Synthesis, Characterization, and Stability of Dendrimer-Encapsulated Palladium Nanoparticles

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Here we report on the synthesis, physical and chemical properties, and stability of Pd nanoparticles encapsulated within poly(amidoamine) (PAMAM) dendrimers. Specifically, amine- and hydroxyl-terminated PAMAM dendrimers ranging in generation from 4 to 8 were studied. Under appropriate conditions, addition of K_2PdCl_4 results in covalent attachment of the $PdCl_3^-$ hydrolysis product of this complex to tertiary amines within the dendrimers. Reduction with $NaBH_4$ results in conversion of dendrimer-encapsulated $PdCl_3^-$ to nearly size monodisperse, encapsulated, zerovalent Pd nanoparticles. Details regarding the Pd species present in solution and within the dendrimer prior to reduction are reported, as is the maximum Pd^{2+} loading of the dendrimers. Dendrimer-encapsulated Pd nanoparticles undergo oxidation in air, but this process is slowed significantly when coordinating ions are removed from solution. In the absence of O_2, dendrimer-encapsulated Pd nanoparticles are stable indefinitely. The oxidation product is not PdO, but rather Pd ions coordinated to the dendrimer interior. Dendrimer generation does not affect the rate of Pd oxidation. The dendrimer itself undergoes irreversible oxidation in the presence of O_2. Finally, the oxidation of dendrimer-encapsulated Pd nanoparticles is reversible. Specifically, H_2 gas can be used to re-reduce partially oxidized Pd nanoparticles without changing their average size.

Introduction

Here we report on the synthesis, physical and chemical properties, and stability of Pd nanoparticles encapsulated within poly(amidoamine) (PAMAM) dendrimers.[1,2] This study is motivated by recent applications of Pd dendrimer-encapsulated nanoparticles (DENs) to catalysis,[1,3−11] and the corresponding need to better understand the fundamental properties of this emerging class of materials. The following four new findings have implications relating to the use of these materials for that purpose. First, the maximum Pd ion loading in the dendrimer is correlated, in a 1:1 stoichiometric ratio, to the number of interior amines available for complexation. Second, Pd DENs can be synthesized within amine-terminated PAMAM dendrimers by controlling solution pH. Third, the oxidative stability of Pd DENs is significantly improved by removal of solution-phase impurities. Fourth, exposure to hydrogen reversibly converts partially oxidized Pd DENs back to the zerovalent state, which is significant in the context of catalyst recycling.

DENs are prepared using a template approach in which metal ions are sequestered within the dendrimer and then reduced (Scheme 1).[1,2,12] As a consequence of this synthetic approach, the encapsulated metal particles do not agglomerate and can be nearly monodisperse in size. Metals such as Pd are of special interest because even when encapsulated within dendrimers a substantial fraction of their surface is unpassivated and therefore catalytically active. Specifically, Pd DENs have been shown to be active for hydrogenation[3−5,7,8,11] and carbon-coupling[6,7,9,10] reactions. Finally, the dendrimer itself can be used to discriminate between substrates, which provides a means for imparting selectivity to intrinsically nonselective Pd catalysts,[3,8,11] and the periphery can be tailored to control solubility of the catalyst.[4−7] Since our original report,[12] other types of metallic,[13−15] bimetallic,[16,17] and semiconductor[18] DENs have been reported by our group and others.

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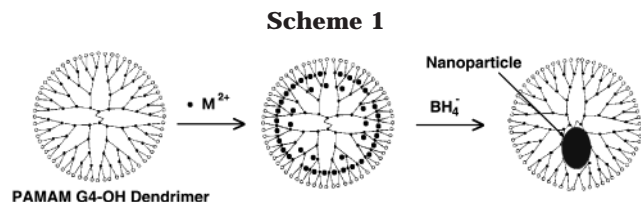(13) Esumi, K.; Suzuki, A.; Aihara, N.; Usui, K.; Torigoe, K. *Langmuir* **1998**, *14*, 3157−3159.

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Scheme 1

The results of this study show that the maximum loading of K_2PdCl_4 into both hydroxyl- and amine-terminated dendrimers correlates with the number of available interior amine binding sites. UV−vis absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) indicate that Pd DENs prepared by chemical reduction are prone to air oxidation. Purification of DENs by dialysis improves their stability, however, and the oxidation by air is reversible upon exposure to hydrogen gas. A key objective of this report is to provide a detailed synthetic procedure for preparing Pd DENs using either hydroxyl- or amine-terminated PAMAM dendrimers and describe the optimal conditions under which they can be stored and used.

Experimental Section

Materials. Hydroxyl-terminated fourth-, sixth-, and eighth-generation (G4-OH, G6-OH, and G8-OH, respectively) and amine-terminated fourth-generation (G4-NH₂) PAMAM dendrimers having ethylenediamine cores were obtained as 10−25% methanol solutions (Dendritech Inc., Midland, MI). Prior to use the methanol was removed under vacuum at room temperature. K_2PdCl_4 (Strem Chemicals Inc.) and $NaBH_4$ (Aldrich Chemical Co., Milwaukee, WI) were used without further purification. 18 MΩ·cm Milli-Q deionized water (Millipore, Bedford, MA) was used to prepare aqueous solutions. Cellulose dialysis sacks having a molecular weight cutoff of 12 000 were purchased from Sigma Diagnostics Inc.

In a typical preparation of G4-OH dendrimers containing nominally 40-atom nanoparticles (G4-OH(Pd₄₀)), 125 μL of a 0.5 mM aqueous solution of G4-OH dendrimer was dissolved in 9.8 mL of deionized water, followed by slow addition of 25 μL of an aqueous 0.1 M K_2PdCl_4 solution with stirring. After the solution was stirred for 1 h, 50 μL of a freshly prepared, aqueous 1.0 M $NaBH_4$ solution was added. G6-OH(Pd₄₀) and G8-OH(Pd₄₀) DENs were prepared via the same route by substituting G6-OH and G8-OH solutions for the G4-OH dendrimer solution. G4-NH₂(Pd₄₀) DENs were prepared by a similar route except that the pH of the G4-NH₂ solution was adjusted to 3 by addition of HCl prior to addition of K_2PdCl_4. After addition of $NaBH_4$ (which results in a significant pH increase), HCl was added to the solution to maintain a pH of ∼8.

Characterization. Absorption spectra were recorded on a Hewlett-Packard HP 8453 UV−vis spectrometer. The optical path length was 1.0 cm, and deionized water or aqueous dendrimer solutions were used as references. XPS data were acquired using an Axis HSi 165 Ultra Kratos instrument (Manchester, UK). XPS data acquisition employed an Al anode set at 15 mA and 15 kV. The carbon peak at 285.0 eV was used as an internal reference. High-resolution transmission electron micrographs (HRTEMs) were obtained with a JEOL-2010 microscope having a point-to-point resolution of 0.19 nm. Samples were prepared by placing a drop of solution on a holey-carbon-coated Cu TEM grid and allowing the solvent to evaporate in air.

Results and Discussion

Figure 1a shows UV−vis spectra of dilute aqueous solutions of K_2PdCl_4 in deionized water. The aqueous Pd salt has two strong ligand-to-metal charge-transfer bands at 207 nm ($\epsilon = 9000$ M⁻¹ cm⁻¹) and 235 nm ($\epsilon = $
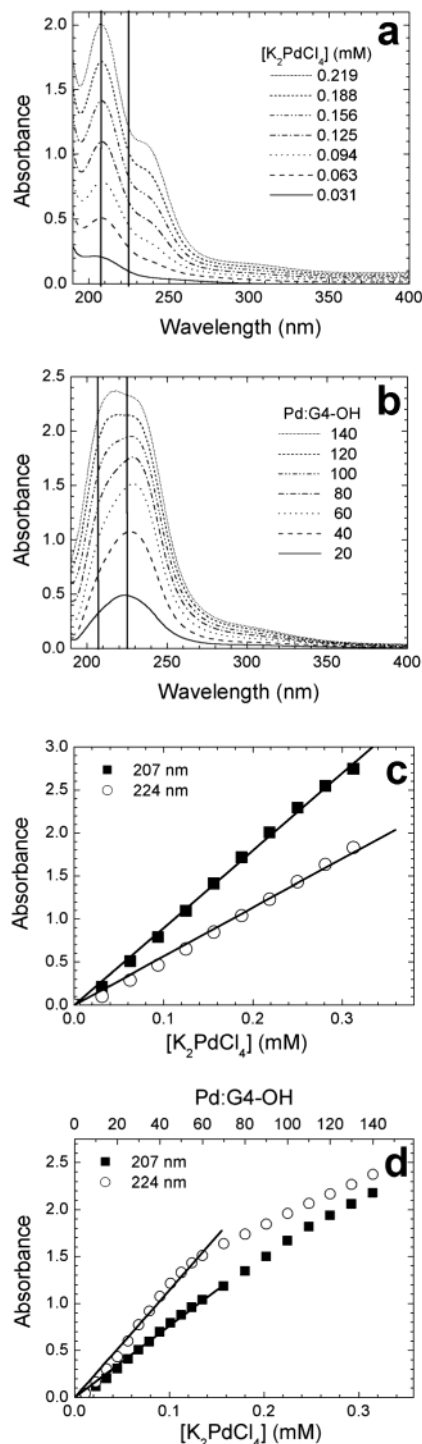

Figure 1. UV−vis absorbance spectra of (a) aqueous K_2PdCl_4 solutions and (b) G4-OH/K_2PdCl_4 solutions containing different Pd/G4-OH ratios. The concentration of G4-OH was 3.125 μM in both cases. Each spectrum was obtained 5 min after addition of K_2PdCl_4; (c) and (d) are Beer−Lambert plots obtained at 207 and 224 nm from the plots of (a) and (b), respectively.

4400 M⁻¹cm⁻¹). These two bands correspond to literature values for the hydrolysis product $PdCl_3(H_2O)^-$.[19] Upon addition of the G4-OH dendrimer, a single UV−vis band is observed at $\lambda_{max} = 224$ nm ($\epsilon = 16\,500$ M⁻¹ cm⁻¹, Figure 1b) at Pd/G4-OH ratios of less than 80. This peak corresponds to a ligand-to-metal charge-transfer (LMCT) band associated with complexation of

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the complex Pd anion to interior tertiary amines of the G4-OH dendrimer.[3] Complexation likely occurs via displacement of water from $PdCl_3(H_2O)^-$, followed by covalent reaction with the interior tertiary amines of the dendrimer. This contention is supported by XPS data indicating a 1:3 Pd/Cl ratio after dialysis of G4-OH$(Pd^{2+})_{40}$ solutions prepared using K_2PdCl_4. Moreover, Ooe et al. have recently shown evidence of a strong interaction between Pd^{2+} and interior amines of PAM-AM dendrimers using ^{14}N NMR.[11] Absorbance spectra of G4-OH$(Pd^{2+})_{40}$ solutions obtained before and after dialysis in water for several days were identical. This means that $PdCl_3^-$ is strongly bound to the G4-OH dendrimer; that is, that the amount of free $PdCl_3(H_2O)^-$ in solution is negligible. At Pd/G4-OH ratios greater than 80, a shoulder is apparent at ~215 nm and the peak at 224 nm broadens significantly. This is a consequence of the superposition of peaks corresponding to both dendrimer-encapsulated $PdCl_3^-$ (224 nm) and free $PdCl_3(H_2O)^-$ in solution (207 and 235 nm) at Pd ion concentrations exceeding that which can be accommodated by the dendrimer.

Figure 1c and d show Beer−Lambert plots at 207 and 224 nm derived from the absorbance spectra shown in Figure 1a and b, respectively. For aqueous K_2PdCl_4 solutions the plot is linear throughout the concentration range studied (Figure 1c), but plots obtained at the same wavelengths for solutions containing both G4-OH and K_2PdCl_4 are linear only up to Pd/G4-OH ratios of ~55 ± 5 (Figure 1d). These results suggest a maximum loading of ~55 ± 5 Pd ions per dendrimer.

The data in Figure 1c and d were used to obtain the titration data shown in Figure 2a. These plots of the concentration of dendrimer-encapsulated and free Pd ions as a function of the Pd/G4-OH ratio were calculated using the Beer−Lambert Law for a multicomponent system (eqs 1 and 2).

$$A(207 \text{ nm}) = \sum \epsilon_1(207 \text{ nm})c_1 l + \sum \epsilon_2(207 \text{ nm})c_2 l \quad (1)$$

$$A(224 \text{ nm}) = \sum \epsilon_1(224 \text{ nm})c_1 l + \sum \epsilon_2(224 \text{ nm})c_2 l \quad (2)$$

Here, c_1 and c_2 are the concentrations of $PdCl_3^-(H_2O)$ and intradendrimer, amine-coordinated $PdCl_3^-$, respectively and l is the path length of the curvette. These results show that there is a maximum loading of 57 ± 5 Pd ions within the G4-OH dendrimers. Because there are 62 interior tertiary amines in G4-OH dendrimer, this result implies that each Pd ion is strongly coordinated with a single tertiary amine.

The behavior of G4-NH$_2$ dendrimers in the presence of K_2PdCl_4 solutions is different from that of the G4-OH dendrimers. Specifically, addition of K_2PdCl_4 to a solution of G4-NH$_2$ in deionized water results in immediate agglomeration and the formation of a white precipitate, presumably due to cross-linking of the dendrimers by Pd ions.[4,20] Such agglomeration is not observed for Gn-OH dendrimers, which emphasizes the poor affinity of Pd ions for hydroxyl groups. Agglomeration is avoided at pH < 5, however, because the peripheral primary amines of the dendrimers are completely protonated and thus unable to cross-link via Pd
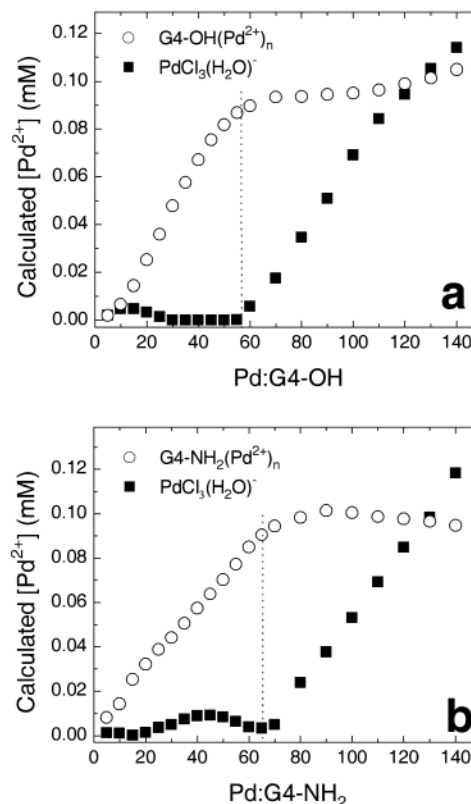

Figure 2. Plots of the concentration of free $PdCl_3(H_2O)^-$ and dendrimer-encapsulated Pd^{2+} as a function of the total Pd/dendrimer mole ratio. In (a) the dendrimer is G4-OH and in (b) it is G4-NH$_2$. The concentrations were calculated using eqs 1 and 2 and values obtained from the Beer−Lambert plots (shown for the G4-OH$(Pd^{2+})_n$ titration in Figure 1; data for G4-NH$_2(Pd^{2+})_n$ not shown).

ions.[4,21,22] Figure 2b shows the results of a spectrophotometric titration of G4-NH$_2$ with K_2PdCl_4 carried out at pH 3. Consistent with the results for G4-OH, a maximum of 65 ± 5 Pd ions coordinate to each G4-NH$_2$ dendrimer under these conditions. That is, the peripheral primary amines remain protonated at low pH, even in the presence of Pd ions, whereas the interior tertiary amines are available for reaction. However, we find that much longer times (5−10 min) are required for complete reaction between $PdCl_3(H_2O)^-$ and G4-NH$_2$ compared to G4-OH (<1 min). A recent report from our group indicates that in the absence of metal ions over 95% of the interior amines in G4-NH$_2$ dendrimers are protonated at pH 3.[22] This suggests that the rate of the covalent reaction between $PdCl_3(H_2O)^-$ and the tertiary amines is slowed by the presence of competing protons. Titration of a G4-NH$_2$ solution with K_2PdCl_4 at pH 1.5 revealed no interaction between the dendrimer and the Pd ions even after 24 h.

Figure 3a shows absorbance spectra of G4-OH$(Pd^{2+})_{40}$ prior to reduction and after reduction with different mole ratios of NaBH$_4$. If the solutions used to obtain these spectra are kept under N$_2$, then they do not aggregate for at least 180 days. Three aspects of these spectra merit comment: first, as the amount of NaBH$_4$ used for the reduction increases, the well-defined LMCT

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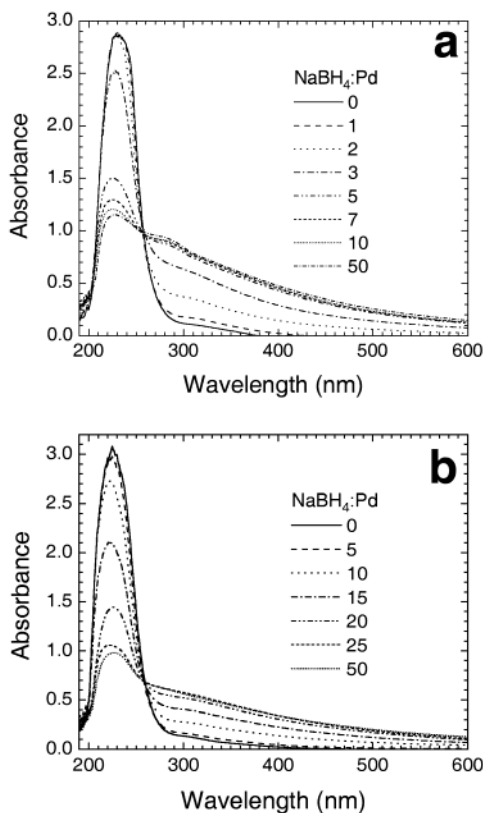(22) Niu, Y.; Sun, L.; Crooks, R. M. *Macromolecules* **2003**, *36*, 5725−5731.

Figure 3. UV−vis absorbance spectra of aqueous solutions initially containing (a) G4-OH(Pd^{2+})$_{40}$ (initial pH = 4) and (b) G4-NH$_2$(Pd^{2+})$_{40}$ (initial pH = 3) as a function of the mole ratio of BH$_4^-$ reducing equivalents per Pd^{2+}. The spectra were obtained in air 5 min after addition of NaBH$_4$.

peak of G4-OH(Pd^{2+})$_{40}$ present at 224 nm decreases; second, there is an increase in the featureless absorbance that monotonically increases toward higher energy; and third, an isosbestic point is present at 258 nm. The first observation indicates that Pd^{2+} is consumed during reduction, and the second observation is a consequence of the continuous absorption arising from interband transitions of the newly formed intradendrimer Pd colloids.[3,23−25] The isosbestic point indicates that the Pd^{2+} present prior to reduction is exclusively converted to a single species, which we identify as zerovalent Pd. A large excess of NaBH$_4$ is required for complete Pd ion reduction, because parasitic proton reduction, which is significant under the conditions used for these experiments (initial pH = 4), competes for reducing equivalents.

Figure 3b shows absorbance spectra analogous to that in Figure 3a, except that G4-NH$_2$ was used to encapsulate the Pd nanoparticles. The initial pH in these experiments was reduced to 3 with HCl to avoid precipitation of the dendrimer (vide supra). After reduction, the absorbance spectra of the G4-NH$_2$(Pd$_{40}$) solutions have the same general features previously described for G4-OH(Pd$_{40}$) (Figure 3a). However, a greater excess of NaBH$_4$ is required to fully reduce G4-NH$_2$-(Pd^{2+})$_{40}$ solutions because of the lower initial pH and correspondingly larger loss of reducing equivalents to

proton reduction. The G4-NH$_2$(Pd$_{40}$) DENs precipitated after a few hours if the solution pH increased above 8 (due to proton reduction by BH$_4^-$). This was avoided by adding HCl to lower the pH; solutions of G4-NH$_2$(Pd)$_{40}$ did not aggregate for up to 30 days if the solution pH was kept below 8. Precipitation at pH > 8 is probably a consequence of dendrimer cross-linking of peripheral amines by Pd^{2+} that arise from air oxidation of Pd DENs (vide infra).

Transmission electron microscopy (TEM) of Pd DENs synthesized in hydroxyl- and amine-terminated dendrimers revealed near-monodisperse Pd nanoparticles having a mean diameter of 1.4 ± 0.4 nm for G4-OH-(Pd$_{40}$) and 1.7 ± 0.5 nm for G4-NH$_2$(Pd$_{40}$) (see Supporting Information).[1,3,8]

Pd DENs are stable toward oxidation for at least 30 days when kept under N$_2$, but begin to oxidize within minutes upon exposure to air.[26,27] Figure 4a shows how the absorbance spectrum of an aqueous pH 8 solution of G4-OH(Pd$_{40}$), adjusted to pH 8 after reduction, changes as a function of time when the solution is stirred in a vial open to the laboratory atmosphere. Under these conditions, the peak at 224 nm, which arises from the presence of G4-OH(Pd^{2+})$_n$, increases and there is a corresponding decrease in the featureless absorption at higher wavelengths. The reappearance of the peak at 224 nm also suggests that any Pd^{2+} ions formed upon oxidation remain sequestered within the dendrimer via reaction with the interior amines. The isosbestic point present at ∼250 nm confirms that zerovalent Pd is converted exclusively to a single species, which we identify as dendrimer-encapsulated Pd ions, upon oxidation. Notice, however, that a small, new peak appears at 285 nm; we believe this feature is due to an irreversible partial oxidation of the G4-OH dendrimers. This point will be discussed in more detail later.

Figure 4b presents a comparison of the oxidation rates of G4-OH(Pd$_{40}$), G6-OH(Pd$_{40}$), and G8-OH(Pd$_{40}$) DENs in an aqueous pH 8 solution. The percentage of oxidized Pd was calculated as using eq 3.

$$\% \, \text{Pd Oxidation} = \frac{A_{224} - A_{224}(\text{Gn-OH}(\text{Pd}_{40}))}{A_{224}(\text{Gn-OH}(\text{Pd}^{2+})_{40}) - A_{224}(\text{Gn-OH}(\text{Pd}_{40}))} \times 100 \tag{3}$$

Here n = 4, 6, or 8, A_{224} is the total absorbance of the solution at 224 nm, and $A_{224}(\text{Gn-OH}(\text{Pd}^{2+})_{40})$ and A$_{224}$-(Gn-OH(Pd$_{40}$)) are the absorbance of Gn-OH(Pd^{2+})$_{40}$ and Gn-OH(Pd$_{40}$) solutions at 224 nm, respectively. The results show that the oxidation rate is essentially independent of dendrimer generation. In all cases the Pd nanoparticles are more than 95% oxidized after 3 days. If the solution pH is adjusted to 5 with HCl, G4-OH(Pd$_{40}$) DENs are more than 95% oxidized after only 1 h. We are uncertain why the acidic chloride medium accelerates oxidation.

Figure 4c shows how the absorbance spectrum of an aqueous pH 8 solution containing G4-NH$_2$(Pd$_{40}$) DENs

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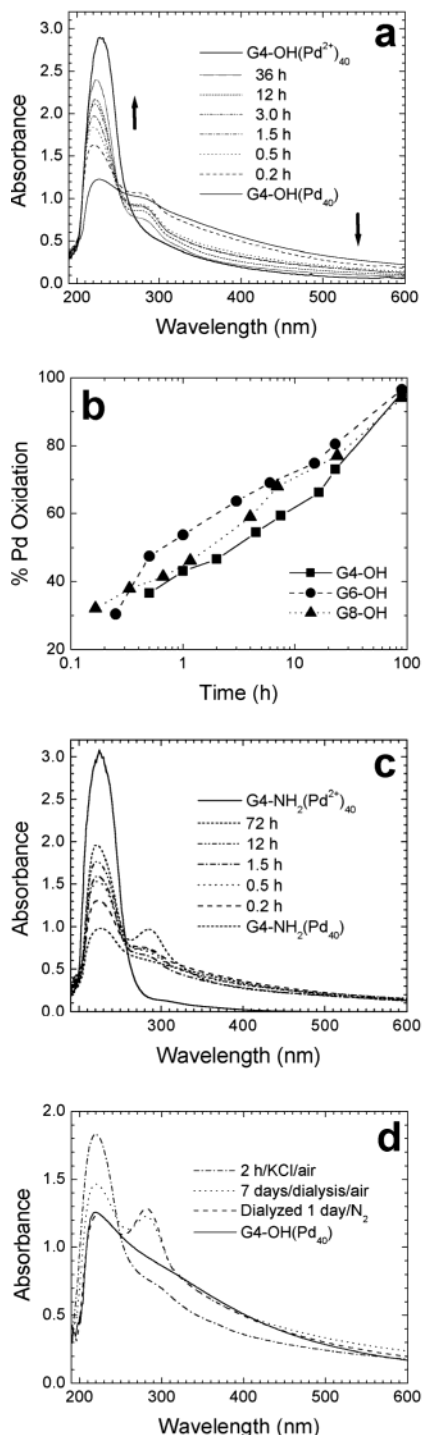
Figure 5. High-resolution XPS spectra of G4-OH(Pd^{2+})$_{40}$ before and after reduction with 20 equiv of NaBH$_4$ (solution pH adjusted to 8 with HCl after reduction), and after partial oxidation by exposure to air for 2 days. The Pd 3d$_{5/2}$ and 3d$_{3/2}$ peaks are shown.

amine groups stabilizing the encapsulated Pd nanoparticles by coordinating with surface Pd atoms.[28]

The oxidative stability of both the G4-OH(Pd$_{40}$) and G4-NH$_2$(Pd$_{40}$) DENs can be dramatically improved by dialyzing the original solution with 10 L of water for 24 h. Figure 4d compares absorbance spectra of G4-OH-(Pd$_{40}$) before and after dialysis, and after exposure to air for 7 days. The solid line is the spectrum of G4-OH-(Pd$_{40}$) prior to dialysis.[23−25] After dialysis for 1 day under N$_2$, a band appeared at 285 nm, which, as will be discussed in detail shortly, is probably due to oxidation of the dendrimer. The rest of the spectrum is essentially unchanged, however. When the same solution was then exposed to air, the oxidation of G4-OH(Pd$_{40}$) was much slower. Specifically, only ∼10% of the Pd oxidized after a period of 7 days (contrast with the data shown in Figure 4a, in which 10% of the Pd oxidized within 0.2 h in the absence of dialysis). To determine if this stability is due to the removal of salts from the solution during dialysis, a stoichiometric amount of KCl (KCl/Pd ratio = 4:1) was added to the dialyzed G4-OH(Pd$_{40}$) solution. This resulted in an immediate increase in the oxidation rate of G4-OH(Pd$_{40}$): ∼30% of the Pd oxidized within 2 h of adding KCl. This suggests that oxidation results in formation of the original G4-OH(Pd^{2+})$_n$ composite, and that this process is facilitated by the presence of coordinating anions.

XPS results confirm that the oxidation of the Pd nanoparticles occurs primarily via reformation of the G4-OH(Pd^{2+})$_{40}$ composite, and not by the formation of an oxide of Pd. Figure 5 shows XPS spectra of solutions containing G4-OH(Pd^{2+})$_{40}$, G4-OH(Pd$_{40}$), and G4-OH-(Pd$_{40}$) after being exposed to air for 24 h. Before reduction, the Pd 3d$_{5/2}$ peak is present at 338.2 eV, but it shifts to 336.1 eV after reduction. After oxidation in air for 24 h, peaks corresponding to both Pd^{2+} (338.2 eV) and zerovalent Pd (336.0 eV) are present. Significantly, no corresponding change in the oxygen 1s signal is observed, suggesting that the oxidation product of the Pd particles in aqueous solution is primarily a coordinated palladium salt and not an oxide of Pd.

Figure 4. (a) UV−vis absorbance spectrum of G4-OH(Pd$_{40}$) as a function of the time the solution was exposed to air after initial reduction. For comparison, a spectrum of G4-OH(Pd^{2+})$_{40}$ is also shown. (b) Plots of % Pd oxidation vs time as a function of the dendrimer generation. The data were calculated using eq 3. (c) Same as (a), except for G4-NH$_2$(Pd$_{40}$). (d) UV−vis absorbance spectra of a G4-OH(Pd$_{40}$) solution before and after dialysis under N$_2$. Spectra are also shown for the dialyzed G4-OH(Pd$_{40}$) solution after exposure to air for 7 days, and then 2 h after addition of KCl (KCl/Pd ratio = 4:1). All data were obtained at pH 8.

changes as a function of time when it is exposed to air. In this case the oxidation rate is slower than for G4-OH(Pd$_{40}$); after 3 days the Pd nanoparticles are only ∼50% oxidized. This may be a consequence of peripheral
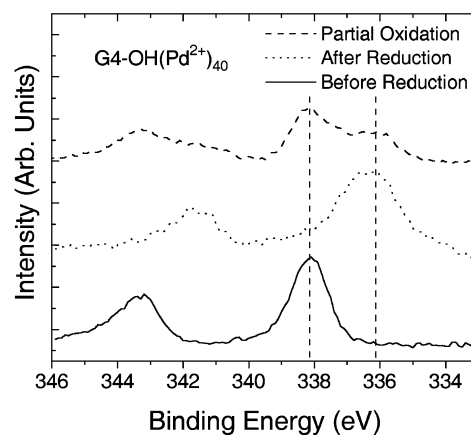
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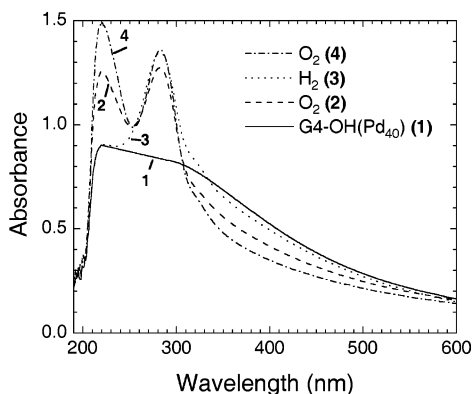
Figure 6. UV−vis absorbance spectra of a G4-OH(Pd$_{40}$) solution after sequential exposure to O$_2$, H$_2$, and O$_2$. The exposures were carried out for 10 min each. The initial reduction was performed using 20 equiv of NaBH$_4$ and the final solution pH was adjusted to 8 with HCl.

To better understand air-induced oxidation of Pd DENs, G4-OH(Pd$_{40}$) solutions were treated with O$_2$ and H$_2$ gas. Figure 6 shows how the absorbance spectrum of G4-OH(Pd$_{40}$) changes upon sequential exposure of the solution to O$_2$ and H$_2$ gases. Upon exposure to O$_2$, the peak at 224 nm resulting from the presence of G4-OH-(Pd^{2+})$_n$ increases and there is a corresponding decrease in the absorbance at higher wavelengths, along with the onset of a new peak at 285 nm. Upon treatment with H$_2$ gas the peak at 224 nm decreases and the intensity of the featureless absorption at high wavelength increases; however, there is no change in the intensity of the peak at 285 nm. This behavior persists over several oxidation/reduction cycles: O$_2$ treatment results in oxidation of the Pd DENs and an increase in the band at 285 nm, whereas H$_2$ treatment results in rereduction of the Pd ions without changing the intensity of the band at 285 nm. It is interesting to note that freshly prepared solutions of G4-OH(Pd^{2+})$_{40}$ cannot be reduced by addition of H$_2$, thus the presence of zerovalent Pd seeds is apparently necessary to drive the H$_2$-induced reduction.

HRTEM images of a G4-OH(Pd$_{40}$) DENs before and after two O$_2$/H$_2$ cycles were similar, with an average particle size after two O$_2$/H$_2$ cycles of 1.2 ± 0.4 nm. (see Supporting Information). Thus, the Pd DENs can be reconstituted after oxidation with no growth in the average nanoparticle size. This finding is consistent with our earlier contention that oxidation does not result in loss of Pd salts from the dendrimer interior. We suspect that the peak at 285 nm, which forms upon O$_2$ exposure, arises from oxidation of the dendrimer. Interestingly, this peak does not appear in the absence of the encapsulated Pd nanoparticles, suggesting that the oxidation reaction is catalyzed by zerovalent Pd. Esumi and co-workers previously showed that a similar dendrimer oxidation peak at 285 nm forms during the in-situ reduction of HAuCl$_4$ salts by UV irradiation in the presence of G4-NH$_2$ dendrimers.[13] We have also found a band at 285 nm that appears when G4-OH dendrimers spontaneously reduce HAuCl$_4$ salts in the absence of an intentionally added reducing agent.[29]

The finding that partially oxidized Pd DENs can be fully reduced by H$_2$ gas is important, because these

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Scheme 2
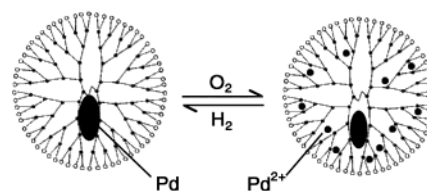
materials have found use as hydrogenation and carbon−carbon coupling catalysts.[3−11] The ability of the dendrimer template to retain oxidized Pd^{2+} ions, which can subsequently be reduced with H$_2$ gas, is a desirable characteristic that provides a means for reactivation and recycling (Scheme 2). In contrast, many colloidal metallic catalysts deactivate when exposed to oxygen and cannot be reactivated.[26,27] The consequences of the oxidation of the dendrimer itself upon exposure to O$_2$ need to be more fully explored, however.

Summary and Conclusions

This paper has reported on the synthesis, physical and chemical properties, and stability of Pd DENs. This type of information is necessary for optimizing the catalytic function of DENs so that their interesting properties can be fully exploited. We have shown that Pd DENs can be synthesized in both G4-OH and G4-NH$_2$ dendrimers, and that the loading of Pd ions into these dendrimers correlates, with a 1:1 stoichiometry, to the number of available interior amines present in the dendrimers. Pd DENs can be synthesized in G4-NH$_2$ dendrimers by selective protonation of the peripheral primary amine groups of the dendrimers. This is important because primary amines are more reactive than hydroxyl groups, and thus are better for linking DENs to surfaces, other polymers, and biological molecules. Pd DENs are stable in the absence of O$_2$, but oxidation occurs in air. Such oxidation can be minimized by dialysis of DEN solutions to remove excess coordinating ligands. The oxidation of Pd DENs is reversible: upon exposure to H$_2$ gas dendrimer-encapsulated metal ions are converted back to zerovalent Pd nanoparticles. The ability of the dendrimer template to retain oxidized Pd^{2+} ions, which can subsequently be reduced with H$_2$ gas in the presence of a zerovalent Pd seed, is a desirable characteristic that provides a means for reactivation and recycling.

Supporting Information Available: Transmission electron microscopy and size-distribution plots of Pd DENs synthesized in hydroxyl- and amine-terminated dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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