

Solution Synthesis of PAMAM-Stabilized Platinum: Evidence for Platinum-Crosslinked Dendrimers Instead of Zero-Valent Nanoparticles

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Abstract

Several research groups, including our own, use poly(amidoamine) (or PAMAM) dendrimers to synthesize noble metal nanoparticles in aqueous solutions. Previous papers claim that PAMAM serves as a template: in principle, a specified number of metal ion precursor molecules complex with each dendrimer molecule in solution, followed by chemical reduction to produce a zero-valent metal nanoparticle composed of the same number of metal atoms. If true, this synthesis route offers the possibility of unprecedented control over the size, shape, and composition of metal nanoparticles. Our work seeks to prove or disprove this templating hypothesis.

We have studied the complexation of Pt precursor (K_2PtCl_4) with hydroxyl-terminated PAMAM using UV-visible spectrophotometry, atomic absorption spectroscopy, ion chromatography, and ^{195}Pt NMR. The results show that complexation of $(PtCl_4)^{-2}$ does not proceed to completion. The extent of complexation depends on precursor concentration and complexation time. Some of the non-complexed Pt can be removed through dialysis.

Next, we focus on results for the reduction of the Pt-PAMAM complex by either $NaBH_4$ or H_2 gas. The final products were characterized by UV-vis, HRTEM, non-contact AFM, XPS, and liquid-phase EXAFS. Starting with the "as-prepared" complex, reduction with $NaBH_4$ leads to a product we describe as Pt-crosslinked PAMAM: HRTEM shows evidence of Pt atoms dispersed throughout each dendrimer; AFM shows two populations of particles, both with average vertical dimensions greater than expected for close-packed metallic Pt nanoparticles; and XPS shows Pt still in the +2 valence state. For reduction with H_2 gas, HRTEM shows additional colloidal Pt particles, too large to be encapsulated, and manifesting lattice fringes; and XPS shows a mixture of +2 and 0 valence states for Pt. The colloidal Pt particles arise from reduction of non-complexed Pt in solution. The colloidal Pt apparently catalyzes further reduction of PAMAM-complexed Pt upon prolonged reduction with H_2 gas.

Dialysis of the complex prior to reduction removes the non-complexed Pt. Upon reduction with either $NaBH_4$ or H_2 gas, HRTEM and AFM show only a single population of particles, but XPS indicates that Pt is still in the +2 valence state. UV-vis spectra do not show the long absorbance tail that we associate with colloidal Pt nanoparticles. EXAFS shows Pt is mostly coordinated with C, N, and O, but not other Pt atoms. All of these results suggest that the product is Pt-crosslinked PAMAM, not PAMAM-encapsulated, zero-valent Pt nanoparticles. Prolonged reduction with H_2 gas eventually leads to arrested precipitation of colloidal Pt nanoparticles, but onset is delayed considerably due to the removal (by pre-dialysis) of the non-complexed Pt.