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Homogeneous Hydrogenation Catalysis with Monodisperse, Dendrimer-Encapsulated Pd and Pt Nanoparticles**

Mingqi Zhao and Richard M. Crooks*

In this report we show that composite materials that consist of noble metal nanoparticles stabilized within dendrimer interiors are suitable for use as homogeneous hydrogenation catalysts. These interesting new materials are prepared by sorbing Pd^{II} or Pt^{II} ions into hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimers (Gn-OH, where Gn represents the *n*th generation) where they complex with interior amine groups. Subsequent chemical reduction of the metal ions with BH₄⁻ yields dendrimer-encapsulated metal nanoparticles that contain the same number of atoms as were preloaded into the dendrimer initially. The resulting composites are soluble in water and stable, either dry or solvated, for at least several months. Thus, the dendrimer acts as both a template for the preparation of monodisperse nanoparticles and a porous stabilizer. Dendrimer-encapsulated Pd clusters exhibit high catalytic activity for the hydrogenation of alkenes in water. Importantly, the catalytic activity can be controlled by adjusting the size (generation) of the dendrimer; that is, the dendrimer acts as a "nanofilter" with a synthetically controllable mesh.

Stabilized noble metal nanoparticles have been used as catalysts and photocatalysts in solutions for many years.^[1–5] The activity of these materials is controlled by their size, crystal structure, and the nature of the stabilizer. Synthetic routes to soluble metal nanoparticles include chemical or electrochemical reduction of metal salts in the presence of stabilizers.^[2, 3, 6] The purpose of the stabilizer is to control the particle size and prevent agglomeration, but strong adsorption of the stabilizers on the active sites may result in a loss of catalytic activity. Ideally, a metal-particle catalyst should be surrounded by a nanofilter or weak adsorbents that permit passage of the substrate and product of the catalytic reaction, but which prevent agglomeration. The dendrimer plays just this role in the experiments described here.

Our approach for the preparation of dendrimer-encapsulated Pd and Pt metal particles is similar to that we,^[7] and later others,^[8] reported previously for Cu. As indicated above, the experiment is quite simple: first, a predetermined quantity of metal ions are extracted into the interior of a Gn-OH dendrimer, and second the ions are chemically reduced with BH4- to yield zerovalent metal particles. Figure 1 shows absorption spectra of dendrimer-encapsulated Pd^{II} and Pt^{II}. For example, a 2mm solution of PtCl₄²⁻ has a strong ligand-metal charge-transfer band at $\lambda_{\max}(\varepsilon) = 214$ nm (8000).^[9] After addition of 0.05 mM G4-OH to this solution, the band at 214 nm decreases and shifts to 221 nm and a new band at 249 nm appears.^[10] These changes are a consequence of the encapsulation of metal ions by the dendrimer. After reduction of the composite the spectrum changes significantly: there is now a much higher absorption intensity at low



Figure 1. a) Absorption spectra of solutions containing 2.0 mM K_2PtCl_4 and 2.0 mM $K_2PtCl_4 + 0.05$ mM G4-OH before and after reduction with a fivefold molar excess of NaBH₄. Curves in b) were obtained under the same conditions as those in a) except 2.0 mM Na₂PdCl₄ was used in place of the K_2PtCl_4 . The optical path length for all UV/Vis measurements was 0.1 cm.

energy, which results from the interband transition of the encapsulated zero-valent metal particles.^[4, 11] Similar spectroscopic results are observed for the G4-OH/Pd^{II} composites. The bands at 217 and 276 nm that result from $PdCl_4^{2-}$

disappear after the addition of G4-OH and new bands are evident at 225 and 300 nm.^[10] A new interband transition is observed after reduction.^[6]

Microscopy confirms that the chemical reduction of PtII or Pd^{II} encapsulated within G4-OH (G4-OH(Pt^{II})_n and $G4-OH(Pd^{II})_n$, respectively) yields intradendrimer metal nanoparticles $(G4-OH(Pt_n))$ and G4-OH(Pd_n), respectively).^[12] High-resolution transmission electron microscopy (HRTEM) images (Figure 2) clearly show that dendrimer-encapsulated particles are quite monodisperse and that their shape is roughly spherical. The diameters of the metal particles for G4- $OH(Pt_{40})$, G4- $OH(Pt_{60})$, and G4-OH(Pd₄₀) particles are $1.4 \pm 0.2, 1.6 \pm 0.2, \text{ and } 1.3 \pm$ 0.3 nm, respectively, which are slightly larger than the theoretical values of 1.1, 1.2, and 1.1, respectively, which are calculated using the as-



Figure 2. HRTEM images of G4-OH(Pt_{40}), G4-OH(Pt_{60}), and G4-OH(Pd_{40}), which show the monodisperse size and shape distribution.

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sumption that the particles are contained within the smallest sphere that circumscribes the Pt and Pd crystals with facecentered cubic packing. We confirmed the elemental composition of the nanoparticles with energy-dispersive spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) also provides elemental compositional information and oxidation states of Gn-OH(M^{II}) and Gn-OH(M). The XPS data indicate the presence of carbon and nitrogen from the dendrimer and that the oxidation state of the metals changes after reduction of Gn-OH(M^{II})_m^[13]

Ligand- or polymer-stabilized colloidal noble metals have been used for many years as catalysts for the hydrogenation of unsaturated organic molecules. Additionally, there is a special interest in the development of methodologies for catalyzing organic reactions in aqueous solutions.^[14] Accordingly, we investigated the catalytic hydrogenation of alkenes in aqueous solutions with these nanocomposite materials. The hydrogenation activities of dendrimer-encapsulated Pt and Pd nanoparticles for a simple alkene (allyl alcohol) and an electron-deficient alkene (N-isopropyl acrylamide) in water are given in Table 1. The product of these hydrogenation reactions was confirmed by GC and NMR spectroscopy. G4-OH(Pd₄₀) shows a high catalytic activity for the hydrogenation of both alkenes, while G4-OH(Pt₄₀) shows a reasonable rate for these reduction reactions. For example, the turnover frequencies (TOFs, mol of H₂ per mol of metal atoms per hour) of G4-OH(Pd_{40}) for the hydrogenation of N-isopropyl acrylamide and for allyl alcohol hydrogenation compare very favorable to water-soluble, polymer-bound Rh^I catalysts,^[15, 16] and are comparable to PVP-stabilized, colloidal Pd dispersions in water (colloid size: 4-60 nm, reaction temperature: 37 °C).^[17] The key result is that dendrimer-encapsulated Pt or Pd particles are accessible to substrates in solution and vield reasonable TOFs for hydrogenation reactions.

Importantly, the hydrogenation reaction rate can be controlled by using dendrimers of different generations. Dendrimer porosity is a function of generation: higher generation materials are less porous and thus less likely to admit substrates to interior metal nanoparticles.^[18] That is, the dendrimer acts as a selective nanoscopic filter that controls the catalytic activity of the composite (Figure 3). For example, the TOFs for G6-OH(Pd₄₀) and G8-OH(Pd₄₀) are only 10%

Table 1. Hydrogenation activity of dendrimer-encapsulated Pt_{40} and Pd_{40} nanoparticles in water. $^{[a]}$

Catalyst	TOF ^[b]	
	<i>N</i> -isopropyl acrylamide	allyl alcohol
G4-OH(Pd)	372	218
G6-OH(Pd)	42	201
G8-OH(Pd)	17	134
G4-OH(Pt)	57	25
G6-OH(Pt)	30	-

[a] Hydrogenation reactions were carried out at 20 ± 2 °C with 2×10^{-4} M Pd⁰ or Pt⁰ composite catalysts. The turnover frequency (TOF) was calculated on the basis of H₂ uptake. The product of the hydrogenation reaction of allyl alcohol or *N*-isopropyl acrylamide was confirmed by GC or NMR spectroscopy. [b] Measured as mol of H₂ per mol of metal atoms per hour.



Figure 3. The hydrogenation rate can be controlled by using dendrimers of different generation: Pd or Pt clusters present within dendrimers of lower generation exhibit the highest catalytic activity. The sterically crowded terminal groups of higher generation dendrimers hinder substrate penetration.

and 5%, respectively, of that for G4-OH(Pd_{40}) with *N*isopropyl acrylamide. This result shows that it is possible to control reaction rates and do selective catalysis by adjusting the "mesh" of the dendrimer "nanofilter".

Finally, dendrimer-encapsulated metal nanoparticles are stable before, during, and after hydrogenation reactions. For example, they do not aggregate for up to four months in water. Additionally they can be isolated as a black powder and redissolved in water to yield a stable, dark-brown solution that is identical to that present before drying. After hydrogenation reactions were run for up to three hours, solutions of G4-OH(Pt₄₀) and G4-OH(Pd₄₀) remained clear and there was no evidence for agglomeration, and also no changes were observed in the UV/Vis or IR spectra.

In summary, we have prepared nearly monodisperse metal particles for catalyst applications that employ dendrimers as both template and stabilizer. Dendrimer-encapsulated Pd nanoparticles show high catalytic activity for the hydrogenation of alkenes in aqueous solution. Dendrimer-encapsulated Pt or Pd particles are quite stable, yet the surface of the particles is accessible to substrates in solution. Importantly, the hydrogenation rate can be controlled by using dendrimers with different generations.

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- [10] The intensity of the absorbance at 249 nm is proportional to the number of Pt^{II} ions in the dendrimer over the range 0–60. Titration results also show by plots of the absorbance at 225 or 300 nm against the number of Pd^{II} in the dendrimer that G4-OH can sorb at least 40 Pd^{II} ions.
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Efficient, Reversible Redox-Switching of Molecular First Hyperpolarizabilities in Ruthenium(II) Complexes Possessing Large Quadratic Optical Nonlinearities**

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Two research areas attracting great interest within the emerging field of "molecular electronics/photonics" are nonlinear optical (NLO) materials^[1] and molecular switches.^[2] It is anticipated that the former will be exploited in optoelectronic technologies, whilst the latter will provide the basis for a range of molecular-scale devices. The fusion of these two

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At the molecular level, quadratic NLO effects are governed by first hyperpolarizabilities, β , which can lead to macroscopic phenomena such as second harmonic generation (SHG). Photoswitching of SHG has been observed recently in solutions of bacteriorhodopsin^[3] and in crystals of *N*-salicylidene-4-bromoaniline.^[4] In other studies focusing on molecular properties, a bis(thienyl)ethene was found to exhibit a change in β on photoisomerization,^[5] and it has been suggested that photoinduced proton-transfer may alter β in nitrobenzyl pyridines.^[7]

Transition metal organometallic and coordination complexes are an important class of NLO molecules,^[1d, 8] for which β data is becoming increasingly available,^[8, 9] largely due to the introduction of the versatile hyper-Rayleigh scattering (HRS) technique.^[10] The presence of redox-active metal centers provides extensive opportunities for modulation of NLO responses, but this has only been addressed previously in SHG photoswitching from $[Ru^{II}(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) derivatives in Langmuir-Blodgett (L-B) films.^[6] In the latter study, a 30% decrease in SHG intensity was ascribed to the change in β upon metal-to-ligand charge-transfer (MLCT) excitation. However, although it has been reported that such octupolar complexes exhibit extremely large β values,^[9b] it now appears that these claims were exaggerated.^[11] Furthermore, only modest β changes occur upon oxidation of $[Ru^{II}(bpy)_3]^{2+}$.^[12]

We have recently discovered that ruthenium(II) ammine complexes of 4,4'-bipyridinium ligands exhibit large, tunable β values which are associated with intense, low-energy MLCT excitations.^[13] The electron-rich, d⁶ centers [Ru^{II}(NH₃)₅]²⁺ or *trans*-[Ru^{II}(NH₃)₄(L)]²⁺ (L = 4-dimethylaminopyridine or 1-methylimidazole) behave as powerful π donors in conjunction with the ligands *N*-R-4,4'-bipyridinium (R = methyl (MeQ⁺), phenyl (PhQ⁺), or 4-acetylphenyl (4-AcPhQ⁺)). These complexes are ideally suited towards redox-switching of NLO responses because although air-stable, they feature completely reversible, one-electron Ru^{III/II} couples at readily accessible potentials (0.46–0.48 V vs SCE for the PF₆⁻ salts in acetonitrile (MeCN)).^[13]

We have previously reported β data for [Ru^{II}-(NH₃)₅(L)](PF₆)₃ (L = MeQ⁺ (1), PhQ⁺ (2), 4-AcPhQ⁺ (3))



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