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Titania-Supported Au and Pd Composites Synthesized from Dendrimer-Encapsulated Metal Nanoparticle Precursors

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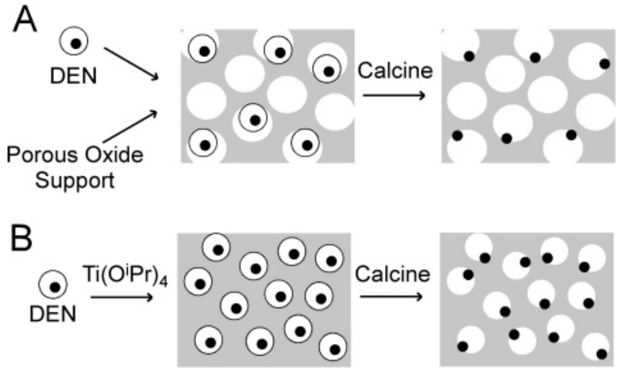
Two different approaches are compared for preparing titania-supported Au and Pd using dendrimer-encapsulated nanoparticle (DENs) precursors. First, preformed dendrimer-encapsulated nanoparticles (1−2 nm in diameter) were deposited onto a commercial solid-oxide support via wetness impregnation. Second, the same DENs were incorporated into an amorphous titania network prepared using sol−gel chemistry. The latter approach is especially interesting, because in this case both the inside and the outside of the dendrimer act as templates: the exterior of the dendrimer templates pores within the sol−gel matrix, and the interior templates the metal nanoparticles. In all cases, the dendrimer can be removed by calcination to leave behind the metal nanoparticles. The wetness impregnation method leads to a 4-fold increase in the average Au nanoparticle size following calcination. Significantly, less than a 2-fold increase in particle size was found for the sol−gel approach.

Introduction

We report herein that dendrimers can be used as templates for deposition of near-monodisperse Au and Pd nanoparticles onto titania supports. Two different approaches for preparing these heterogeneous catalytic composites are compared. First, preformed dendrimer-encapsulated nanoparticles (DENs)[1−3] can be deposited onto commercial solid-oxide supports via wetness impregnation (Scheme 1A). Second, DENs can be incorporated into an amorphous titania network prepared using sol−gel chemistry (Scheme 1B). The latter approach is especially interesting, because in this case both the inside and the outside of the dendrimer act as templates: the exterior of the dendrimer templates pores within the sol−gel matrix, and the interior templates the metal nanoparticles. In all cases, the dendrimer can be removed by calcination to leave behind just the metal nanoparticles.

Scheme 1



Dendrimer-encapsulated nanoparticles (DENs) are synthesized by sequestering metal ions within appropriate dendrimers and then chemically reducing the resulting composite.[1−3] In many cases, the resulting nanoparticles are nearly monodisperse in size. Moreover, the size of the nanoparticles can be tuned by varying the metal-to-dendrimer ratio prior to reduction. This method has proven to be useful for synthesizing a wide variety of metallic,[4−9] bimetallic,[10−12] and semiconducting[13] DENs. Encouraged by their catalytic activity for hydrogenation[6,10−12,14−17] and carbon−carbon

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coupling[18-21] reactions in solution, we sought to investigate whether DENs could be used to prepare Pd and Au catalysts supported on titania. We previously showed that DENs can be immobilized on surfaces[7,22-24] and used as heterogeneous catalysts.[7,22] Others have subsequently expanded upon these findings in a number of interesting ways.[25-29] In all of these reports, one of two approaches has been used for preparing the supported catalyst. In the first case, the dendrimer is fixed to a support and used as the active catalyst.[25,26] In the second case, the dendrimeric template is removed by calcination following immobilization, leaving behind a naked supported-nanoparticle catalyst.[27-29] Here, we focus on the latter approach.

There have been several examples of dendrimers being used to deliver nanoparticles to solid supports, followed by removal of the dendrimer to leave behind the supported, naked metal nanoparticle. The first route involves deposition of DENs onto a preexisting support followed by calcination of the dendrimer. For example, we previously investigated the calcination of Pd DENs on graphite and found that the Pd nanoparticles aggregated at the step edges of the graphite when the dendrimer was removed.[22] In a particularly important and relevant report, Chandler and co-workers showed that Pt DENs could be deposited onto commercial silica and calcined at 300 °C to yield supported Pt catalysts that nearly retain their original size distribution.[29] Choi et al. deposited G6-OH PAMAM dendrimers loaded with 60 Fe^{3+} ions onto oxide supports, calcined the composite, and observed supported 1.2 ± 0.5 nm-diameter Fe_2O_3 particles. These turned out to be catalytic for the growth of carbon nanotubes.[28] A second means for delivering nanoparticles to surfaces using dendrimers involves the incorporation of the dendrimer into a sol–gel matrix. This route has the benefit that the dendrimer can act as a template to control the porosity of the final material.[30-36] For example, Larsen and co-workers incorporated Cu^{2+}-loaded poly(propylene)imine dendrimers into amorphous silica gels, and then calcined the composites to yield CuO particles dispersed on a porous silica matrix.[27] Other groups have examined the incorporation of dendrimer-stabilized CdS[37] and Au[38] particles into silica matrixes, although in both cases no attempt was made to remove the dendrimer from the resulting support.

In this paper, we compare the synthesis of two different types of supported-nanoparticle materials. In both cases, the active metal is introduced as either Au or Pd nanoparticles prepared within fourth-generation, quaternary ammonium- or amine-terminated dendrimers. The first type of material involves deposition of Au DENs onto a commercial titania support via wetness impregnation, followed by calcination of the dendrimer at 500 °C. This route leads to a significant increase in size of the DENs from 1.7 ± 0.4 to 7.2 ± 3.6 nm. The second approach involves addition of titanium isopropoxide ($Ti(O^iPr)_4$) to methanolic solutions of Au and Pd DENs. The DENs are incorporated into the amorphous titania network upon hydrolysis and condensation of the alkoxide precursor. Upon calcination at 500 °C, the resulting supported Au and Pd nanoparticles grow only slightly in size. For example, Au DENs increase from 2.0 ± 0.6 nm in diameter to 2.7 ± 0.6 nm following calcination at 500 °C, and to 4.4 ± 0.8 nm when the temperature is raised to 550 °C. The dendrimer has a dual templating role in these materials, as it defines the size and monodispersity of both the nanoparticles and the pore structure in the titania framework. Specifically, the experimentally determined average BJH pore size of 4.0 nm in the calcined titania/G4-NH_2(Pd_{55}) composite material provides strong evidence that the imprint of the 4.5 nm-diameter G4-NH_2 dendrimer remains in the titania after calcination.

Experimental Section

Materials. Amine-terminated fourth- and sixth-generation (G4-NH_2 and G6-NH_2, respectively) PAMAM dendrimers having ethylenediamine cores were obtained as 10–25% methanol solutions (Dendritech Inc., Midland, MI). K_2PdCl_4, $HAuCl_4$ (Strem Chemicals Inc., Newburyport, MA), glycidyltrimethylammonium chloride (~90%, Fluka Chemie AG), $Ti(O^iPr)_4$ (99.999%), and $NaBH_4$ (Aldrich Chemical Co., Milwaukee, WI) were used without further purification. 18 MΩ-cm Milli-Q deionized water (Millipore, Bedford, MA) and HPLC-grade MeOH were used as solvents. The synthesis of partially quaternized, fourth-generation PAMAM dendrimers (G4-Q_{32}, where 32 is the number of quaternary amines per dendrimer) has been previously published by our group.[23]

Preparation of Au/Titania Materials by Wetness Impregnation with Au DENs. The following procedure was followed to synthesize 2 μM G4-Q_{32}(Au_{55}) DEN solutions.[39] The synthesis was carried out to yield a TiO_2 powder containing 1% w/w Au. The synthesis starts by addition of 100 mL of a 10 μM solution of G4-Q_{32} to 400 mL of 99% MeOH, followed by addition of 550 μL of 0.10 M $HAuCl_4$. After the mixture was stirred for 5 min, 550 μL of a 1.0 M solution of $NaBH_4$ in 0.3 M aqueous NaOH was added. Next, the MeOH solvent was removed from the resulting 2 μM G4-Q_{32}(Au_{55}) DEN solution

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by rotary evaporation, and the remaining water was removed by placing the remaining 5 mL of solution over P_2O_5 in a desiccator overnight. A slurry was prepared by mixing together 1.0 mL of methanol, the Au DEN powder, and 0.99 g of Degussa P25 titania (surface area = 45 m^2/g). The slurry was dried in a desiccator overnight and then calcined at 500 °C in air for 3 h.

Preparation of Au and Pd DENs for Sol−Gel-Based Nanoparticles. The following procedure was followed to synthesize a 0.92 μM G4-$NH_2(Au_{55})$ DEN solution.[39] First, 0.0924 g of a 14.2% w/w solution of G4-NH_2 (0.92 μmol) in MeOH was added to 1 L of 99% MeOH, and then 510 μL of a 0.10 M $HAuCl_4$ solution was added. After the mixture was stirred for 5 min, 510 μL of a 1.0 M $NaBH_4$ solution in 0.3 M aqueous NaOH was added (10× excess). The solution was stirred for several hours and used for the sol−gel synthesis described below. G4-$NH_2(Pd_{55})$ DENs were prepared by nearly the same procedure. Specifically, 20 μL of 0.3 M HCl was added to a solution of G4-NH_2 in 1 L of 99% MeOH, followed by the addition of 510 μL of 0.10 M K_2PdCl_4. The HCl was added to prevent cross-linking of the G4-NH_2 dendrimer by the Pd^{2+} ions (Pd^{2+} is used to designate $PdCl_4^{2-}$ and any hydrolysis products present in the MeOH solution).[24,40] After being stirred for 30 min, 1 mL of a 1.0 M solution of aqueous $NaBH_4$ was added (20× excess). The solution was stirred for several hours under N_2 and was used for the sol−gel synthesis described below.

Sol−gel Synthesis of Au- and Pd-Based Nanoparticles on Titania Supports. The 1 L MeOH solutions of 0.92 μM G4-$NH_2(Au_{55})$ or G4-$NH_2(Pd_{55})$ described in the previous section were used for the sol−gel preparations. The synthesis was carried out to yield a TiO_2 powder containing 1 wt % Au or Pd. To a solution of G4-$NH_2(Au_{55})$ or G4-$NH_2(Pd_{55})$, 0.3 M HCl was added to neutralize excess $NaBH_4$ and NaOH. This step is necessary to avoid reduction of the $Ti(O^iPr)_4$. After the mixture was stirred for several hours, 3.52 g of $Ti(O^iPr)_4$, dissolved in 5 mL of MeOH dried over molecular sieves, was added dropwise to the solution. The solution became turbid over a period of 30−60 s as the alkoxide precursor hydrolyzed. After 5 min, 100 mL of H_2O was added. The resulting solution was left for 24 h at 22 ± 2 °C, and then the precipitate was filtered and dried at 100 °C for 24 h. Typical yields based on the mass of titania for all of the syntheses were 30−60%. 100% yield corresponds to complete conversion of the titania precursor to crystalline titania. The powder was then calcined at 500 °C in flowing air for 3 h. Samples with higher dendrimer-to-Ti ratios were also prepared to gain improved resolution for TGA and elemental analysis. For these catalysts, 9.2 μM G4-$NH_2(Au_{55})$ or G4-$NH_2(Pd_{55})$ solutions were used, followed by the addition of 3.52 g of $Ti(O^iPr)_4$ as described earlier.

Characterization. Micrographs were obtained using a JEOL-2010 high-resolution transmission electron microscope (HRTEM) having a point-to-point resolution of 0.19 nm. Solution samples were prepared by placing a drop of the methanolic DEN solution onto a carbon-coated Cu TEM grid (400 mesh, Electron Microscopy Science, Fort Washington, PA). Powdered samples were examined by placing a drop of an EtOH slurry of the titania powder onto the Cu TEM grid. Thermogravimetric analyses (TGA) were conducted using a TA Instruments Q500 TGA with a heating rate of 10 °C/min under a flow of air. Adsorption−desorption isotherms were obtained using a Micromeritics ASAP 2010 volumetric adsorption analyzer. The samples (~0.05−0.15 g) were outgassed under vacuum at a temperature of 100 °C for 24 h. The isotherms were obtained at 77 K and analyzed using the BET model.[41] Pore-size distributions were calculated using the BJH method.[42] The X-ray powder diffraction data were collected with a Bruker D8 diffractometer using Cu Kα radiation. C, H, N elemental analyses were performed by Quantitative Technologies Inc. (QTI, Whitehouse, NJ). The weight percents of metals were determined by ICP-MS analysis using a Perkin-Elmer quadrupole DRCII ICP-MS (Perkin-Elmer/Sciex) and Perkin-Elmer's ELAN software. A quartz concentric Meinhard nebulizer and quartz cyclonic spray chamber with nickel cones were used. The composite materials were digested by refluxing in ultrapure aqua regia for 3 h, followed by removal of any undissolved titania by filtration. The samples were then diluted, and the Au content was analyzed by ICP-MS using standard Au ICP-MS solutions. Bi was used as an internal standard.

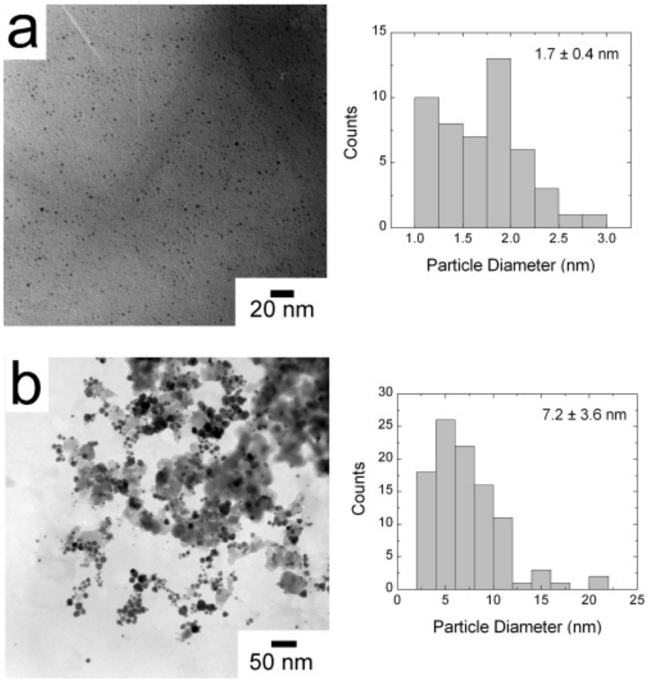

Figure 1. TEM images and particle-size histograms for G4-$Q_{32}(Au_{55})$ DENs synthesized in 99% MeOH: (a) after removal of solvent; and (b) after deposition onto P25 Degussa titania followed by calcination at 500 °C for 3 h in air.

Results and Discussion

Deposition of Au DENs onto a Commercial Titania Support. We previously reported the synthesis of G4-$Q_{32}(Au_{55})$ DENs in aqueous solutions,[39] and the same synthesis in 99% MeOH was found to yield comparable particle sizes of 1.3 ± 0.3 nm. However, the average particle size increased to 1.7 ± 0.4 nm when the solvent was removed by rotary evaporation (Figure 1a), indicating some agglomeration. After removal of the mixed MeOH/H_2O solvent, the dry G4-$Q_{32}(Au_{55})$ powder was redissolved in 1.0 mL of MeOH and mixed with a commercial Degussa P25 titania support. The resulting slurry was dried and calcined in air at 500 °C for 3 h. Figure 1b shows the resulting material. Note that the Au nanoparticles have aggregated significantly with the average particle size increasing to 7.2 ± 3.6 nm. This result differs from earlier work reported by Chandler and co-workers who showed that Pt nanoparticles could be delivered to commercial silica supports using Pt DENs with significantly better particle-size retention.[29] Importantly, a calcination temperature of 300 °C was found to be sufficient to remove the PAMAM dendrimer from Pt DENs, presumably because decomposition of the dendrimer is catalyzed by the encapsulated Pt nanoparticles. However, thermogravimetric analysis of Au

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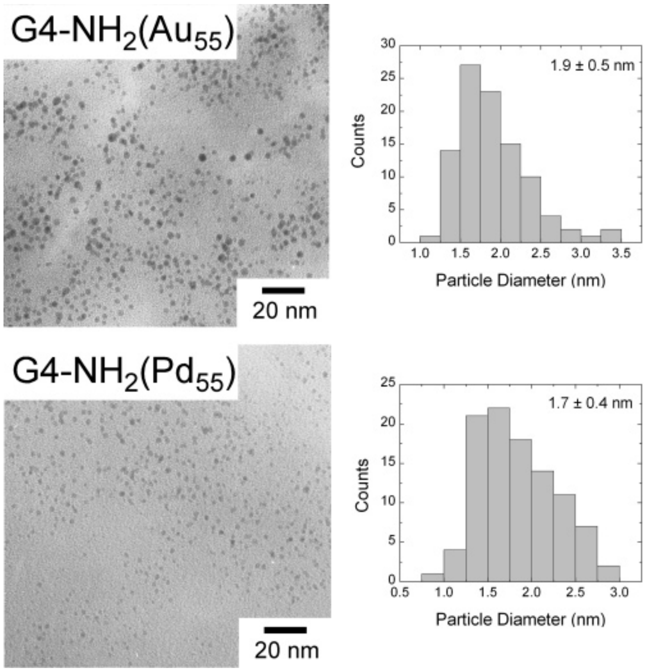

Figure 2. TEM images and particle-size histograms of 0.92 μM Au and Pd DENs synthesized in 99% MeOH.

DENS, which is discussed later, indicates that the dendrimer is not fully decomposed until a calcination temperature of ~500 °C is achieved. Milder decomposition conditions, such as treatment with ozone or an oxygen plasma, may lead to less agglomeration.[43]

Incorporation of Au and Pd DENs into Sol−Gel-Synthesized Titania. The synthesis and characterization of Pd[14,15,24,40] and Au DENs[5,8,39] in amine-terminated PAMAM dendrimers have previously been reported by our group and others. Here, G4-NH$_2$(Au$_{55}$) and G4-NH$_2$(Pd$_{55}$) DENs were synthesized in 99% MeOH solutions by loading Au^{3+} and Pd^{2+} ions into G4-NH$_2$ dendrimers, and then reducing the composite with NaBH$_4$. For convenience, we denote AuCl$_4^-$ and PdCl$_4^{2-}$ and their hydrolysis products as Au^{3+} and Pd^{2+}, respectively.[40]

Figure 2 shows TEM images of the Au and Pd DENs used in this part of the study. The average particle sizes of the G4-NH$_2$(Au$_{55}$) and G4-NH$_2$(Pd$_{55}$) DENs are 1.9 ± 0.5 and 1.7 ± 0.4 nm, respectively. The size of the G4-NH$_2$(Au$_{55}$) DENs is larger than the average particle size of 1.3 ± 0.3 nm we have previously measured for G4-NH$_2$(Au$_{55}$) nanoparticles synthesized in aqueous solutions.[39] We are not certain why the particles appear larger when synthesized in MeOH, but it may be related to the difference in dielectric constant between water and MeOH.[44] The G4-NH$_2$(Pd$_{55}$) DENs are also larger than the anticipated value of 1.2 nm calculated for a 55 atom, close-packed, spheroidal particle, but this has also been found to be typical for Pd DENs synthesized in aqueous solution.[6,16,24,40]

After synthesizing the metallic DENs, excess NaBH$_4$ was neutralized with HCl and a methanolic solution of Ti(O^{i}Pr)$_4$ was added.[45] After addition of Ti(O^{i}Pr)$_4$, the solution slowly becomes turbid over a period of 30−60 s as the alkoxide precursor undergoes hydrolysis and condensation,[46] and an orange (Au) or brown (Pd) precipitate settles out after several minutes. Five minutes later, 100 mL of H$_2$O was added to ensure full hydrolysis of the alkoxide precursor. After aging at room temperature for 1 day, the precipitate was filtered, and a clear, colorless filtrate was observed. It is important to note that only primary amine-terminated dendrimers were incorporated into the sol−gel matrix. Dendrimers terminated in hydroxyl groups (G4-OH(Au$_{55}$)) or those having partially quaternized surfaces (G4-Q$_{32}$(Au$_{55}$)) were not incorporated into the sol−gel matrix. That is, there was considerable phase separation, and most of the DENs remained in solution after filtration of the precipitate. We conclude that primary amines form covalent bonds with the alkoxide precursor, which upon slow hydrolysis and condensation yields the amorphous titania/DEN composite. Other groups have also successfully incorporated dendrimers into sol−gel materials through covalent and electrostatic interactions.[27,30−38,47−49] Specifically, the strategy used here is similar to the ligand-assisted templating strategy developed by Ying and co-workers for the synthesis of mesoporous oxide materials using interactions between alkylamine surfactants and metal alkoxide precursors prior to hydrolysis.[50]

After filtration of the titania/DEN composite material, the powder was dried at 100 °C for 1 day, and the resulting purple (Au) or brown (Pd) powder was characterized by TGA and elemental analysis to determine the optimal calcination temperatures. For these studies, composites having a higher synthetic dendrimer-to-titania mass ratio (0.13 as compared to 0.013 used for the earlier preparations, see Experimental Section) were used to enhance the signal-to-noise ratio of the TGA and elemental analysis results. Thermogravimetric analysis of the amorphous titania/G4-NH$_2$(Au$_{55}$) and titania/G4-NH$_2$(Pd$_{55}$) composites in air indicated that the weight loss attained its maximum value in the range 500−525 °C (Supporting Information). Typical weight losses after decomposition of the dendrimer were in the range of 35−45%. These values compare to a weight loss of only 12% measured for a titania-only preparation (no DENs present), which likely corresponds to loss of water upon condensation of the sol−gel. We conclude that the residual weight loss of 23−33% arises from pyrolysis of the dendrimer. However, because only 13 wt % of the precursor solution corresponds to dendrimer, it is clear that all (or nearly all) of the DENs are incorporated into the final product even though the overall synthetic yield is only ~40 wt %. In other words, the moderate yield associated with the synthesis is associated with incomplete incorporation of the titania precursor.

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Table 1. Elemental Analysis of Titania/DEN Composites Before and After Calcination at 500 °C for 3 h

sample	elemental analysis[b] C %	H %	N %
titania/G4-$NH_2(Au_{55})$ before calcination	18	3.4	7.4
titania/G4-$NH_2(Au_{55})$ calcined at 500 °C	7.4	0.3	4.8
titania/G4-$NH_2(Au_{55})$ calcined at 550 °C	0.39	0.34	0.29
titania/G4-$NH_2(Pd_{55})$ before calcination	17	3.3	7.1
titania/G4-$NH_2(Pd_{55})$ calcined at 500 °C	0.25	<0.1	<0.05
titania standard[a] before calcination	1.9	1.69	<0.05
titania standard[a] calcined at 500 °C	1.3	<0.1	<0.05

[a] Standard prepared by hydrolysis and condensation of $Ti(O^iPr)_4$ in the absence of dendrimer. [b] The composites used to obtain the data in this table were prepared with higher dendrimer-to-titania percentages (13%) than were used for other preparations reported in this paper (1.3%) to improve the accuracy of the elemental analysis results (see Experimental Section).

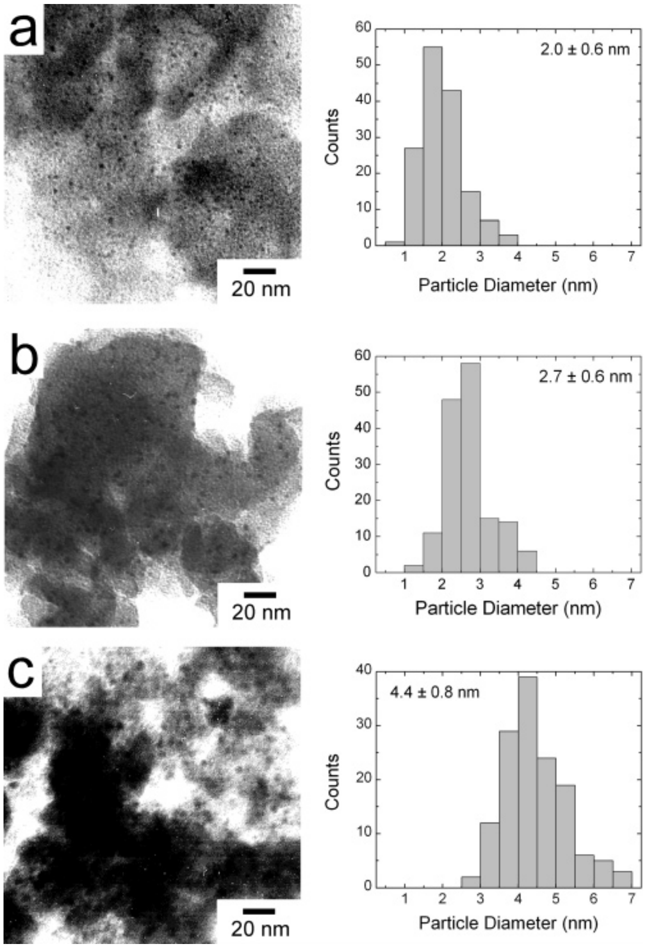

Figure 3. TEM images and particle-size histograms for G4-$NH_2(Au_{55})$ DENs incorporated into a titania matrix: (a) prior to calcination; (b) after calcination at 500 °C; and (c) after calcination at 550 °C. Calcinations were carried out under flowing air, and the final temperature was maintained for 3 h.

Elemental analysis indicated that significant percentages of C and N were still present in titania/G4-$NH_2(Au_{55})$ after calcination at 500 °C for 3 h, while the titania/G4-$NH_2(Pd_{55})$ composite had negligible amounts of these elements following calcination using the same conditions (Table 1). The more efficient removal of the dendrimer from the titania/G4-$NH_2(Pd_{55})$ composite may be a consequence of the catalytic properties of the Pd nanoparticles.[29] The presence of catalytic centers inside dendrimers has previously been shown to aid in dendrimer decomposition. For example, poly(propylene)-imine dendrimers could be removed at ~300 °C when Cu^{2+} ions were complexed within the dendrimer, but they were not decomposed until temperatures of 550−575 °C were attained in the absence of Cu^{2+}.[27] As mentioned previously, Pt DENs have also been shown to catalyze dendrimer decomposition.[29]

The extent of Au incorporation into a titania/G4-$NH_2(Au_{55})$ composite prepared using a titania-to-dendrimer mass ratio of 0.013 and calcined at 550 °C was determined by ICP-MS elemental analysis. The results indicated a Au content of 3.2 wt % (Supporting Information), which is higher than the expected value of 1.0 wt % Au based on 100% yield. The ca. 300% increase in the Au content is consistent with the overall mass yield of 35% in this preparation and the earlier discussion, indicating that all of the dendrimer (and therefore all of the Au), but only ~1/3 of the titanium alkoxide, is incorporated into the composite after hydrolysis and condensation.

TEM images of the amorphous titania/G4-$NH_2(Au_{55})$ composite before and after calcination at 500 and 550 °C in air for 3 h are shown in Figure 3. The average particle size of the Au nanoparticles in the amorphous titania/G4-$NH_2(Au_{55})$ composite is 2.0 ± 0.6 nm, indicating that the Au DENs retain their average size and dispersity after incorporation into the titania matrix (size before incorporation into the composite: 1.9 ± 0.5 nm). However, upon calcination at 500 °C, the average particle size increases to 2.7 ± 0.6 nm, and further increases to 4.4 ± 0.8 nm after calcination at 550 °C. The average particle sizes are likely somewhat overstated, however, because particles out of the focal plane of the image appear larger than they actually are. In addition, it is difficult to image nanoparticles within the titania matrix that have sizes <1.5 nm, and therefore the histograms shown in Figure 3 are biased toward larger particle sizes. We speculate that growth of the Au nanoparticles as the calcination temperature increases from 500 to 550 °C is mainly a consequence of the removal of the residual organic stabilizers, presumably decomposition products of the dendrimer, which elemental analysis indicates are still present after calcination at 500 °C but absent after calcination at 550 °C (Table 1). The limited increase in size of the Au nanoparticles is somewhat surprising in view of findings that Au monolayer-protected clusters[51] incorporated within titania substrates by the sol−gel method undergo growth from 2 to 5−10 nm after calcination at just 425 °C.[52] We believe that the improved retention of the average nanoparticle size for the sol−gel route as compared to the deposition route described earlier (7.2 ± 3.6 nm at 500 °C) is a consequence of the Au nanoparticles being well-dispersed in the titania matrix, which inhibits agglomeration.

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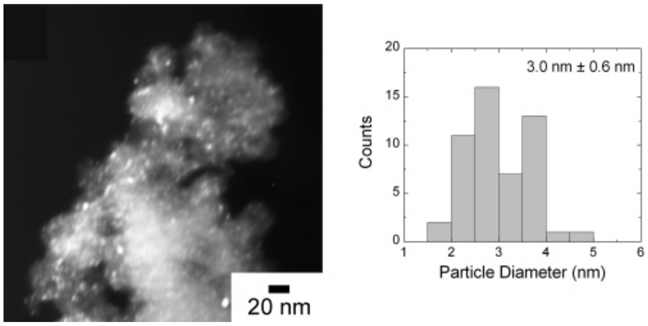

Figure 4. Dark-field TEM image and particle-size histogram for a titania/G4-$NH_2(Pd_{55})$ composite after calcination at 500 °C for 3 h in flowing air.

Figure 4 shows a dark-field TEM image of the titania/G4-$NH_2(Pd_{55})$ composite after calcination at 500 °C in air for 3 h. TEM images of the Pd nanoparticles prior to calcination could not be obtained due to the low electron-density contrast between the Pd nanoparticles and the underlying titania support. Indeed, even after calcination of the dendrimer, the particles cannot be easily visualized by bright-field TEM. The micrograph and corresponding histogram indicate an average nanoparticle size of 3.0 ± 0.6 nm. This value is likely significantly overstated due to the poor contrast of the particles even in dark-field mode. As mentioned earlier, it is difficult to image nanoparticles within the titania matrix that have sizes <1.5 nm, and therefore the histograms shown in Figure 4 are likely biased toward larger particle sizes. Nevertheless, the Pd nanoparticles agglomerate less than the corresponding Au nanoparticles after complete removal of the dendrimer template (4.4 ± 0.8 and 3.0 ± 0.6 nm for Au and Pd, respectively).

Effective heterogeneous catalyst supports must have high surface areas, as well as a significant degree of meso- and macroporosity, to allow for the ingress and egress of reactants and products.[52] Several groups have previously shown that PAMAM and PPI dendrimers can be used as templates for the synthesis of disordered mesoporous silica materials.[30−35] Therefore, we anticipated that it would be possible for DENs to also act as templates to control porosity in the titania composites following calcination. Figure 5a shows N_2 adsorption/desorption plots for the titania/G4-$NH_2(Pd_{55})$ composite before and after calcination at 500 °C for 3 h, as well as a titania control (no dendrimer present) prepared by hydrolysis and condensation of $Ti(O^iPr)_4$ and calcined at 500 °C. Before calcination, the titania/G4-$NH_2(Pd_{55})$ composite displayed a type III isotherm, which is typical of a macroporous material, and had a BET surface area of 34.0 m^2/g.[41] After calcination, the composite revealed a significant hysteresis at intermediate partial pressures, which is typical of mesoporous materials, and the BET surface area increased to 50.2 m^2/g. In contrast, the titania-only control sample had a surface area of 11.7 m^2/g and displayed a typical type III isotherm indicating macroporosity. The increase in surface area upon calcination of the composite is likely a consequence of the mesoporosity introduced by the dendrimer template.

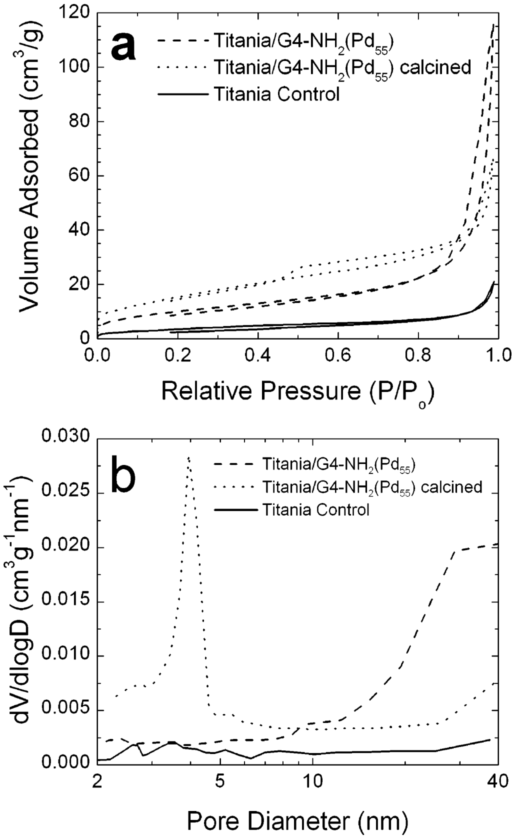

Figure 5. (a) N_2 adsorption/desorption isotherms for (a) titania/G4-$NH_2(Pd_{55})$ composites before and after calcination at 500 °C for 3 h in flowing air, and a titania control also calcined at 500 °C; and (b) BJH pore-size distributions for the same composites.

The total pore volume of the titania/G4-$NH_2(Pd_{55})$ composite decreases from 0.18 to 0.10 cm^3/g upon calcination at 500 °C. This is probably due to loss of macroporosity arising from crystallization of the titania matrix upon calcination. Indeed, powder X-ray diffraction indicates that the composites are amorphous prior to calcination, but at least partially convert to the crystalline anatase phase after calcination at 500 °C (Supporting Information).[53]

Figure 5b shows the calculated BJH pore-size distributions for the three composites compared in Figure 5a.[42] A sharp pore-size distribution centered around 4.0 nm is observed for the calcined titania/G4-$NH_2(Pd_{55})$ composite, but this feature is absent in both the control (no dendrimer) and the titania/G4-$NH_2(Pd_{55})$ composite prior to calcination. The average pore size of 4.0 nm in the calcined titania/G4-$NH_2(Pd_{55})$ composite material provides strong evidence that the imprint of the G4-NH_2 dendrimer remains in the titania after calcination, because the solution-phase diameter of G4-NH_2 dendrimer is ~4.5 nm.[1]

Summary and Conclusions

We have compared two approaches for immobilizing Au and Pd nanoparticles onto titania substrates. In both cases, the precursor nanoparticles are encapsulated within dendrimers. The first route involves the deposition of Au DENs onto a commercial P25 Degussa support, followed by calcination at 500 °C. Using this approach, a 4-fold increase in nanoparticle size is observed following calcination. The second route in-

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volves incorporation of Au and Pd DENs into an amorphous titania network followed by hydrolysis and condensation of the alkoxide. In this case, there is only a 40% increase in size for the Au nanoparticles following calcination at 500 °C and a 80% increase in size for the Pd nanoparticles. In addition, the dendrimer template controls the porosity of the titania. Forthcoming reports will focus on the relationship between the structure of these composite materials and their catalytic function.

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Supporting Information Available: Thermogravimetric analysis, ICP-MS analysis, and powder X-ray diffraction spectra of titania/G4-NH_2(Au_{55}) and titania/G4-NH_2(Pd_{55}) composite materials (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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