

Bimetallic Palladium–Platinum Dendrimer-Encapsulated Catalysts

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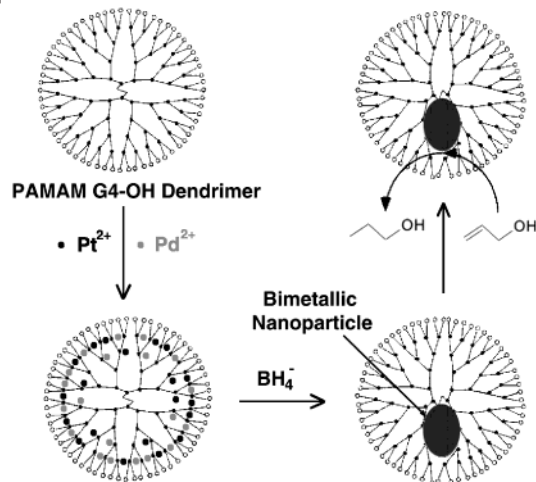
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We report the synthesis, characterization, and catalytic activity of bimetallic Pd–Pt dendrimer-encapsulated catalysts (DECs).^{1,2} These materials are prepared by co-complexing different ratios of palladium and platinum salts with the interior tertiary amines of hydroxyl-terminated polyamidoamine (PAMAM) dendrimers (Scheme 1). Chemical reduction of these composites yields stable, fairly monodisperse, water-soluble bimetallic DECs having sizes on the order of 1.9 ± 0.4 nm. Evidence that these nanoparticles are bimetallic comes from single-particle X-ray energy dispersive spectroscopy (EDS) and catalysis experiments. The latter indicate that the hydrogenation rate of allyl alcohol is enhanced in the presence of the bimetallic nanoparticles compared to DECs containing only platinum or only palladium nanoparticles. These findings are significant, because at present there are no methods for preparing nearly monodisperse, bimetallic nanoparticles that are catalytically active and soluble in solvents ranging from water to supercritical CO₂.² In addition, dendrimer templates offer the possibility of multistep sequential design of bimetallic catalysts that could allow for the synthesis of a large range of bimetallic architectures.²

We,^{1–3} and others,^{4–6} have previously reported the synthesis and characterization of monometallic palladium and platinum DECs and showed that they can be used as catalysts for hydrogenation, oxygen reduction, and Heck-coupling reactions. Such catalysts can be solubilized in a range of solvents, including fluoros and supercritical fluids.² We also previously described a methodology for preparing Pd–Pt DECs, but it was not possible at that time to unambiguously prove the central claim of the present paper: that individual nanoparticles are bimetallic.² More recently, Chung and Rhee used this same approach to prepare Pd–Pt DECs.⁷ They successfully demonstrated a cooperative catalytic effect, which was attributed to the presence of bimetallic metal nanoparticles, but it was not possible to provide direct evidence for the catalytically active bimetallic phase. The single-particle EDS results described here address this key issue.

We chose to explore the synthesis and characterization of Pd–Pt bimetallics, because other groups have previously shown that this system exhibits synergistic catalytic effects.^{8,9} The synthesis of these materials was carried out using a slight modification of the procedure we previously reported for the synthesis of monometallic palladium and platinum DECs (Scheme 1).² A mixture of K₂PdCl₄ and K₂PtCl₄ was added to a dilute aqueous solution of a fourth-generation, hydroxyl-terminated PAMAM dendrimer (G4-OH). The total-metal-ion-to-dendrimer ratio was fixed at 40:1, and therefore the composites had a stoichiometry of G4-OH[(Pd²⁺)_x(Pt²⁺)_{40-x}] where *x* varies between 0 and 40. The metal ion/G4-OH solutions were stirred for 4 days prior to addition of the reducing agent to ensure complete complexation of the ions with interior tertiary amines. This extended time period is required, because while

Scheme 1. Schematic Diagram Showing the Synthesis of Bimetallic Pd–Pt DECs Utilizing PAMAM G4-OH Dendrimers as Templates



PdCl₄²⁻ is very quickly complexed with the dendrimer, PtCl₄²⁻ requires several days to completely react. A 20-fold excess of BH₄⁻ was used to reduce G4-OH[(Pd²⁺)_x(Pt²⁺)_{40-x}] to G4-OH[(Pd)_x(Pt)_{40-x}], which causes the color of the solution to change from pale yellow to dark brown. The resulting bimetallic DECs were stable in solution (no aggregation or color change) for up to 6 months.

UV–vis spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to examine G4-OH[(Pd²⁺)_x(Pt²⁺)_{40-x}] and G4-OH[(Pd)_x(Pt)_{40-x}]. Prior to reduction, strong ligand-to-metal charge-transfer (LMCT) bands, corresponding to palladium and platinum ions coordinated to the interior tertiary amines of the dendrimer, are observed at 224 and 250 nm, respectively (see Supporting Information). These positions are identical to the LMCT bands observed for monometallic composites.² After reduction, a monotonically increasing absorption, arising from the interband transition, indicates formation of zerovalent metal particles.¹⁰ XPS analysis following reduction indicates that the palladium salt is completely reduced, while the platinum salt is nearly completely reduced: the palladium 3d_{5/2} peak shifts from 338.2 to 336.1 eV upon reduction, and a shift from 72.8 to 71.3 eV was found for the platinum 4f_{7/2} peak. These XPS results are very similar to those found for monometallic DECs.

Bright-field, high-resolution transmission electron microscopy (HRTEM) of G4-OH[(Pd)₃₀(Pt)₁₀] indicates that the particles are 1.9 ± 0.4 nm in diameter (Figure 1a). Figure 1b shows these same DECs in high-angular annular dark-field mode. Here, the particles were found to be 2.1 ± 0.6 nm in diameter. EDS analysis of the entire area shown in Figure 1b indicates that the atom %'s of Pd and Pt are 74 and 26%, respectively. These values agree very well with the mol %'s of PdCl₄²⁻ and PtCl₄²⁻ used in the original

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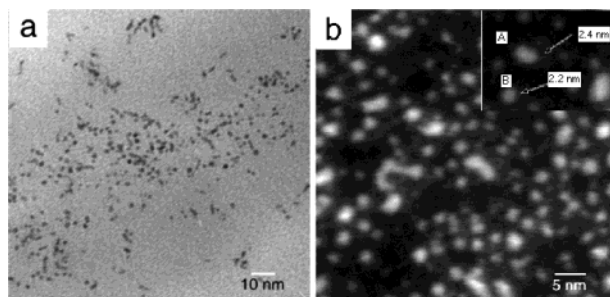


Figure 1. TEM images of bimetallic G4-OH[(Pd)₃₀(Pt)₁₀] particles. (a) bright-field HRTEM. (b) high-angular annular dark-field mode STEM. The inset is a high-resolution image of two individual particles that were analyzed by EDS.

synthesis mixture (75 and 25%, respectively). The inset of Figure 1b shows a region of the sample in which the nanoparticle density on the TEM grid was low enough to allow EDS analysis of individual nanoparticles. Particle A has an elemental composition of 73% Pd and 27% Pt, and particle B has a composition of 63% Pd and 37% Pt. These single-particle EDS measurements unambiguously confirm that bimetallic nanoparticles (rather than physical mixtures of monometallic nanoparticles) are present within the dendrimer. The difference in the atom %'s of Pd and Pt within individual nanoparticles is mainly a consequence of the low X-ray count rates arising from the small number of atoms within each particle.

In some cases, hydrogenation rates can provide information about the atomic composition of noble metal catalysts.^{9,11} Accordingly, we measured turnover frequencies (TOFs) for the hydrogenation of allyl alcohol in water using G4-OH[(Pd)_x(Pt)_{40-x}] DECAs as a function of the atomic ratio of Pd and Pt. Briefly, 5 mL of a 25 μ M aqueous G4-OH[(Pd)_x(Pt)_{40-x}] DEC solution was added to 45 mL of deionized water in a Schlenk flask, and the solution was stirred under H₂ for 1 h prior to the addition of 10 mmol of allyl alcohol. The progress of the reaction was followed by monitoring the change in the H₂ volume as a function of time. TOFs were determined from the slope of plots of turnover mol (H₂(mol Pd + Pt)⁻¹) vs time. Nine different G4-OH[(Pd)_x(Pt)_{40-x}] DECAs were examined over the range $x = 0-40$, and a plot of TOF as a function of the mol % PdCl₄²⁻ used to prepare the DECAs is shown in Figure 2. Each data point represents the average of two measurements; replicate measurements were within ± 10 mol H₂(mol Pd + Pt)⁻¹ h⁻¹. DECAs containing only Pt yielded the lowest TOF (50 mol H₂(mol Pd + Pt)⁻¹ h⁻¹), while Pd-rich DECAs (65–90%) gave TOFs larger than those obtained from Pd-only DECAs (TOF = 193 mol H₂(mol Pd + Pt)⁻¹ h⁻¹). The values obtained for the monometallic Pd- and Pt-containing DECAs agree with those we have previously reported for the hydrogenation of allyl alcohol in water.^{2,3} Importantly, physical mixtures of Pd and Pt DECAs did not show enhanced TOFs (Figure 2). The higher TOFs observed for Pd-rich DECAs are thought to arise from a synergistic electronic (ligand) effect.^{8,9,11} Thus, the observation of enhanced TOFs provides additional evidence for our central claim that these materials are bimetallic.

To summarize, EDS analysis of individual nanoparticles confirms that these DECAs contain both Pd and Pt atoms and have ap-

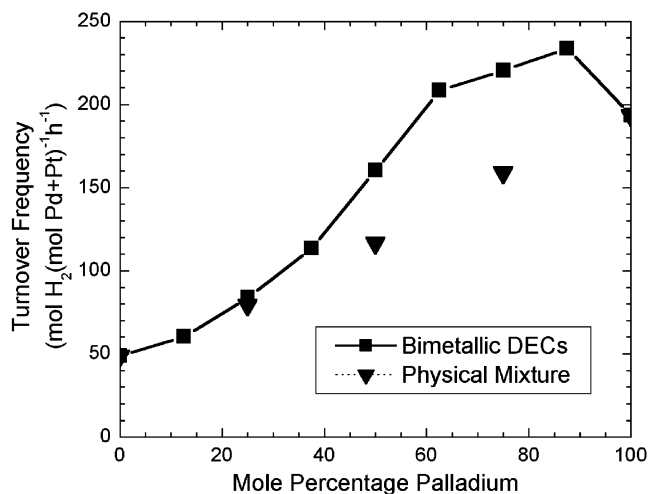


Figure 2. Plot of turnover frequency (TOF) vs the mol % of PdCl₄²⁻ used to prepare the DECAs. The filled squares indicate the results for bimetallic nanoparticles and the filled triangles are for physical mixtures of dendrimers containing either only Pt or only Pd. Reaction conditions: [allyl alcohol] = 200 mM, [Pd + Pt] = 0.095 mM, substrate:metal ratio = 2100:1, $T = 19$ °C.

proximately the same atomic composition as the ratio of the metal salts in the original reaction mixture. Hydrogenation of allyl alcohol with bimetallic DECAs shows a definitive synergistic effect at high Pd loadings. These results are important because they provide a means for preparing nearly monodisperse bimetallic metal catalysts under easily controlled conditions. Forthcoming reports will describe bimetallic nanoparticles prepared from different combinations of metals and having controlled (core–shell) architectures.

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Supporting Information Available: UV–vis data for Pd, Pt, and bimetallic DECAs before and after reduction (PDF). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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