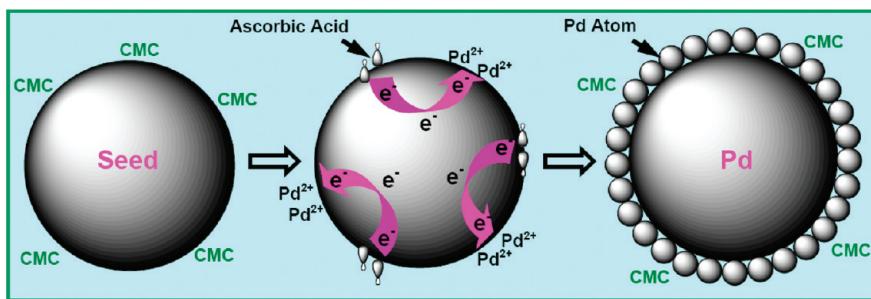


Figure 10. FT-IR spectra (on the left) of Pd nanoparticles obtained from the seed-mediated growth process where low concentration ascorbic acid solution (0.03 M) was employed during the growth stage. The mean particle sizes are (a) 6.4 nm and (b) 7.8 nm (see Figure 5). Also, digital images of the Pd nanoparticle precipitates and their redispersion in water are provided (on the right).

Scheme 1. Potential Mechanism Illustrating the Ascorbic Acid Induced Seed-Mediated Growth of the Pd Nanoparticles^a



^aThis process leads to the formation of Pd atoms homogeneously accumulated on the surface of the Pd nanoparticle seeds, thus allowing the subsequent growth of the Pd nanoparticles.

onto the surface of the Pd nanoparticle seeds, as reflected by the broad size distributions (Figure 4). On the other hand, gradual addition of ascorbic acid in low concentration not only avoids the formation of new nucleation sites but also allows even reduction of Pd²⁺/accumulation of Pd atoms on the surfaces of the Pd nanoparticle seeds (Figures 5 and 7).

4.4. Stabilization of Pd Nanoparticles by CMC Molecules after Growth. Stabilization of the Pd nanoparticles by the CMC after the growth is important to prevent agglomeration. The Pd nanoparticles obtained after the ascorbic acid (0.03 M) induced growth were separated from the aqueous solution via centrifugation (6000 rpm) with the assistance of the antisolvent ethanol. The centrifugation results in Pd nanoparticle precipitates, which could be completely redispersed in the aqueous phase via simply shaking the centrifuge tube, revealing good stabilization of Pd nanoparticles by the CMC molecules in water (see Figure 10 on the right). FT-IR spectra of these Pd nanoparticles are presented in Figure 10. Interestingly, the relative intensity of the unassociated carboxylic acid stretching peak at 1732 cm⁻¹, as compared to the asymmetric $\nu_{as}(COO^-)$ or symmetric $\nu_s(COO^-)$ stretching peaks, increases as the size of the Pd nanoparticles becomes larger upon sequential growth (Figures 2c and 10). Nevertheless, the appearance of significant asymmetric $\nu_{as}(COO^-)$ or symmetric $\nu_s(COO^-)$ stretching peaks as well as the -OH peaks in each of these cases (Figures 2c and 10) confirms the attachment of the -COO and -OH functional groups, thereby providing the steric stabilization for the Pd nanoparticles.^{8,13} Evidently, the CMC molecules sustain

their ability to stabilize the Pd nanoparticles within the aqueous solution even during/after the seed-mediated growth process.

5. Potential Mechanism for This Seed-Mediated Growth of Pd Nanoparticles. It has been reported that small metal particles generally act as a relay system for electron transfer from donor to acceptor.⁴⁶ As a result, reduction of the Pd²⁺ is prone to occur at the surface of the Pd nanoparticle seeds. The enlargement of the Pd nanoparticles via the reduction of Pd²⁺ could principally occur in the following way: Ascorbic acid donates electrons to the Pd seed surface where the electrons are stored, and subsequently Pd²⁺ is reduced into Pd⁽⁰⁾. This process leads to a formation of Pd atoms and their homogeneous sequential accumulation on the surface of the Pd seeds, thereby achieving atomic-level control over the size of the Pd particles. A potential growth mechanism is illustrated in Scheme 1. The Pd nanoparticle seeds function as catalysts in this system and significantly decrease the energy barriers for the reduction reaction from Pd²⁺ into Pd⁽⁰⁾. As such, this does not allow the extremely weak reducing agent, ascorbic acid, to reduce the Pd²⁺ in the bulk solution that would form new nucleation centers. Rather, it facilitates the sequential growth of Pd atoms on the surface of Pd seeds. Accordingly, the ascorbic acid based reduction of the Pd²⁺ into Pd⁽⁰⁾ is predominantly a surface-mediated reduction in this case. While the adsorbed CMC molecules can function as effective capping agents to prevent the Pd nanoparticles from agglomerating, an inhibition of growth in the presence

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of the CMC molecules was not observed. The CMC used in this study is a linear polysugar with a molecular weight of 90 000, resulting in a bulky monolayer with a higher degree of steric hindrance.⁸

Conclusions

In this work, small (approximately 3.4 nm) Pd nanoparticles with narrow size distribution ($SD = 0.7$ nm) were synthesized using CMC as a capping agent and ascorbic acid as a reducing agent in aqueous solution at 95 °C. Using these CMC-Pd nanoparticles as seeds coupled with a seed-mediated growth method where low concentration ascorbic acid (0.03 M) was employed as reducing agent, we accomplished precise control over the size of Pd nanoparticles spanning from 3.4 to 7.6 nm in approximately 1.4 nm increments through Pd^{2+} reduction on the surfaces of the Pd seeds. Also, the extraction of these Pd nanoparticles from the aqueous phase into an organic phase was accomplished with no significant change in their sizes. Thus, the use of CMC as capping agent and ascorbic acid as reducing agent in water allowed green chemistry principles to be incorporated into both the nanoparticle seed synthesis and seed-mediated

growth process. This “green” seed-mediated growth process provided stoichiometric control over Pd nanoparticle size, thereby achieving desired Pd nanoparticles size.

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Supporting Information Available: Images of the aqueous dispersions of CMC-Pd nanoparticles synthesized at room temperature and 95 °C; TEM images of CMC-Pd nanoparticles synthesized at room temperature using ascorbic acid as the reducing agent along with the histogram of these Pd nanoparticles; plot of the Pd nanoparticle size and size distribution as a function of the system temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.