

## Synthesis of Mono- and Bimetallic Nanoparticle Catalysts Utilizing Solid Phase Dendrimer Templates

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### Introduction

Starburst polyamidoamine (PAMAM) dendrimers are a specific class of nearly monodisperse, hyperbranched polymers that can be employed in nanoparticle syntheses.<sup>1</sup> PAMAM dendrimers, which have open interiors and porous peripheries, can be used to both template and stabilize a wide variety of mono- and bimetallic metal nanoparticles (NPs). In this synthetic scheme, metal precursors are first bound to the interior amine groups of the PAMAM dendrimer; addition of a reducing agent prepares particles that are essentially trapped within the dendrimer interior. The dendrimer mediated synthesis allows for greatly increased control over particle size and composition. For bimetallic particles, well-mixed and core-shell particles on the order of 2 nm in diameter can be selectively prepared.

Solution syntheses of dendrimer encapsulated nanoparticles (DENs) have been well studied for a variety of metals and metal combinations. DENs are active homogeneous catalysts, with the dendrimer imparting size and shape selectivity in hydrogenation reactions, as well as solubility in either aqueous or organic solvents.<sup>1</sup> However, as with any homogeneous system, catalyst separation is problematic. Additionally, dendrimer mediated syntheses often require aqueous solvents for nanoparticle preparation or extraction, which is problematic for oxidizable metals.

To address these issues, we developed synthetic methodologies for anchoring PAMAM dendrimers to solid supports. The anchored dendrimers can be used as precursors for heterogenized DEN catalysts. Additionally, anchored dendrimers can be employed as synthetic NP templates, allowing for rapid PAMAM dendrimer recycling.

### Materials and Methods

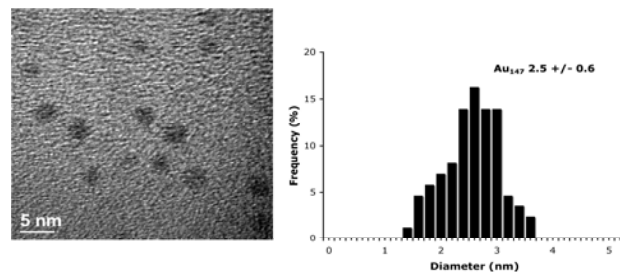
Amine terminated generation 5 PAMAM dendrimers (G5NH<sub>2</sub>) were anchored to polystyrene resin beads (EMD Biosciences) and alkylated with 1,2-epoxydodecane (Aldrich) to produce G5C12<sub>anch</sub>. Anchoring on templated silica was accomplished similarly, first treating the silica with anhydride terminated silanes purchased from GelEst. Dendrimer encapsulated nanoparticles (DENs) were prepared by adapting literature syntheses. Metal salt precursors (HAuCl<sub>4</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, K<sub>2</sub>PtCl<sub>4</sub>), NaBH<sub>4</sub>, and C<sub>10</sub>SH were purchased from Aldrich and used without further purification. SiO<sub>2</sub> (Davisil) and TiO<sub>2</sub> (Degussa p-25) was calcined at 500 °C overnight. SILANE (GelEst) was used as received. TiO<sub>2</sub> supported Au MPCs were activated at 290 °C under flowing H<sub>2</sub>/N<sub>2</sub> (5%) for 16 hours. SiO<sub>2</sub> supported DENs were activated at 290 °C under flowing O<sub>2</sub> for 16 hours.

### Results and Discussion

Amine terminated PAMAM dendrimers were anchored onto anhydride terminated polystyrene resins through a direct reaction in DMF. The surfaces of the anchored dendrimers were then rendered hydrophobic by reacting the remaining (unreacted) primary amines

with 1,2-epoxydodecane producing G5C12<sub>anch</sub>. Solution <sup>1</sup>H NMR and ATR-FTIR spectroscopies were used to follow and confirm the anchoring and alkylation reactions. Spectrophotometric titration of G5C12<sub>anch</sub> with toluene solutions of CoCl<sub>2</sub> showed that the anchored dendrimers bound 150 equivalents of Co<sup>2+</sup>, in good agreement with the value obtained for G5C12 in toluene solution (165 eq.). Control experiments with unmodified resin beads showed no uptake of CoCl<sub>2</sub> or HAuCl<sub>4</sub> over several hours. Based on these results, the dendrimers were successfully anchored on the resin beads and were functionally similar to solution G5C12 PAMAM dendrimers.

Au DENs were prepared by adding HAuCl<sub>4</sub> in EtOH to a toluene slurry of G5C12<sub>anch</sub> followed by reduction with NaBH<sub>4</sub>. Reflectance UV-Visible spectroscopy of the anchored DENs was comparable to solution spectra of the corresponding Au DENs. The Au NPs were extracted from the dendrimer interior by vigorously stirring with decanethiol in toluene. The TEM micrograph and particle size distribution histogram in Figure 1 show that the extracted nanoparticles are slightly larger than those prepared via solution syntheses, but are still small and relatively monodisperse. Further, after a brief NaCN, a second batch of NPs with similar particle sizes and distribution were prepared, in comparable yield.



**Figure 1.** TEM image and corresponding particle size histogram (100 particles) for (C<sub>10</sub>SH) Au<sub>147</sub> MPCs synthesized from G5C12<sub>anch</sub>.

The extracted NPs were deposited onto P-25 titania and the alkyl thiol was thermally removed. The resulting materials were active CO oxidation catalysts, and were comparable to the World Gold Council test catalysts. The solid phase protocol was extended to the NiAu, CoAu, and CuAu bimetallic systems. The synthesis and extraction of these bimetallic DENs in nonaqueous solution (toluene) was investigated and shown to behave similarly to the Au monometallic system.

### Significance

This new preparative method allows for the facile synthesis and extraction of NPs (both mono and bimetallic) in nonaqueous solvents. This provides a new opportunity for the synthesis and study of NP catalysts made from metals that are easily oxidizable.

### References

1. Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. *J. Phys. Chem. B*, 109, 692 (2005).