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FEATURE ARTICLE

Synthesis, Characterization, and Applications of Dendrimer-Encapsulated Nanoparticles

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In this article we describe the synthesis, characterization, and applications of dendrimer-encapsulated nanoparticles (DENs). These materials are synthesized by a template approach in which metal ions are extracted into the interior of dendrimers and then subsequently chemically reduced to yield nearly size-monodisperse particles having dimensions of less than 3 nm. Monometallic, bimetallic (including core/shell), and semiconductor nanoparticles have been prepared by this route. The dendrimer component of these composites serves not only as a template for preparing the nanoparticle replica but also to stabilize the nanoparticle, makes it possible to tune solubility, and provides a means for immobilization of the nanoparticle on solid supports. These materials have a number of potential applications, but the focus here is on catalysis. Homogeneous catalytic reactions, including hydrogenations, Heck coupling, and Suzuki reactions, in water, organic solvents, biphasic fluorous/organic solvents, and liquid and supercritical CO_2 are discussed. In many cases it is easy to recycle catalytic DENs. DENs can also be immobilized on supports, such as silica and titania, and used for heterogeneous catalysis. Bimetallic DENs are shown to have particularly interesting catalytic properties. In addition to a discussion of current progress in this field, a number of intriguing questions related to the properties and potential applications of these materials are examined.

1. Introduction

This article summarizes the synthesis, characterization, and applications of dendrimer-encapsulated nanoparticles (DENs), which were first reported by our group in 1998.[1−4] Briefly, these nanocomposite materials are synthesized by complexing metal ions within dendrimers and then reducing the composites to yield zerovalent DENs (Scheme 1). DENs are interesting, because they combine the desirable physical and chemical properties of the encapsulated nanoparticles with the tunable solubility and surface reactivity of the dendrimer template. Furthermore, the nanoparticle size, composition, and structure can be controlled by taking advantage of the dendrimer structure and the means by which the metal ions are introduced into the dendrimer. DENs have a number of potential applications, but here emphasis is placed on their use as catalysts.

Many new classes of dendrimers have been reported since the first synthesis of poly(propyleneimine) (PPI) dendrimers by Vögtle et al. in 1978.[5] Examples include Tomalia's Starburst poly(amidoamine) (PAMAM) dendrimers,[6,7] the arborols of Newkome and co-workers,[8] and the polyether dendrimers described by Fréchet et al.[9] Dendrimers have attracted attention because of their well-defined structures and chemical versatility. Specifically, the structure and chemical properties of dendrimers can be logically controlled by modification of the core, the type and number of repetitive branch units, and the terminal functional groups. Crowding of surface functional groups on higher-generation dendrimers leads to a close-packed spherical periphery surrounding interior cavities. The synthesis and a two-dimensional representation of the structures of generation-four amine-terminated (G4-NH_2) and hydroxyl-terminated (G4-OH) PAMAM dendrimers are shown in Figure 1.[3,10] G4-NH_2 and G4-OH dendrimers are approximately 4.5 nm in diameter and contain 62 interior tertiary amine groups and 64 peripheral functional groups.

SCHEME 1

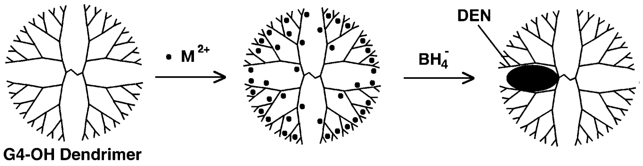

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Table 1 shows that the physical characteristics of PAMAM dendrimers are a function of generation.[3] For example, dendrimer diameter increases roughly linearly with generation, while the number of functional groups on the periphery increases exponentially. An important consequence of this is that the distance between functional groups on the dendrimer surface, and consequently the flexibility of peripheral groups, decreases with generation. For example, an amine group on the surface of G4, G6, and G8 PAMAM dendrimers occupies an area of 4.0, 2.2, and 1.2 nm^2, respectively.[11] We have illustrated the importance of this dendrimer property by showing that the distance between peripheral groups can be used to control access of small molecules to encapsulated catalysts. Another important property of amine-functionalized dendrimers relates to the relative basicity of the interior tertiary amines and the primary

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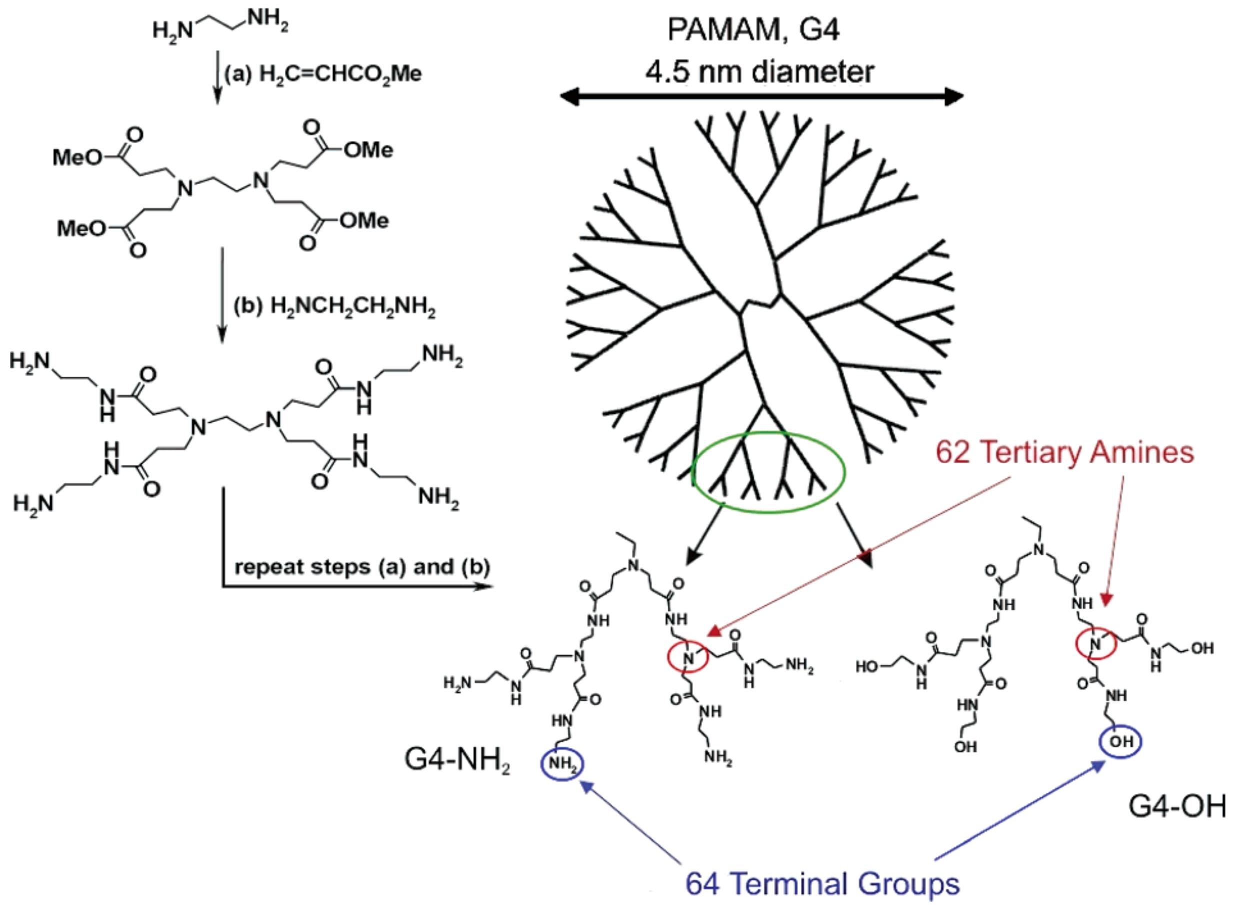

Figure 1. Representation of synthesis and structures of fourth-generation, amine-terminated (G4-NH$_2$) and hydroxyl-terminated (G4-OH) PAMAM dendrimers.

TABLE 1: Physical Characteristics of PAMAM Dendrimers

generation	number of surface groups	number of tertiary amines	molecular weight[a]	diameter (nm)[b]
0	4	2	517	1.5
2	16	14	3,256	2.9
4	64	62	14,215	4.5
6	256	254	58,048	6.7
8	1024	1022	233,383	9.7
10	4096	4094	934,720	13.5

[a] Molecular weight is based on defect-free, ideal-structure, amine-terminated dendrimers. [b] Molecular dimensions determined by size-exclusion chromatography.

amines on the dendrimer surface. Specifically, the peripheral amines are more basic than those in the interior (pK_a = 9.23 and 6.30, respectively). This makes it possible to selectively protonate just the peripheral amines, which can be important for the synthesis of DENs within amine-terminated dendrimers.[12,13]

Depending on the reagent used for the final amidation reaction, the dendrimer surface can be terminated with either reactive groups, such as amines or carboxylic acids, or less reactive groups, such as hydroxyls and hydrocarbon chains. For example, hydroxyl-terminated PAMAM dendrimers are synthesized by substituting ethanolamine for ethylenediamine in the last step of the PAMAM dendrimer synthesis. A consequence of the presence of polar tertiary amines in the interior, along with the ability to tune the exterior functional groups, is a means for controlling the dielectric gradient across the dendrimer. This property can be used to selectively concentrate metal ions or other small molecules (for example, catalytic substrates) within the dendrimer.[14,15]

While a number of dendrimer structures have been reported that have metals at their core, at branch points, and attached to peripheral functional groups,[4,16] we have focused on the synthesis of metal nanoparticles housed within the interior void spaces.[1−4,17] In the mid-1990s several groups recognized that both the interior tertiary amines and the exterior functional groups of PAMAM and PPI dendrimers could complex metal ions, such as Cu^{2+}, Co^{2+}, Pt^{2+}, and Pd^{2+}.[1,17−21] The driving force for encapsulation of metal ions within dendrimers is usually based on covalent bond formation, electrostatic interactions, complexation reactions, or a combination thereof. Metal ions can be complexed exclusively within the interior of dendrimers by functionalizing the periphery with noncomplexing entities, such as hydroxyl groups, or by adjusting the solution pH to selectively protonate peripheral amine or acid groups.[12] Once the metal ions are encapsulated, we,[1−4,17] and others,[22−24] have demonstrated that they can be reduced to yield DENs (Scheme 1).

Monodisperse nanoparticles have potential applications in fields such as catalysis, optoelectronics, magnetism, and chemical sensing. Chemical routes to stable metal nanoparticles typically involve the reduction of metal salts and capping of the resulting nanoparticles with polymers or surfactants to stop growth and prevent agglomeration.[25,26] Alternatively, templates can be used to synthesize nanoparticles having well-defined sizes and shapes: examples of templates include porous alumina and track-etched membranes,[27] and reverse micelles.[28,29] These methods generally yield nanoparticles that are passivated by steric or electrostatic stabilizers, which limits their use for applications in fields such as catalysis. That is, one cannot have catalytic activity without access to surface sites, but removal of stabilizers to allow such access usually leads to aggregation. DENs address this issue, because the dendrimer allows for kinetic (templated) control of the nanoparticle size (and possibly shape), but it also prevents aggregation of the nanoparticles without passivating all of the active sites on the nanoparticle surface.

There are three other potentially useful properties of DENs. First, it is easy to control the chemical composition of the peripheral groups on the dendrimer,[30] and this provides a means for attaching DENs to supports and for solubilizing them in nearly any solvent.[12,15,31,32] Second, we have shown that the dendrimer periphery can function as a size-and-shape selective molecular filter, thereby providing a means for introducing selectivity to intrinsically nonselective metal catalysts.[2,11] Third, the dendrimer can, in some cases, provide a means for controlling product selectivity.[31] Although we have not made an effort to understand and control this function yet, it will likely prove to be important. One disadvantage of PAMAM-based DENs is the limited thermal stability of PAMAM dendrimers, which undergo retro-Michael addition at temperatures beyond 100 °C. However, PPI dendrimers do not contain internal amido groups and have been shown to be stable at temperatures up to 470 °C,[33] allowing PPI DENs to be used as high-temperature catalysts.[31] Finally, we should point out that although the high cost of PAMAM and PPI dendrimers limits their usefulness as industrial catalysts, both dendrimer families are commercially available.[34]

It is important to distinguish DENs, or *intra*dendrimer-encapsulated nanoparticles, in which the nanoparticle resides within the interior void space of the dendrimer, from *inter*dendrimer-stabilized nanoparticles, in which the nanoparticle surface is stabilized by multiple dendrimers. Evidence for encapsulation of 1−3 nm-diameter nanoparticles within single dendrimers comes from TEM staining studies and small-angle X-ray scattering (SAXS) analysis of DENs.[24] The high degree of DEN size monodispersity, the relationship between particle size and the dendrimer-to-metal-ion ratio used in their preparation,[35] and the selectivity of catalytic DENs for particular substrates are also consistent with the structural model of DENs represented in Scheme 1. All of these points will be expanded upon later.

There have been many reports of dendrimer−metal nanocomposites prepared using amine- or carboxylic acid-terminated dendrimers. These dendrimers typically complex metal ions both on their periphery and in their interior, so that when the composites are reduced they yield mixtures of both inter- and intradendrimer nanoparticles.[36,37] This review focuses on the synthesis and properties of intradendrimer nanoparticles, but there is an extensive literature relating to interdendrimer nanocomposites that will be briefly touched upon later. There are also many reports relating to the catalytic properties of dendrimers having metal ions at their cores, branch points, and on their periphery, but this topic is beyond the scope of the present review and interested readers are directed to the many excellent recent reviews that address this subject.[16,38−42]

2. Synthesis

The nomenclature used to describe the dendrimers and DENs referred to in this paper is as follows. Dendrimers loaded with metal ions are referred to as Gx-R(M^{p+})$_n$, where x is the generation of the PAMAM or PPI dendrimer, R is the terminal group of the dendrimer (in most cases R = −OH or −NH_2), and M^{p+} and n refer to the type and average number of metal ions complexed to the interior of each dendrimer. After reduction of the metal, the resulting DENs are referred to as Gx-R(M_n) where M_n is the zerovalent metal nanoparticle containing n atoms.

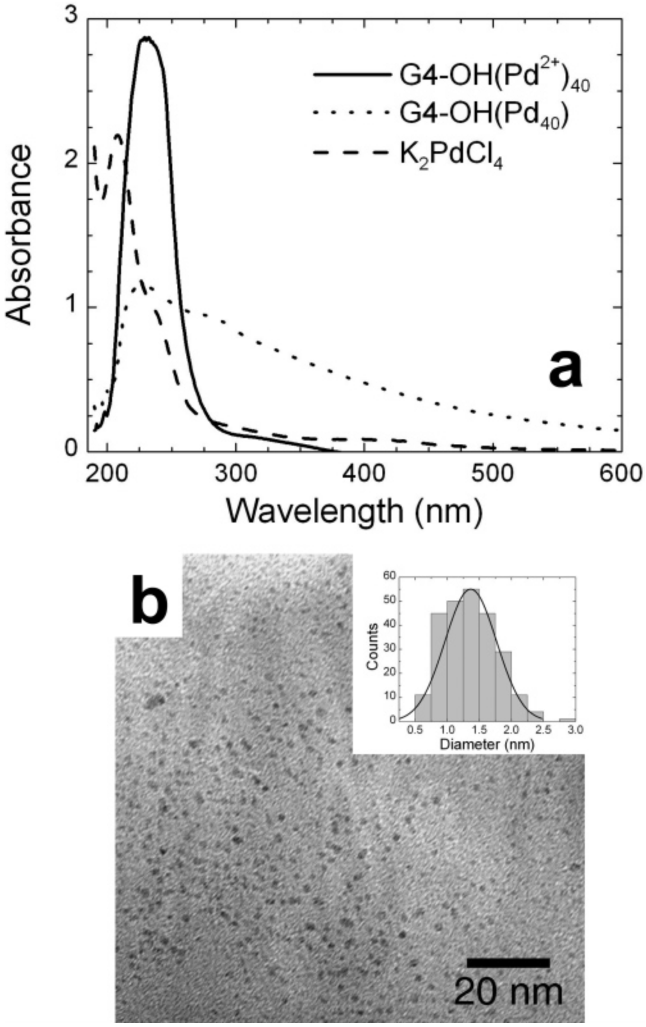

Figure 2. (a) UV−vis spectra of aqueous solutions containing K_2PdCl_4, G4-OH(Pd^{2+})$_{40}$, and G4-OH(Pd_{40}). In each case the [Pd] = 0.5 mM. Dendrimer-only backgrounds were subtracted from the G4-OH-(Pd^{2+})$_{40}$ and G4-OH(Pd_{40}) spectra. (b) HRTEM and particle-size distribution for G4-OH(Pd_{40}) DENs.

Since the first synthesis of dendrimer-encapsulated Cu nanoparticles,[1−4] many different types of DENs have been prepared. As mentioned earlier, the first step of the synthesis involves complexation of metal ions with interior tertiary amine groups of the dendrimer (Scheme 1). Once this reaction is complete, a reducing agent, often excess BH_4^-, is added to the solution with vigorous stirring. In addition to Cu, it is also possible to prepare Pd and Pt DENs using K_2PdCl_4 or K_2PtCl_4, respectively, in conjunction with either amine-[12,13] or hydroxyl-terminated[11,17,43,44] PAMAM[11−13,17,43,44] or PPI[31,32] dendrimers. For example, Figure 2a shows UV−vis spectra of a solution containing K_2PdCl_4 only, as well as solutions containing a 40:1 molar mixture of K_2PdCl_4 and G4-OH before (G4-OH(Pd^{2+})$_{40}$) and after (G4-OH(Pd_{40})) chemical reduction.[44] Here, we denote all forms of Pd ions in solution as Pd^{2+}, but in fact the principal species in solution is probably the $PdCl_3(H_2O)^-$ hydrolysis product.[44] The solution containing only K_2PdCl_4 displays a peak at 207 nm and a shoulder at 235 nm that correspond to $PdCl_3(H_2O)^-$. When the dendrimer is added to this solution, a strong LMCT band appears at 224 nm, which arises from the covalent attachment (via a Cl ligand displacement reaction) of

Pd^{2+} to the interior tertiary amines of the dendrimer. Spectrophotometric titrations show that a maximum of 62 Pd^{2+} ions can be incorporated into a G4-OH dendrimer in aqueous solution.[13,44] When an excess of $NaBH_4$ is added to this solution, it turns from pale yellow to dark brown, signaling formation of zerovalent Pd DENs.[45,46] A HRTEM image of these materials is presented in Figure 2b. Note that only the Pd nanoparticles have sufficient contrast to appear in this micrograph; the dendrimer itself is transparent. The average particle size of 1.4 ± 0.4 nm is larger than the calculated value for a 40-atom fcc packed Pd cluster (1.1 nm).[17] While we do not fully understand this discrepancy, it has been reported by others and is highly reproducible.[11,17,44,47,48] The larger-than-expected size may be a consequence of steric constraints within the dendrimer interior, which could cause clusters to adopt non-symmetrical geometries.

Pd and Pt DENs can also be prepared within amine-terminated PAMAM dendrimers by controlling the pH to ensure selective protonation of just the terminal primary amines.[12,13] If a substantial fraction of both the interior and exterior amines are unprotonated, then addition of K_2PdCl_4 to a solution of G4-NH_2 results in the formation of a white precipitate, presumably due to cross-linking of the dendrimers by Pd^{2+}.[49] However, precipitation can be avoided between pH 2 and 5, because in this range the peripheral primary amines are selectively protonated and are thus unable to react with Pd^{2+}, while the interior tertiary amines are mostly unprotonated and therefore able to extract Pd^{2+} from solution.[12,13,50,51] Nearly all the primary and tertiary amines are protonated below pH 2, and it is therefore not possible to sequester Pd^{2+} within the dendrimers in this pH range.[13,50,51] Reduction of G4-$NH_2(Pd^{2+})_{40}$ prepared in a suitable pH range results in formation of Pd DENs that have essentially the same properties as the corresponding materials synthesized in G4-OH. The ability to prepare DENs within amine-terminated dendrimers is important, because primary amines are reactive and therefore provide a synthetic handle for linking DENs to surfaces,[13,52] polymers,[53,54] and biological molecules.

Recently, we investigated the synthesis of Pd, Pt, and Au DENs using fourth- and sixth-generation quaternary ammonium-terminated dendrimers (G4-Q_{32} and G6-Q_{116}, where 32 and 116 are the number of quaternary amines per dendrimer).[35,52] These quaternary ammonium-terminated dendrimers exhibit positively charged surfaces at all pHs, which avoids the types of aggregation and precipitation problems alluded to earlier.[52] Moreover, quaternary amines (as well as primary amines) are stable in the presence of metal salts. In contrast, the hydroxyl groups of Gn-OH dendrimers have sufficient reducing power to prematurely convert $AuCl_4^-$ to zerovalent Au.[35,55] Micrographs of G4-Q_{32}-(Au_{55}), G6-$Q_{116}(Au_{55})$, and G6-$Q_{116}(Au_{140})$ DENs are shown in Figure 3. The size distributions (insets) indicate that the average diameters of these materials are 1.3 ± 0.4 nm, 1.3 ± 0.3 nm, and 1.6 ± 0.3 nm, respectively.[35] The average sizes of the Au_{55} and Au_{140} nanoparticles measured by HRTEM are very close to the values of 1.2 and 1.6 nm calculated by assuming that these materials are spherical in shape. These results illustrate an important property of DENs: the size of the particle is dependent on the metal-to-dendrimer ratio but independent of the dendrimer generation, provided that there are sufficient interior groups to coordinate with the metal ions.

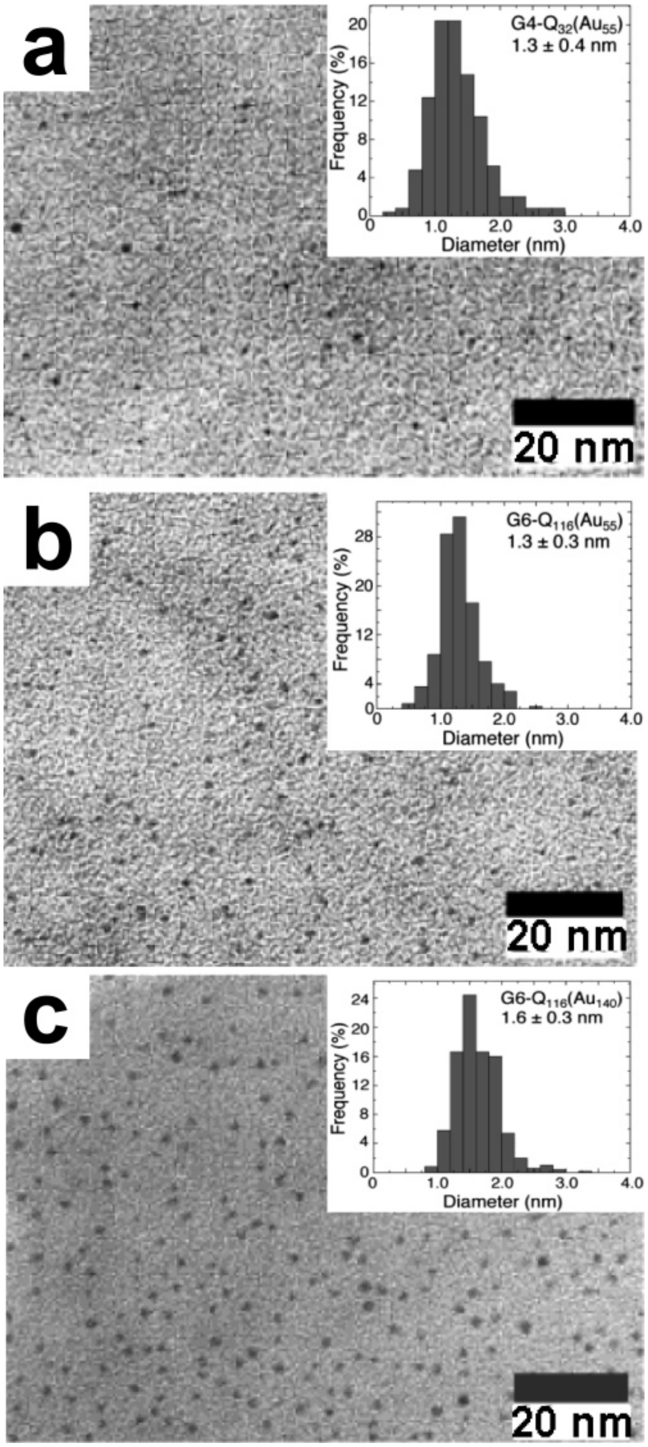

Figure 3. HRTEM images of (a) G4-$Q_{32}(Au_{55})$, (b) G6-$Q_{116}(Au_{55})$, and (c) G6-$Q_{116}(Au_{140})$ DENs and the corresponding particle-size distributions. Reprinted with permission from *Chem. Mater.* **2004**, *16*, 167−172. Copyright 2004 American Chemical Society.

Other groups have previously shown that Au DENs can be synthesized in high-generation dendrimers. For example, using staining-HRTEM, small-angle X-ray scattering (SAXS), and neutron scattering (SANS), Gröhn et al. showed that Au nanoparticles prepared using amine-terminated G6-G10 PAMAM dendrimers result in the formation of Au DENs, whereas larger *inter*dendrimer particles are formed with lower generation, amine-terminated dendrimers.[24] Interestingly, they observed individual Au particles in the G8-$NH_2(Au_{1024})$ DENs, whereas two or three nanoparticles were observed within the G10-NH_2 dendrimers. They suggested that the increased mass density within the largest dendrimers may be responsible for the formation of multiple particles; that is, there could be insufficient flexibility in the structure to allow for the formation of single Au_{4096} nanoparticles. These results underscore an important point: the mechanism and kinetics by which single, zerovalent atoms convert to nanometer-scale metal clusters within dendrimers have not been addressed.

In addition to preparing DENs via precursors that rely on specific interactions between metal ions and dendrimers, it is also possible to take advantage of solubility differences between metal ions in solution and within dendrimers. For example, we have used this route to synthesize Cu and Pd DENs within amphiphilic PPI dendrimers.[56] Previous studies have shown that Cu^{2+} ions cannot complex with functional groups inside PPI dendrimers;[20,57] however, PPI dendrimers modified on their periphery with hexanoyl or palmitoyl groups encapsulate Cu^{2+} from $CHCl_3$/MeOH (4:1, v/v) solutions. In fact, the amount of Cu^{2+} encapsulated within these modified PPI dendrimers is four times greater than in the corresponding PAMAM dendrimers.[1,22] This indicates that the amount of Cu^{2+} in the modified PPI dendrimers cannot be accounted for only by a fixed-stoichiometry interaction such as metal−ion complexation. Similarly, Pd^{2+} can also be driven into these same modified PPI dendrimers using solubility differences. For both the Cu^{2+} and Pd^{2+} PPI composites, chemical reduction leads to the corresponding DENs. Pd DENs synthesized by this route are catalytically active.[56]

While chemical reducing agents are usually used to prepare DENs, several alternative routes have been investigated. UV irradiation is effective for the preparation of both Au[23] and Ag[58] DENs. In addition, Ottaviani and co-workers have shown that X-rays can be used to form Ag/dendrimer nanocomposites, but in this case the Ag nanoparticles were not encapsulated within individual dendrimers.[59] An especially effective means for converting one type of DEN to another involves an intradendrimer redox displacement reaction.[60] In this approach DENs prepared from a particular metal, such as Cu, can be exchanged with another metal, such as Ag, as long as the latter is more noble than the former. Equation 1 expresses this concept for the Ag/Cu case. Depending on the pH of the solution in which this reaction is carried out, the Cu^{2+} ions resulting from the displacement reaction may remain trapped within the dendrimer. This opens up some interesting possibilities for carrying out intradendrimer reactions that require both a catalyst and a cocatalyst. As discussed in a later section, it also provides a means for synthesizing bimetallic nanoparticles having highly structured geometries.

$$Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag \qquad (1)$$

While we have focused mainly on the synthesis of metal DENs, the synthesis of semiconductor DENs has also attracted attention, especially the formation of CdS quantum dots. Murphy and co-workers reported the first synthesis of *inter*dendrimer-stabilized CdS semiconductor quantum dots in 1998.[36] By controlling solution properties, we were able to show that it was also possible to prepare CdS DENs.[61] Moreover, by changing the dendrimer generation, it was possible to form larger CdS nanoparticles: larger dendrimers gave rise to larger quantum dots. Specifically, the CdS diameters obtained for 1:1 ratios of Cd^{2+} to the number of tertiary amines in the outermost shell of the dendrimers were 1.3, 1.8, and 2.3 nm for G4-OH, G6-OH, and G8-OH dendrimers, respectively. Importantly, light-scattering experiments unambiguously showed that there was no aggregation of these materials.

3. Applications

Catalysis. At present, DENs have the highest potential for applications in the field of catalysis for the following reasons.[2−4] First, the dendrimer provides a means for controlling the chemical composition of the catalyst, while simultaneously providing a means for controlling solubility for homogeneous catalysis and a handle for immobilization for heterogeneous catalysis.[13,52] Second, while the dendrimer prevents aggregation of the encapsulated nanoparticles, it does not passivate all of the active sites on the metal surface. Third, we have shown that DENs can be recylced.[15,31,44] Fourth, the host dendrimer can be configured to provide both reactant[11,31] and product[11,31,32] selectivity.

In structure and function, catalytic DENs are intermediate between what we normally think of as homogeneous and heterogeneous catalysts. The reasons for this will become apparent later in this section. Therefore, we somewhat arbitrarily refer to DENs as homogeneous catalysts if they are dissolved in solution and heterogeneous catalysts if they are attached to a support. Using this definition, we have shown that DENs can be used as homogeneous hydrogenation and carbon-coupling catalysts in water,[11,17,43,62] organic solvents,[12,56] biphasic fluorous solvents,[15,31] and even supercritical CO_2.[32] DENs also function as heterogeneous electrocatalysts for the reduction of oxygen,[43,63] and, after removal of the dendrimer, as supported catalysts for hydrogenation and oxidation reactions.[64−66] In the following sections we expand upon some of these findings, particularly as they relate to the four previously mentioned unique aspects of catalytic DENs.

Size-Selective Hydrogenation Catalysts. The catalytic hydrogenation activity of Pd DENs is related to the density of functional groups on the dendrimer periphery, which is itself a function of dendrimer generation. This principle is illustrated in Scheme 2 and confirmed by the results shown in Table 2; smaller substrates more easily penetrate low-generation dendrimers compared to larger substrates or higher generation dendrimers. Accordingly, there are, on average, more encounters per unit time between the smaller substrates and the catalysts encapsulated in low-generation dendrimers.[11,17] For example, the turnover frequency (TOF) for allyl alcohol decreases by a factor of about four when the calculated edge-to-edge distance between OH end-groups decreases from 8.2 Å (G4-OH(Pd_{40})) to 3.2 Å (G8-OH(Pd_{40})).[11] Likewise, for the intermediate-generation G6-OH(Pd_{40}) DENs, the hydrogenation TOF for the largest branched allylic alcohol, 3-methyl-1-penten-3-ol, is a factor of 10 smaller than the TOF for the smallest substrate, allyl alcohol. These results show that the dendrimer periphery acts as a size- and shape-selective "nanofilter". Ooe et al. have recently reported similar selectivities, based on substrate size and polarity, for Pd DENs hosted by PPI dendrimers functionalized on the periphery with triethoxybenzamide groups.[48] Specifically, they found that the rate of catalytic hydrogenation of cyclic conjugated dienes by Pd DENs in chloroform decreased in the order of cyclopentadiene > 1,3-cyclohexadiene > 1,3-cyclooctadiene, whereas no such changes in hydrogenation rates were observed when the reactions were carried out using Pd/C catalysts. In addition, the Pd DENs showed remarkable selectivity toward polar substrates: in competitive reactions between 3-cyclohexene-1-methanol and cyclohexene, only the 3-cyclohexene-1-methanol was hydrogenated. The authors attributed these results to the strong interaction of the polar substrates with the interior tertiary amines of the dendrimers; that is, the enhanced solubility of polar substrates within the dendrimer.

To demonstrate the generality of the nanofilter concept, we examined the hydrogenation TOFs for three related allylic alcohols using DENs prepared from a single dendrimer generation terminated in functional groups having different degrees

SCHEME 2

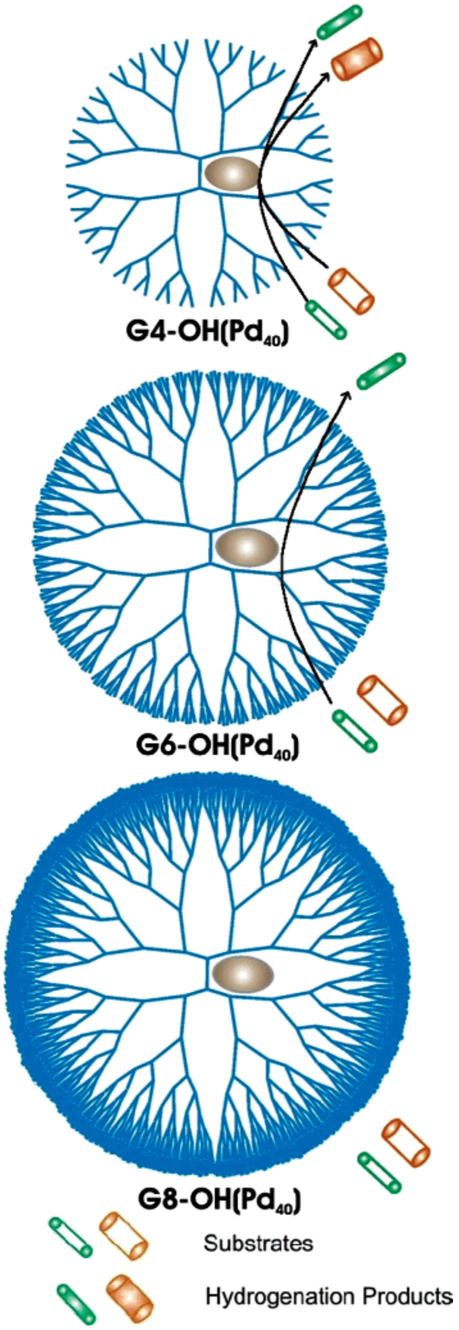

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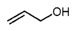
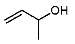
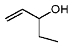
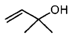
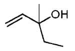
TABLE 2: Hydrogenation Reaction Rates Using Gx-OH(Pd_{40}) Catalysts for Structurally Related Allylic Alcohols[a]

Substrates	TOF[mol H_2(mol Pd)$^{-1}$ h^{-1}]		
	G4-OH(Pd_{40})	G6-OH(Pd_{40})	G8-OH(Pd_{40})
	480/470[1]	450/460[1]	120
	450/460[1]	380	93
	260	280	68
	150	75	62
	100	40	50

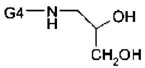
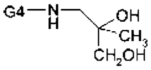
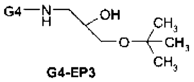
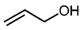
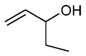
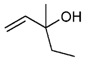
[a] Hydrogenation reactions were carried out at 25 ± 2 °C using 2 × 10^{-4} M Gx-OH(Pd_{40}) catalysts in MeOH−H_2O (4:1 v/v) mixtures. The turnover frequency (TOF) was calculated based on H_2 uptake. [1]Duplicate measurements were performed to illustrate the level of run-to-run reproducibility. Reprinted with permission from *J. Am. Chem. Soc.* **2001**, *123*, 6840−6846. Copyright 2001 American Chemical Society.

of steric bulk. In this case, G4-NH_2 PAMAM dendrimers were modified with a series of epoxides having increasingly larger distal functional groups.[67] The resulting α-amino alcohol-terminated PAMAM dendrimers (G4-EPx, $x = 1-3$, Table 3) served as templates for the preparation of Pd_{40} nanoparticles, and then as hydrogenation catalysts. Table 3 shows a clear trend indicating that DENs functionalized with bulkier peripheral groups are poorer catalysts than those having less steric bulk on their surface. Thus, regardless of whether the average spacing between dendrimer branches is controlled by modulating the dendrimer generation or the size of the terminal groups, the result is the same. A close examination of Tables 2 and 3 indicate that there are some deficiencies in this simple model based on steric factors, however, and it is likely that other factors such as the number and distribution of interior tertiary amine groups, differences in solvent properties within different generation dendrimers, and differences in the physical and electronic structure of the DEN itself, will also affect the catalytic properties of DENs. Nevertheless, these two examples provide guidance for conferring selectivity to intrinsically nonselective metal catalysts. Presumably other types of peripheral modifications of the dendrimer surface could function as charge-selective or enantioselective nanofilters, but such investigations have not as yet been carried out.

Hydrogenation of Molecular Rulers. We have shown that “molecular rulers” consisting of catalytically active allyl groups and cyclodextrin “stoppers” spanned by intervening alkyl chains having different lengths (0.5, 0.9 and 1.3 nm) can be used to estimate the average distance between the dendrimer surface and the surface of the encapsulated metal nanoparticles (Scheme 3).[4,68] By making some key structural and mechanistic assumptions, and then using NMR to measure the relative hydrogenation rates of these rulers, it was possible to estimate that the surfaces of encapsulated nanoparticles in G4-OH(Pd_{40}) DENs are an average of 0.7 nm ± 0.2 nm from the surface of the dendrimer. This estimate agrees fairly well with SAXS measurements reported for Au DENs by Gröhn et al., who found that the Au particles had to be significantly displaced from the center of the dendrimer in order for models to properly represent the experimental scattering profiles.[24]

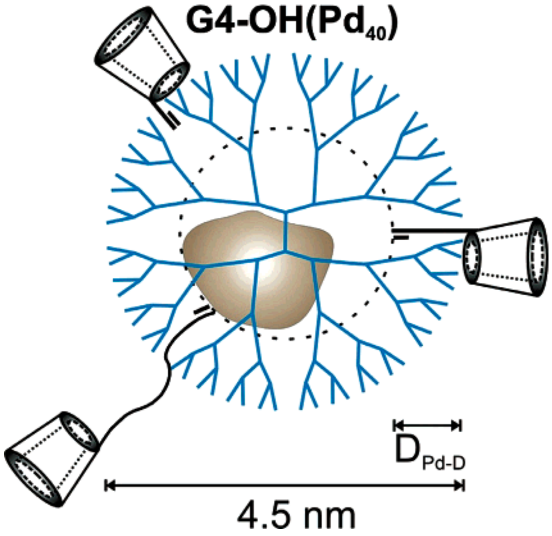
Heterocoupling Catalysts. In addition to catalyzing hydrogenation reactions, Pd DENs have been used as catalysts for carbon-coupling reactions by our group[31,32] and others.[47,69] For example, we have shown that Pd DENs prepared using PPI dendrimers modified on their periphery with perfluorinated polyether chains can catalyze the Heck coupling of *n*-butylacrylate with a range of aryl halides in biphasic fluorous/organic solvents.[31] The Pd DENs catalyzed the reaction at 90 °C, compared to temperatures in excess of 120 °C used for other

TABLE 3: Hydrogenation Reaction Rates Using Fourth-Generation, Epoxide-Modified Catalysts for Structurally Related Allylic Alcohols

Solvent	Substrate	TOF[mol H_2(mol Pd)$^{-1}$ h^{-1}]			
		G4-OH(Pd_{40})	G4-EP1(Pd_{40})	G4-EP2(Pd_{40})	G4-EP3(Pd_{40})
		G4-OH	 G4-EP1	 G4-EP2	 G4-EP3
MeOH:H_2O (1:1)		125	83/62[1]	62/62[1]	43
		105	62/56[1]	60/56[1]	53
		50	55/50[1]	43/43[1]	31

[1] Duplicate measurements were performed to illustrate the level of run-to-run reproducibility.

SCHEME 3



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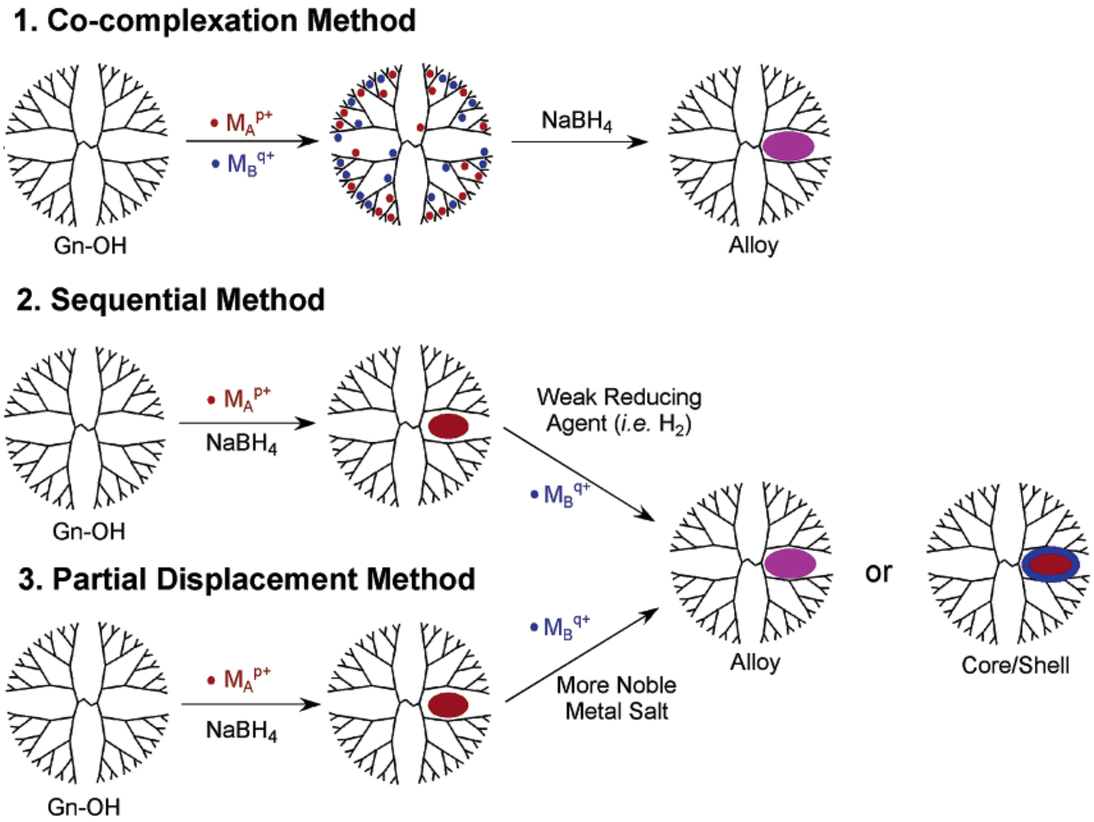
colloidal Pd Heck catalysts.[31] In addition, the reaction was 100% selective for the trans isomer of *n*-butyl-formylcinnamate. Other colloidal Pd catalysts in fluorous solvents have exhibited selectivities for this reaction in the 74−98% range.[70,71]

The same highly fluorinated Pd DENs catalyze Heck reactions in both liquid and supercritical CO_2 ($scCO_2$).[32] This was the first example of the use of metal nanoparticles to perform a catalytic reaction in environmentally friendly $scCO_2$, and so there is potentially some technological significance to these results. Of greater importance, however, we found that coupling of aryliodides and methacrylate yields the highly unfavorable 2-phenylacrylic acid methyl ester isomer, rather than the preferred cinnamate products. This finding suggests that judicious tuning of solvent conditions, dendrimer structure, and catalyst composition may provide a means for enhancing product selectivity (contrast this with the previous sections that focused on reactant selectivity).

Li and El-Sayed have compared the catalytic efficiency of Pd DENs for the Suzuki carbon-coupling reaction with Pd nanoparticles stabilized by either poly(vinylpyrrolidone) (PVP) or a polystyrene-poly(sodium acrylate) block copolymer.[47] They found that G4-OH DENs had the highest stability but also the lowest catalytic activity. Lower generation DENs, including those encapsulated by G3-OH and G2-OH dendrimers, were more catalytically active than G4-OH but their TOFs remained inferior to those of the PVP- and block-copolymer-stabilized nanoparticles. These results suggest that there is an inverse relationship between nanoparticle stability and catalytic activity. Whether reduced catalytic activity in the higher-generation dendrimers is a consequence of the greater resistance to mass transfer imposed on substrates seeking to encounter the catalyst, or a higher percentage of the nanoparticle surface being passivated by functional groups within the higher generation dendrimers, is an open (and important) question. One thing is certain, however: the synthesis of dendrimers specifically designed to increase catalytic activity without reducing stability is a worthwhile research objective.

Bimetallic Catalysts. The successful synthesis of catalytically active bimetallic DENs is a recent key development in this field. Scheme 4 outlines three different approaches for preparing such materials.[2] The co-complexation route leads to alloy-type bimetallics, and the other two methods can lead to alloy or core/shell materials depending on the identity of the two metals and the details of how the synthesis is carried out. For example, bimetallic alloys consisting of Pd and Pt can be prepared via the co-complexation route using K_2PdCl_4 and K_2PtCl_4 complex ions and G4-OH dendrimers.[62] The resulting PdPt bimetallic DENs are water-soluble, stable for over 1 year in solution, and nearly monodisperse in size. HRTEM indicates that G4-OH-$(Pd)_{30}(Pt)_{10}$ DENs have an average diameter of 1.9 ± 0.4 nm, which is significantly larger than the value of 1.1 nm calculated for a fcc-packed PdPt particle containing 40 atoms. Previous investigations of monometallic Pd and Pt DENs have also revealed a discrepancy between the calculated and experimentally determined diameters,[11,17,43,44,47,48] and, although we are uncertain of the origin of this effect, it may be related to steric constraints within the dendrimer interior that lead to particles having unusual shapes. Single-particle EDS verified that the ratio of K_2PdCl_4 and K_2PtCl_4 used to prepare the DENs controls the composition of individual particles. For example, large-area EDS analysis of G4-OH$(Pd)_{30}(Pt)_{10}$ DENs indicated that the atomic percentages of Pd and Pt are 74% and 26%, while two individual particles had elemental compositions of 73% Pd and 27% Pt, and 63% Pd and 37% Pt, respectively. Importantly, TOFs for the hydrogenation of allyl alcohol are significantly higher for the Pd-rich bimetallic DENs compared to physical mixtures of the single-metal analogues (Figure 4).[62] Such an

SCHEME 4



enhancement has previously been documented for 1−2 nm-diameter PdPt bimetallic particles and is thought to be due to synergistic electronic (ligand) effects.[72] Chung and Rhee have also recently reported synergistic effects for the hydrogenation of cyclohexene by PdPt DENs[73] and the partial hydrogenation of 1,3-cyclooctadiene by PdRh DENs.[74]

In addition to alloy-type bimetallics, it is also possible to prepare core/shell structures using the sequential dendrimer-templating approach illustrated in Scheme 4. For example, our group has recently synthesized [Au](Pd) core/shell structures (brackets indicate the core metal and parentheses indicate the shell metal) by selectively reducing $PdCl_4^{2-}$ onto G6-Q_{116}(Au_{55}) seeds using H_2.[75] Figure 5 shows representative HRTEM micrographs and particle-size distributions for G6-Q_{116}(Au_{55}), G6-Q_{116}[Au_{55}](Pd_{95}), and G6-Q_{116}[Au_{55}](Pd_{455}) DENs. The average particle sizes for these materials are 1.3 ± 0.3, 1.8 ± 0.5, and 2.3 ± 0.4 nm, respectively, which compare well to calculated values of 1.2, 1.8, and 2.6 nm, respectively.[75] Single-particle EDS experiments confirmed that all the [Au](Pd) core/shell nanoparticles are bimetallic and have compositions related to the ratio of Pd to Au used to prepare the DENs. Compared to Pd-only monometallic DENs, the hydrogenation of allyl alcohol in water is significantly enhanced when these core/shell DENs are used as catalysts. Bimetallic DENs having a Pd core and a Au shell can also be prepared using Pd DEN seeds and H_2 or ascorbic acid to reductively deposit the Au shell.[75] However, for reasons that we do not understand at the present time, the [Pd](Au) core/shell DENs are not stable when used as catalysts for hydrogenation reactions.

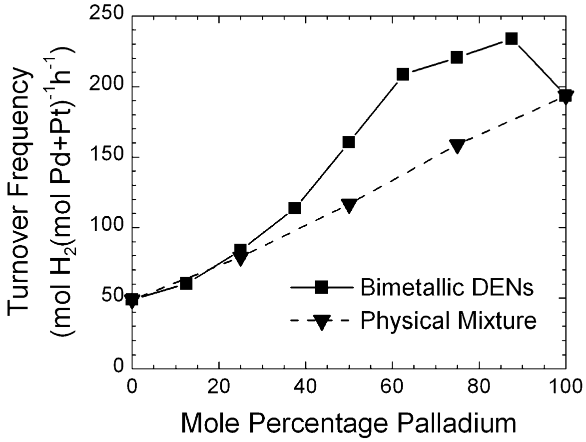


Figure 4. Plot of turnover frequency (TOF) vs the mole percentage of $PdCl_4^{2-}$ used to prepare the DENs. The squares indicate the results for bimetallic nanoparticles and the triangles are for physical mixtures of Pt-only or Pd-only DENs. Reaction conditions: [allyl alcohol] = 200 mM, [Pd+Pt] = 0.095 mM, substrate/metal ratio = 2100:1, T = 19 °C. Reprinted with permission from *J. Am. Chem. Soc.* **2003**, *125*, 3708−3709. Copyright 2003 American Chemical Society.

Heterogeneous Catalysts. Heterogeneous catalysts can be prepared using DENs by immobilizing the dendrimer template onto a solid support. After this step it may be desirable to remove the dendrimer from the encapsulated nanoparticle, but removal of the dendrimer may lead to an increase in both the particle size and the particle-size distribution.

We previously showed that monolayers of Pt DENs terminated with hydroxyl functional groups could be immobilized on Au surfaces and used for the electrocatalytic reduction of O_2.[43] Although these materials demonstrated a clear catalytic function, they were not very stable and tended to be easily displaced from the electrode surface. Accordingly, we have sought to improve the stability of electrocatalytic DENs. For example, Pd and Pt DENs encapsulated within amine-terminated dendrimers and partially quaternized amine-terminated dendrimers can be covalently linked to acid-terminated mercaptoundecanoic acid (MUA) self-assembled monolayers (SAMs)

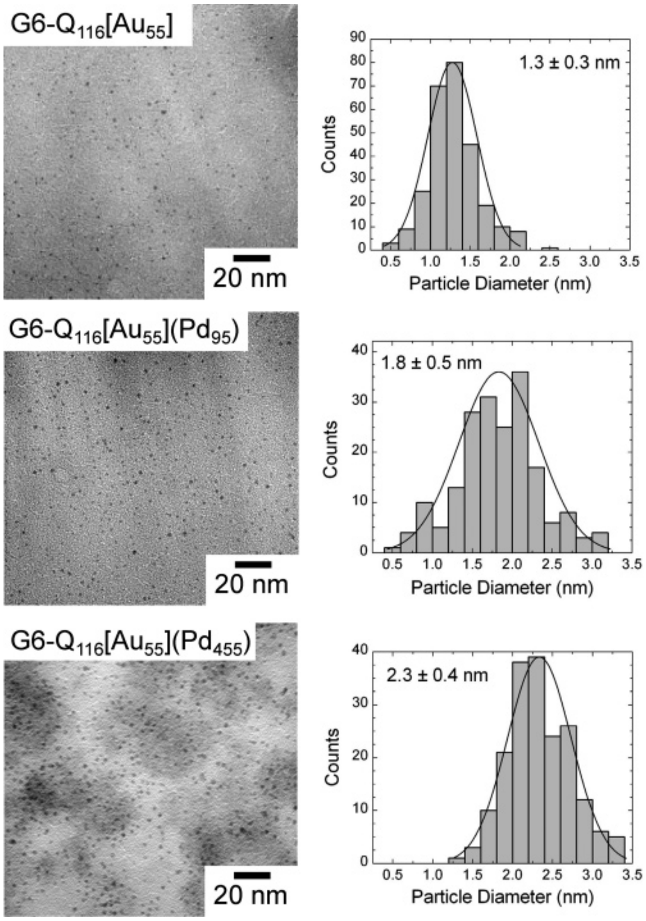
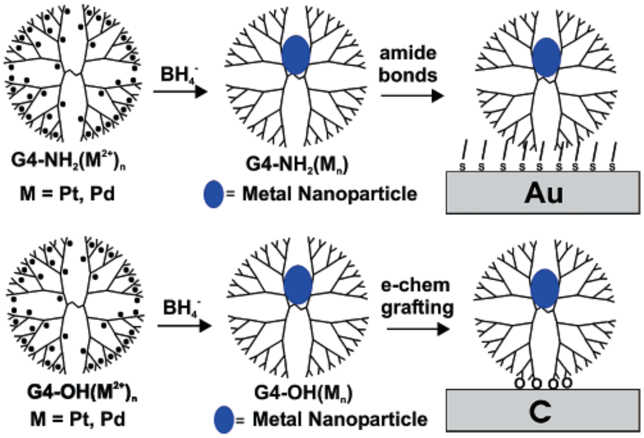


Figure 5. HRTEMs and particle-size distributions for G6-Q_{116}(Au_{55}), and G6-Q_{116}[Au_{55}](Pd_{95}) and G6-Q_{116}[Au_{55}](Pd_{455}) bimetallic DENs synthesized by H_2 reduction of K_2PdCl_4 onto Au_{55} seeds. Reprinted with permission from *J. Am. Chem. Soc.* **2004**, *126*, 15583−15591. Copyright 2004 American Chemical Society.

SCHEME 5



attached to Au surfaces via thiol groups (top panel of Scheme 5).[13,52] The resulting films were durable even after sonication under acidic conditions, whereas films prepared by electrostatic attachment of the dendrimer to the MUA monolayer were less robust. However, Pt catalysts formed by this route were not active for the electrocatalytic reduction of O_2, presumably due to the insulating SAM layer separating the Au surface from the DENs.

This problem was resolved by electrochemically grafting Pt DENs to glassy carbon electrodes (bottom panel of Scheme 5).[63] This approach was inspired by previous reports demonstrating that alcohols and glycols could be linked to carbon surfaces at positive potentials.[76,77] G4-OH(Pt_{40}) DENs were electrochemically grafted to glassy carbon electrodes by cycling the potential from 0 to 1.0 V (vs Ag/AgCl, 3M NaCl) three times. The maximum current for the electrocatalytic reduction of O_2 occurs at 0.22 V for the G4-OH(Pt_{40})-modified electrodes, while the reaction takes place at negative potentials for Pt-free G4-OH-modified electrodes (Figure 6). Importantly, the resulting films are stable: no change in the peak position or current magnitude was observed for the G4-OH(Pt_{40})-modified electrodes after 50 electrochemical cycles, or after sonication for 10 min in aqueous 0.5 M H_2SO_4.

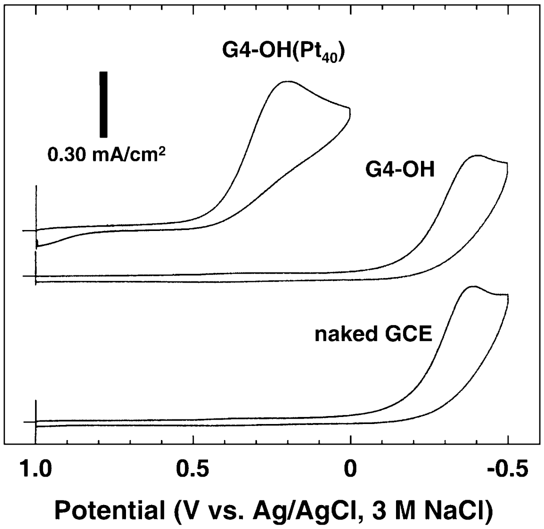


Figure 6. Cyclic voltammograms demonstrating the electrocatalytic reduction of O_2 by G4-OH(Pt_{40}). The catalysts were prepared by electrochemically grafting the hydroxyl-terminated dendrimers onto glassy carbon electrodes. Note the positive shift in peak potential, which demonstrates the electrocatalytic effect, for the electrode modified with Pt DENs. Experimental conditions: electrolyte solution, aqueous 0.5 M H_2SO_4 saturated with O_2; scan rate, 50 mV/s; electrode area, 0.071 cm^2.

DENs can also be incorporated into conducting polymer matrixes. This may provide a means for carrying out electrocatalytic reactions using electronically switchable polymers. To demonstrate the preparation of these materials, we synthesized thiophene-terminated PAMAM dendrimers and showed they could be co-electropolymerized with poly(3-methylthiophene).[53] Moreover, Pt ions could be coordinated within the dendrimers and reduced to form DENs within the co-polymerized matrix.[78] Although we have shown that such films retain their desirable electronic properties after incorporation of DENs, we have not yet demonstrated that the DENs communicate electronically with the polythiophene matrix or that the DENs are catalytically active.

In addition to preparing heterogeneous catalysts from intact DENs, it is also possible to remove the dendrimer after immobilization. In this case, the only function of the dendrimer is to provide a means for synthesizing the nanoparticles and then dispersing them onto a solid support without agglomeration. Our focus has been on preparing catalysts using preformed DENs, but others have shown that dendrimers can also be used to prepare supported catalysts by calcining dendrimers loaded with unreduced metal ions.[79−81] In principle, removal of the dendrimer leads to a more active catalyst because the substrate has easier access to the metal surface. This is particularly important for gas-phase reactions, because in the absence of a solvent the dendrimer collapses around the nanoparticle and renders it catalytically inactive.[64] The major difficulty in making

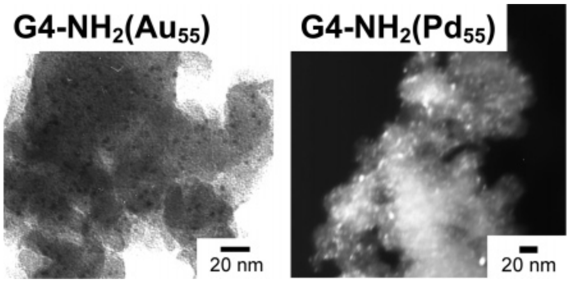


Figure 7. TEM micrographs of G4-NH_2(Au_{55}) and G4-NH_2(Pd_{55}) DENs incorporated into a titania matrix and then calcined at 500 °C under a flow of air for 3 h. Reprinted with permission from *Chem. Mater.*, published online 11/23/2004, http://dx.doi.org/10.1021/cm049279z. Copyright 2004 American Chemical Society.

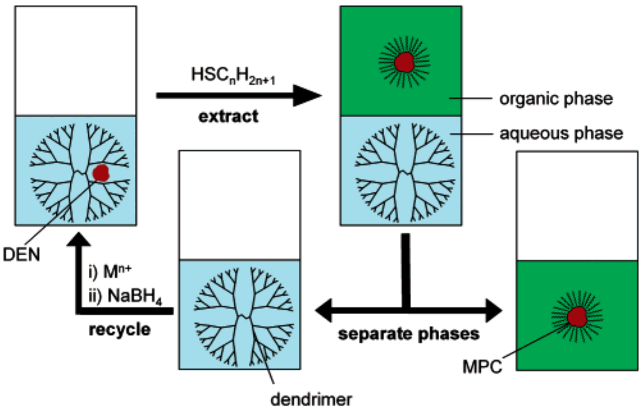
dendrimer-free heterogeneous catalysts using this approach is that methods suitable for removing the dendrimer usually lead to growth in the average particle size and size-distribution of the nanoparticles.

Our first efforts to prepare dendrimer-free heterogeneous catalysts using DEN precursors focused on Pd DENs supported on mica or highly oriented pyrolytic graphite (HOPG).[82] For example, Pd DENs encapsulated within G6-NH_2 were found to have strong interactions with the step edges of HOPG surfaces. However, upon calcination at 630 °C the particles grew into large aggregates. A much more successful example of this general approach was recently demonstrated by Chandler and co-workers, who showed that G5-OH(Pt_{50}) and G5-OH(Pt_{100}) DENs could be deposited onto commercial silica supports and then calcined at 300 °C in a O_2/He flow to yield supported Pt catalysts that largely retained their original size.[64] For example, calcination of G5-OH(Pt_{100}) under these conditions led to an increase in the average particle size from 1.9 ± 0.3 nm to 2.2 ± 0.5 nm. In this case, the removal of the dendrimer was accelerated by the presence of the catalytic Pt nanoparticles. In contrast, we have recently shown that temperatures of ∼500 °C (in air) are required to remove PAMAM dendrimers from Pd or Au DENs supported on titania.[65] Calcination using these conditions leads to particle growth; for example, the average particle size of G4-Q_{32}(Au_{55}) nanoparticles deposited on titania increased from 1.7 ± 0.4 nm to 7.2 ± 3.6 nm.[65] However, lower temperature routes to removal of the dendrimer template, such as oxygen plasma treatment, could lead to improved retention of the particle size.[83]

In addition to depositing DENs onto surfaces, it is also possible to incorporate them into inorganic matrixes to yield catalytically active heterogeneous materials. For example, we have shown that such materials can be prepared by incorporating DENs into sol−gel matrixes, and then calcining the composite to remove the dendrimer. This approach minimizes particle growth, because individual nanoparticles are isolated within the sol−gel framework. We demonstrated the viability of this approach by incorporating Au and Pd DENs into amorphous titania networks and then removing the dendrimers by calcination.[65]

Figure 7 shows HRTEM images of Au and Pd nanoparticles, derived from G4-NH_2(Au_{55}) and G4-NH_2(Pd_{55}) DENs, supported on titania. The important conclusion is that the average particle size and size distribution do not increase much following calcination.[65] Specifically, the Au_{55} particles increase from 2.0 ± 0.6 nm in diameter to 2.7 ± 0.6 nm following calcination at 500 °C. Another interesting aspect of this approach is that the dendrimer has a dual templating role: it defines the size and monodispersity of both the nanoparticles and the pore structure in the titania framework.[65]

SCHEME 6



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Supported bimetallic nanoparticles can also be prepared via this sol−gel route, and even after calcining to remove the dendrimer the size and chemical composition of individual particles are largely retained.[66] For example, supported PdAu catalysts formed from G4-NH_2($Pd_{27.5}Au_{27.5}$) DENs were found to have an average particle size of 1.8 ± 0.4 nm and 3.2 ± 0.9 nm before and after calcination, respectively. Moreover, single-particle EDS analysis following calcination of G4-NH_2($Pd_{14}Au_{41}$) DENs indicated average Pd and Au compositions of 19 ± 2% and 81 ± 2%, respectively, which are in good agreement with the molar percentages of $PdCl_4^{2-}$ and $AuCl_4^{-}$ used in their preparation.

These first few attempts to prepare supported monometallic and bimetallic catalysts from DENs demonstrate that it is possible to preform nanoparticles within dendrimer templates, deliver these materials to metal oxide supports, and then remove the dendrimer without too much change in the size and composition of the particles. Additional studies of this type will undoubtedly lead to additional improvements in the materials synthesis and hence to more efficient and selective heterogeneous catalysts.

Extraction of Metal Nanoparticles from within Dendrimers. We recently demonstrated that DENs can be extracted from within dendrimer templates and transferred to an organic phase using *n*-alkanethiol surfactants.[84−87] As shown in Scheme 6, the extraction is carried out as follows. DENs are prepared in an aqueous phase, and then an organic phase containing an *n*-alkanethiol is added. The two-phase system is shaken, and the nanoparticles are extracted into the organic phase as monolayer-protected clusters (MPCs).[88] The dendrimeric templates remain in the aqueous phase. There are three interesting aspects of this extraction process. First, it provides a simple route to nearly monodisperse MPCs that does not require subsequent purification. Second, because the dendrimer templates remain in the aqueous phase, they can be recycled and used to prepare additional DENs. Third, it is scientifically interesting that objects as large as DENs can be extracted from within the dendrimer interior given the steric crowding on the periphery.

Figure 8 shows HRTEM micrographs and particle-size distributions for G4-OH(Pd_{40}) DENs before extraction, and the corresponding Pd_{40} MPCs after extraction.[84] Before extraction, the Pd DENs have an average diameter of 1.7 ± 0.4 nm, while after extraction the particle size decreases slightly to 1.5 ± 0.3 nm. These results very strongly suggest that individual nanoparticles are extracted from the dendrimer without significant

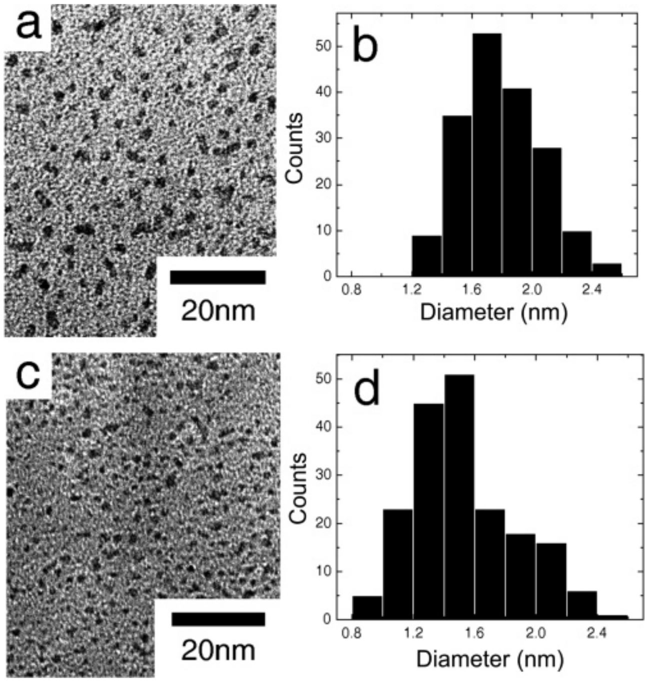

Figure 8. HRTEM micrographs and size-distribution histograms for (a),(b) G4-OH(Pd_{40}) and (c),(d) Pd_{40} MPCs (MPC−Pd_{40}) after extraction with a toluene solution containing 500 μM *n*-hexanethiol. Reprinted with permission from *J. Am. Chem. Soc.* **2003**, *125*, 11190−11191. Copyright 2003 American Chemical Society.

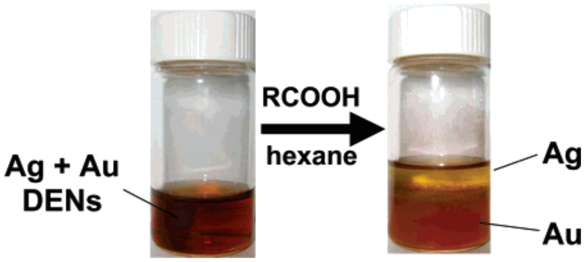

Figure 9. Photographs illustrating the selective extraction of DENs. The vial on the left contained a mixture of 0.20 mM G4-OH(Au_{147}) and 0.18 mM G4-OH(Ag_{110}) DENs in water. When an *n*-hexane solution containing 0.25 M *n*-decanoic acid was added and the vial shaken, the Ag nanoparticles were extracted into the organic phase as monolayer-protected clusters. Reprinted with permission from *Chem. Mater.* **2004**, *16*, 4202−4204. Copyright 2004 American Chemical Society.

loss of metal or aggregation. FT-IR spectroscopy was used to ascertain the whereabouts of the dendrimer after extraction: the amide bands, which are characteristic of PAMAM dendrimers, were only observed in the aqueous phase. In addition to Pd, we have shown that it is also possible to extract Au, Ag, and bimetallic AuAg DENs using *n*-alkanethiol surfactants.[85−87]

While *n*-alkanethiols were the obvious choice for the initial extraction experiments due to their well-known affinity for metal surfaces (in particular Au), we thought it might be possible to extract particular metals from a mixture using ligands having different affinities for different materials. This type of selective extraction is analogous to the concept of orthogonal assembly first described in 1989 by the Wrighton and Whitesides groups, who showed that two different surfactants could selectively interact with a patterned surface composed of two different materials.[89] Figure 9 demonstrates the selective extraction concept. The left photograph shows a vial containing an aqueous mixture of monometallic Au and Ag DENs. When a hexane solution containing *n*-decanoic acid is added and the vial shaken, only the Ag nanoparticles are extracted to the organic phase as MPCs.[87] We believe this is due to the presence of an oxide layer on the surface of the Ag DENs, which facilitates selective adsorption of *n*-alkanoic acids only onto the surface of the Ag DENs.[90,91] Because *n*-decanoic acid does not interact strongly with zerovalent Au, Au DENs are not converted to MPCs and therefore they are not transported to the organic phase.

In addition to selective extraction of monometallic DENs, it is also possible to use this method to characterize bimetallic nanoparticles. This is a particularly important consequence of this extraction experiment, because there are very few methods for confirming core/shell structures for particles having diameters of less than 3 nm. The idea is that [Au](Ag) core/shell DENs (having a Ag oxide layer on their surface) should selectively extract in the presence of an *n*-alkanoic acid and [Ag](Au) core/shell DENs should selectively extract in the presence of an *n*-alkanethiol. Indeed, it turns out that this approach to structural characterization works very well.[86]

4. Future Outlook

One of the most promising aspects of the work described here involves the synthesis and characterization of structured bimetallic nanoparticles (Scheme 4). In the future we hope to show that it is possible to synthesize particular structures based on a first-principles understanding of catalytic selectivity. This goal will require, among other things, better synthetic methodologies for nanoparticle fabrication. Some guidance as to how this might be accomplished comes from Yamamoto and co-workers who have studied the interaction of $SnCl_2$, as well as other metal salts, with phenylazomethine dendrimers.[92] They found that $SnCl_2$ complexes with the imine groups of the dendrimer in a stepwise radial fashion.[92] Such precise spatial control of metal loading could potentially be used to synthesize multishell nanoparticles for catalytic and other applications.[93]

Another interesting avenue for further research is the exploration of DEN catalysts as natural enzyme mimics; that is, systems in which several catalytic sites can act in concert to yield desirable products. Indeed, we previously found that when Cu DENs are converted to Ag DENs by redox displacement (eq 1), Cu^{2+} remains complexed within the dendrimer over a broad range of pHs.[60] This suggests that dendrimer-based catalysts could be designed for reactions that require the cooperative action of a zerovalent metal catalyst and an ionic co-catalyst in close proximity. A well-known example of such a reaction, which we are presently studying,[94] is the Stille cross-coupling reaction between aryl and vinyl halides with organostannanes using a zerovalent Pd catalyst. It has been shown that Cu(I) salts have a significant co-catalytic effect in this reaction.[95]

Since its origins in solid-phase peptide synthesis, combinatorial chemistry has impacted fields ranging from catalysis to agriculture as a route to more cost-effective product development.[96] In its simplest form, combinatorial chemistry involves preparation of a large number of related chemical entities from a relatively small number of building blocks, and then subsequent screening of these entities for activity. Building DENs through combinatorial chemistry might be an attractive route to synthesize multi-metallic alloys having well-defined particle sizes and tunable solubility as improved catalysts for such reactions as the electrooxidation of methanol in fuel cells or ester hydrolysis. DEN libraries consisting of metal catalysts and ionic co-catalysts could also be prepared. Such a combinatorial study has already been reported for constructing a combinatorial library of polymer-bound catalyst contenders.[97]

In addition to catalysis, there are other fields that might benefit from DENs. For example, dendrimer-encapsulated semiconductor nanoparticles (or quantum dots, QDs) having controlled sizes, and thus well-defined luminescence properties, have already been prepared.[61] Such materials might be useful as biological labels, because QDs have highly desirable characteristics compared to organic dyes[98] and because the luminescent properties of QDs are not affected by the surrounding dendrimers to an appreciable extent. Moreover, the dendrimer itself possesses many functional groups on its periphery that can be used as handles for attachment to biomolecules or surfaces. Additional possibilities for using DENs include the integration of nanoparticles into dendrimers that can harvest light and transfer the energy to a reaction center.[99] Such composite DENs could be used for light-induced hydrogen evolution using colloidal Pt or bimetallic catalysts.[100,101] Another possible application is the formation of magnetic DENs, composed of metals or bimetallic alloys,[102] that could find use in the field of data storage.

5. Summary and Conclusions

This article has provided an overview of progress in the synthesis and characterization of dendrimer-encapsulated nanoparticles. We have shown that these materials can serve as models for addressing scientific questions and that they may also have some technological significance.

It is worthwhile to summarize what we know and what we do not know about DENs. We know, for example, that metal ions having an affinity for tertiary amines are sequestered within the interior of PAMAM and PPI dendrimers. Following chemical reduction, HRTEM, SAXS, and catalysis experiments confirm that these ions are reduced to atoms and that the atoms aggregate into nanoparticles having sizes that reflect the original metal-ion-to-dendrimer ratio. TEM indicates that DENs can be quite monodisperse in size, but there are some limitations of this method that make it necessary to qualify this statement. First, TEM does not clearly resolve particles smaller than ∼1 nm, which means that if particles in this size range are present they are not counted in particle-size distributions. Likewise, the inherent resolving power of the TEM used to obtain the data reported here is ±0.19 nm, and therefore it is difficult to draw definitive conclusions regarding monodispersities of DENs that approach this value. Clearly, better methods are required for measuring particle sizes (and shapes) in the range of 0−3 nm.

In addition to monometallic DENs, it is also possible to prepare bimetallic materials that have either random alloy or core/shell structures. DENs are stable for long periods of time, although some metals, such as Cu and Ag, easily oxidize in air. This is partly a consequence of the fact that the redox potential of metals shift positive as their size decreases.[103] DENs can be rendered soluble in water, organic and fluorous solvents, and even in liquid and supercritical CO_2, and this provides a major opportunity to study metal-particle-catalyzed reactions in unusual solvent environments. We also know that DENs can be extracted from within the interior of dendrimers without aggregation and without major changes in size or chemical composition. Selective extraction experiments also provide a sensitive means for studying the structure of bimetallic core/shell DENs.

With regard to catalysis, we know that dendrimers can act as size-selective “nanofilters” that confer a degree of substrate selectivity to intrinsically nonselective metal catalysts. However, as with all selective filters there is a cost, and in this case the cost is reduced turnover frequency. This means that the rates of reactions catalyzed by DENs are often rather slow. We know that DENs catalyze hydrogenation and carbon-coupling reactions, but the full scope of reactions that can be catalyzed by DENs is unknown. For example, it seems reasonable to expect that dendrimers could be prepared that exhibit regioselectivity and enantioselectivity. We know that catalytic reactions occurring within DENs can lead to unusual product distributions, but the scope and underlying reasons for this observation are not known. We also know that catalytically active DENs can be recycled by attaching appropriate functional groups on the periphery of the dendrimer.

We know that DENs can be immobilized on surfaces and used for electrocatalysis and other forms of heterogeneous catalysis. We also know that in the absence of solvent or in the presence of a poor solvent, dendrimers collapse around the encapsulated metal nanoparticle and that this shuts off catalytic activity. However, surface-confined DENs can be activated by removing the dendrimer, and in favorable cases this does not lead to too much aggregation.

There are a few other interesting questions about DENs that have not yet been addressed. For example, can DENs provide a platform for studying catalytic quantum-size effects in homogeneous solution or as supported catalysts?[104,105] Is it possible to control the shape as well as the size of nanoparticles using dendrimer templates? What does the surface of a DEN look like? That is, what percentage of the atoms on the surface of a DEN are catalytically active? Although we have some idea where DENs are located inside dendrimers, it would be interesting to know the distribution of locations and how the presence of the nanoparticle affects the dynamics of dendrimer motion.

Clearly, there are many interesting questions about DENs that remain unanswered. We hope this article will stimulate others to bring their particular expertise to bear on DENs and related materials. It would be particularly interesting to examine the properties of nanoparticles encapsulated in other families of dendrimers, and it would also be useful to devise characterization methods that would provide additional insight into the properties of DENs.

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