Controlled Synthesis of Pd Clusters in Subnanometer Range Using Poly(propylene imine) Dendrimers

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Tailor-made synthesis of Pd clusters in the subnanometer range was achieved using dendrimers as tunable host materials. The subnano Pd clusters consisting of a specific number of Pd atoms of Pd_4, Pd_8, and Pd_{16} were obtained by preorganization of Pd ions within the PPI dendrimers and subsequent reduction.

The size- and shape-selective syntheses of metal nanoparticles are of much interest in the areas of materials physics and chemistry, because of their high potential for catalysts, optics, and electronics.[1] Among naked metal nanoparticles, small clusters ranging in diameters less than 1 nm, "subnano metal clusters," are highly expected to open a new realm in materials science,[2] since they bridge the gap between mononuclear metal atoms and nanoparticles.[3] However, the subnano metal clusters are prone to aggregate into larger particles or bulk metals, which obstruct their study under practical conditions. Size-controlled synthesis of the subnano metal clusters is a current topic in the development of highly functionalized materials.[4]

Palladium is at the heart of catalytic molecular transformations in areas of organic synthesis and environmental pollution control.[5] One of the promising synthetic methodologies for producing subnano Pd clusters is by reduction of Pd ions in the presence of stabilizing agents such as polymer micelles,[4a] zeolites,[4b] and clays.[4c] Such hosts have subnano-ordered spaces to protect the small metal nuclei from aggregation. However, systematic control over the nuclearity of "naked" subnano Pd clusters by bottom-up process has not been achieved yet.[6]

Dendrimers are highly branched molecules with monodispersed molecular weight having the following characteristics: 1) tunable chemical and physical properties by designing core, branch, and surface units, 2) sterically confined nanovoids, and 3) a highly congested surface with increasing generation.[7] Due to the above combination of attributes, dendrimers have been attracting attention as unimolecular capsules for entrapping metal nanoparticles.[8] Although there are many reports on dendrimer-encapsulated metal nanoparticles with diameters ranging from 1 to 3 nm,[9] the precise control of the cluster sizes within the confined nanovoids is still challenging.

We describe here a selective synthesis of Pd clusters in the subnanometer range (Pd_n: n denotes the numbers of Pd atoms) using a fifth generation poly(propylene imine) (PPI) dendrimer functionalized with 3,4,5-triethoxybenzamide (TEBA) groups on the periphery (Figure 1A). To the best of our knowledge, this is the first report on precise control of the number of Pd atoms in such subnano clusters within the dendrimer, e.g., Pd_4, Pd_8, and Pd_{16}.

The PPI dendrimer was used as a nanocapsule on the basis of its high compatibility with Pd^{2+} ions. The primary amino groups

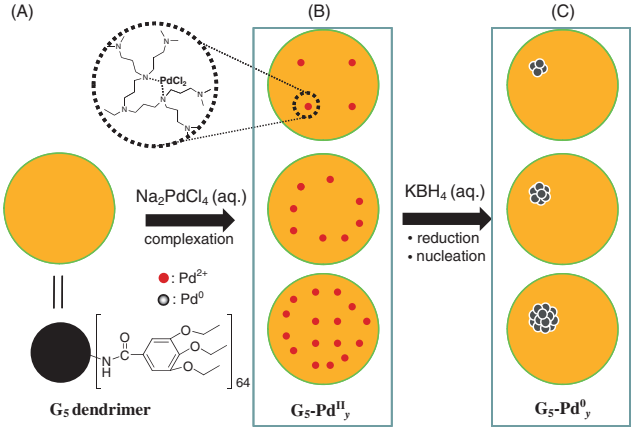

Figure 1. (A) The fifth generation of PPI dendrimer functionalized with 3,4,5-triethoxybenzamide groups (G_5 dendrimer). The number of tertially amino groups within G_5 was 62. (B) G_5–$Pd^{II}{}_y$ ($y = 4$, 8, and 16) and (C) subnano Pd clusters within G_5 dendrimers: G_5–$Pd^0{}_y$ ($y = 4$, 8, and 16). Detailed procedures are in Supporting Information.[13]

of the third to fifth generations of PPI dendrimers were functionalized with 3,4,5-triethoxybenzoic acid chloride to construct unimolecular capsules having congested shell on the surface (G_x, x denotes the generation number of the dendrimer; $x = 3$–5).[9f] An appropriate amount of aqueous solution of Na_2PdCl_4 was added to a chloroform solution of G_x, giving G_x–$Pd^{II}{}_y$ dendrimers where y represents the number of precursor Pd ions in one dendrimer ($y = 4$, 8, and 16). The G_x–$Pd^{II}{}_y$ dendrimers were further treated with an aqueous solution of KBH_4 under vigorous stirring. The light brown solution turned dark brown indicating the formation of Pd(0) clusters.

The Pd K-edge X-ray absorption fine structure (XAFS) of G_x–$Pd^{II}{}_8$ ($x = 3$–5) was examined before treatment with KBH_4: the $k^3\chi(k)$ Fourier transforms of these dendrimers showed peaks at 1.6 and 1.9 Å corresponding to Pd–Cl and Pd–N shells, respectively (Supporting Information[13]). Curve-fitting analyses suggest that the Pd^{2+} species are surrounded by two Cl and two N atoms, i.e., the $PdCl_2$ species are immobilized at the two nitrogen atoms of the dendritic branch as illustrated in Figure 1B.

Addition of KBH_4 yielded Pd^0 clusters with a new peak at 2.5 Å attributable to a Pd–Pd bond, accompanied by the diminution of the peak from the Pd–Cl shell.[10] Coordination numbers (CN) of the Pd–Pd shell of G_x–$Pd^0{}_8$ were calculated as 6.0, 5.1, and 4.6 for $x = 3$, 4, and 5, respectively.[11] Diameters of the Pd clusters for G_x–$Pd^0{}_8$ were estimated to be less than 1 nm, i.e., 0.99, 0.84, and 0.76 nm for $x = 3$, 4, and 5, respectively (Table 1 and Supporting Information[13]). Interestingly, in the

Table 1. Curve-fitting results of the Pd K-edge EXAFS[a]

Sample	Shell	CN[b]	R/Å[c]	σ^2/Å[d]	N[e]	d/nm[f]
G_5–$Pd^{II}{}_4$	Pd–N[g]	1.9	2.08	0.0004	—	—
	Pd–Cl[g]	1.8	2.29	0.0048	—	—
G_5–$Pd^0{}_4$	Pd–Pd	3.1	2.73	0.0069	4	0.50
	Pd–N	2.0	2.05	0.0034	—	—
G_5–$Pd^{II}{}_8$	Pd–N[g]	2.1	2.05	0.0044	—	—
	Pd–Cl[g]	1.9	2.26	0.0074	—	—
G_5–$Pd^0{}_8$	Pd–Pd	4.6	2.76	0.0074	8	0.76
G_5–$Pd^0{}_{16}$	Pd–Pd	5.9	2.73	0.0092	16	0.97
G_4–$Pd^0{}_8$	Pd–Pd	5.1	2.75	0.0074	10	0.84
G_3–$Pd^0{}_8$	Pd–Pd	6.0	2.75	0.0076	17	0.99

[a]The region of 1.0–2.9 Å in FT of the reduced samples was inversely transformed. [b]Coordination number. [c]Interatomic distance. [d]Debye–Waller factor. [e]Number of Pd atoms in a cluster.[11] [f]Diameter of Pd clusters.[13] [g]Before addition of aqueous KBH_4 solution.

case of the fifth generation of the dendrimer (G_5–$Pd^0{}_8$), the Pd cluster of 0.76 nm can be determined to contain 8 Pd atoms which are the same as that of the preorganized Pd^{2+} ions within one dendrimer before the KBH_4 reduction.

Next, it was attempted to control the other number of Pd atoms such as Pd_4 and Pd_{16} in the subnano clusters by using the G_5 dendrimer as a unimolecular capsule (Table 1 and Figure 1C). For $y = 4$ and 16, subnano Pd clusters having diameters of 0.50 and 0.97 nm were obtained, which correspond to the clusters composed of 4 and 16 Pd atoms, respectively. Notably, the subnano clusters composed of a specific number of Pd atoms (i.e., Pd_4, Pd_8, and Pd_{16}) were obtained by preorganization of Pd ions within one dendrimer molecule (Figure 1C).

Surface congestion and nanovoids derived from the regulated branching units of the dendrimers play important roles in the fine control of size of the subnano Pd clusters. Introduction of the bulky TEBA groups on the surface makes a highly congested shell on the G_5 PPI dendrimer. This then affords a unimolecular capsule capable of sterically confining the Pd clusters within the G_5 dendrimer.[12] In the cases of the G_3 and G_4 dendrimers, the relatively loose surface shell allows the bimolecular nucleation process that results in the formation of larger Pd clusters together with empty dendrimers.

In summary, we have succeeded in the controlled synthesis of subnano-ordered Pd clusters consisting of a specific number of Pd atoms of Pd_4, Pd_8, and Pd_{16} by preorganization of Pd ions within the PPI dendrimers and subsequent reduction. Fine tuning of the void sizes of dendrimers by changing core and branch units will expand the tailor-made synthesis of Pd particles from subnano to nano range.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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