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Engineered Polymer for Controlled Metal Nanoparticle Synthesis

Baosong Fu,[†,‡] Michael N. Missaghi,[†]
Christopher M. Downing,[§] Mayfair C. Kung,*[,†]
Harold H. Kung,*[,†] and Guomin Xiao[‡]

[†]*Department of Chemical and Biological Engineering, and*
[§]*Department of Chemistry, Northwestern University,*
Evanston, Illinois 60208-3120, and [‡]*School of Chemistry and*
Chemical Engineering, Southeast University,
Nanjing 211189, P.R. China

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Metal nanoparticles of a narrow size distribution are valuable in diverse applications including catalysis, information storage, optoelectronics, and sensors. Uniformity of particle size minimizes the dispersion of important properties critical in these operations, such as surface chemical activity and magnetic and electronic properties. Thus, there has been great interest in recent years to develop methods to synthesize monodispersed nanoparticles in high yields.[1−4] Conventional methods, such as precipitation, deposition onto a support, or ion exchange, typically result in broad size distributions. Recent approaches involve confining the metal precursors in a limited space, such as in a micelle or reverse micelle,[5] microemulsion,[6] dendrimer,[7] or functionalized polymer,[8] and resin.[9,10] Tuning of the size is achieved by adjusting the precursor concentration or density of ligating groups used to stabilize the precursors or the metal particles in the dendrimer or polymer. Although elegant, these methods are limited in their scalability, tunability, control, and/or cost. For example, micelles are stable only in high dilution, which greatly limits the throughput. Dendrimers offer excellent control of the particle size, but they are expensive and only limited types of dendrimers are readily available. In addition, the strong chemical interactions employed to stabilize the precursor or the particle often demand harsh removal treatments that cause significant coarsening of the metal particles.

Metal loading is a common vehicle to change the metal particle size−lower loadings for smaller sizes. An ideal synthetic method should permit independent control and tuning of these two variables. Here we report a simple method to achieve this by controlling separately the density of a ligating function that governs the particle size and the metal loading by the density of a reducing function or the amount of precursor used. Very importantly, by incorporating both ligating and reducing functions into a single oligomer molecule, their proximity to and interaction with the metal precursor and the metal particle can be defined, resulting in atomic-level control of the metal reduction and nucleation process and subsequent stabilization of the metal particle. We prepared Pd nanoparticles using this approach, with a linear, designer siloxane oligomer containing hydrido, silanol, and cyanopropyl groups, which is derived from poly(methylhydrosiloxane). The Si−H groups provide the reducing function, the −CN groups coordinate to surface Pd atoms and stabilize the particles from agglomeration, and the Si−OH groups can be used to form an oxide support to separate the metal particles. The final Pd particle size is controlled by the ratio of the cyanopropyl groups to the total Pd atoms, which reflects the surface to bulk ratio of Pd atoms. The use of −CN groups differentiates our method from the literature reports that used monomeric hydrosilane or hydridosiloxane oligomers or polymers,[11−13] where Si−H serves primarily as a reducing agent, although there is a possibility that it also helps stabilize small Pd particles.[14]

Scheme 1 illustrates our method. A commercially available polymethylhydrosilane (PMHS, **I**) was oxidized with water, using a $Pd_2(dba)_3$ catalyst, to convert some of its Si−H to Si−OH to form **II** (step 1).[15] The extent of oxidation was determined by the amount of water added, and could be followed by quantifying the H_2 gas evolution. After removing the water, we added a predetermined amount of 3-cyanopropylchlorodimethylsilane to react quantitatively with a desired amount of silanol (step 2) to form a cyanopropyl-modified polymethylhydrosiloxane (**III**). The ^{1}H NMR spectrum of **I** (Figure 1, spectrum 1a) shows three resonances at 0.1 (terminal Si−CH_3), 0.2 (internal Si−CH_3), and 4.7 ppm (Si−H). From the peak area ratios of terminal Si(CH_3)$_3$ to internal SiH(CH_3), the average degree of polymerization of **I** (i.e., *n*) was

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*Corresponding author.

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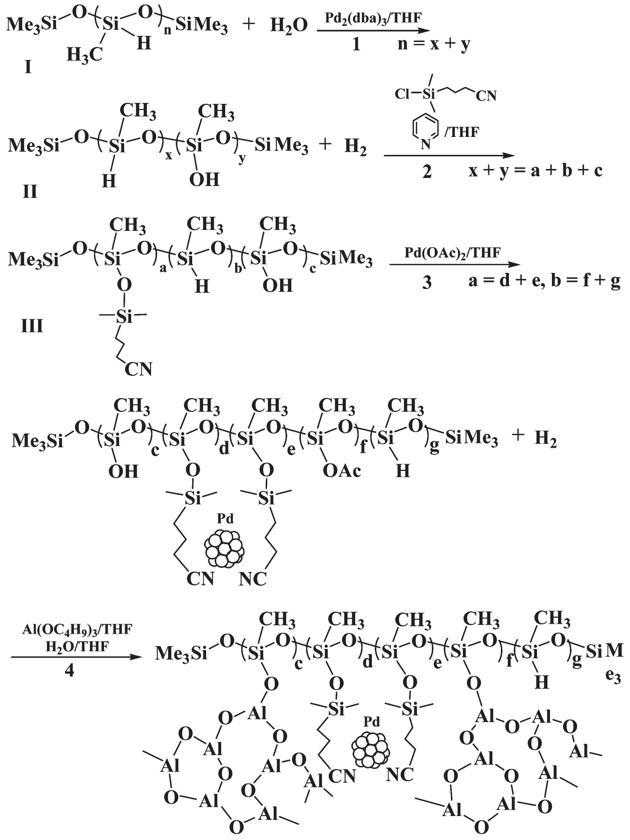
Scheme 1



estimated to be 25.7. The ^1H NMR spectrum of a partially oxidized PMHS, **II** (spectrum 1b), shows an additional broad singlet at 5.8 ppm (Si$-$O*H*), in addition to a number of new Si$-$CH_3 peaks between 0.0 and 0.2 ppm. **III** shows a ^1H NMR spectrum (spectrum 1c) with resonances at 4.7 ppm (Si$-$*H*), at around 0.1 ppm (Si$-$CH_3), as well as at 0.7, 1.7, and 2.35 ppm assigned to $-CH_2(\alpha)$, $-CH_2(\beta)$, and $-CH_2(\gamma)$ of the cyanopropyl ligand. The ^{29}Si NMR spectrum of **III** (spectrum 1d) exhibits three groups of peaks centered at around -12 (O*Si*$(CH_3)_2R$), -33 ($-$O*Si*R$(CH_3)O-$), and -62 ppm ($-$O*Si*$(OR)(CH_3)O-$).[16]

Pd particles were formed upon adding $Pd(OAc)_2$ to **III** in dry THF (step 3). In these experiments, substoichiometric amounts of $Pd(OAc)_2$ with respect to Si$-$H were added, such that the metallic Pd contents were determined by the amount of $Pd(OAc)_2$ used. Finally, aluminum(III) s-butoxide was added to react with the remaining silanols to form a gel, which could be calcined to form an oxidic support for the Pd particles. Typically, the samples were dried by heating in air to 60 °C or in vacuo for 2 h.

Samples with similar Pd particle sizes but different metal loadings were prepared by adding different amounts of $Pd(OAc)_2$ to **III** while maintaining the molar ratio of CN/Pd close to 10 (Table 1, samples 1$-$4). Representative TEM images of these samples are shown in Figure 2a$-$d and their size distributions in Figure S3 in the Supporting Information. These samples contained small Pd particles, averaging 1.3 nm and with similar size distributions, and the density of particles increased with Pd loading. Notably, the particle size remained small, even for a high loading of 5%.

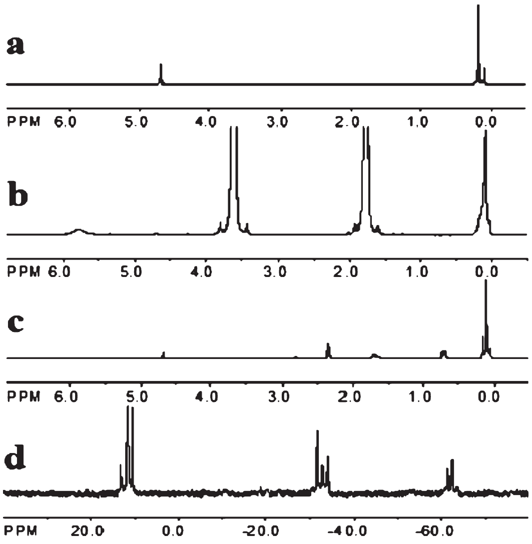


Figure 1. ^1H NMR spectra of (a) PMHS, **I**; (b) partially oxidized PMHS, **II**; and (c) **III**; and (d) ^{29}Si NMR of **III**. In spectrum b, the large resonances at around 1.8 and 3.7 ppm are solvent (THF) peaks.

Tuning the particle size distribution for a given Pd loading was achieved by using **III** of different CN densities while maintaining the amount of Pd unchanged. For samples 3, 5, 6, and 7 in Table 1, the Pd loading was 2.4$-$3.3 wt %, whereas the CN/Pd ratios varied from 0 to ~10. Figure 2e$-$g shows the TEM images of samples 5, 6, and 7, and Figure S4 in the Supporting Information shows their size distributions. The size was the smallest (~1.3 nm) for the sample with the highest CN/Pd ratio (sample 3, Figure 2c), and increased with decreasing CN/Pd ratio, from sample 7, to 6, and finally to 5, where the average particle size was 3.0 nm.

These Pd particles were quite thermally stable against sintering. When sample 3 was heated to 500 °C in air for 5 h and 400 °C in H_2 for 1 h to form sample 9, the particle size increased only from ~1.3 to ~2.8 nm (Figure 2h, Table 1, and Figure S5 in Supporting Information).

The advantages offered by the close proximity of nitrile ligands and the reducing function (Si$-$H) in stabilizing the Pd particles was illustrated by comparing Sample 3 with Sample 8. Both samples were prepared with a solution containing the same concentration of nitrile groups (6 mmol butanenitrile for sample 8 and 6 mmol nitrile in **III** is sample 3, in 15 mL THF), $Pd(OAc)_2$ (corresponding to 3 wt % Pd in the final product), and the same concentration of reducing equivalent (as **I** for sample 8, as **III** for sample 3). Sample 8 showed a significantly larger particle size (2.2 versus 1.3 nm, Figure 2i and Figure S6 in the Supporting Information).

The metal dispersions, determined by H_2 chemisorption (Table S1) confirmed the conclusion based on TEM images: the dispersion decreased in the order sample 1 > 3 > 5, and decreased after calcinations to 500 °C. The high dispersion (53$-$88%) measured also indicated that

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[16] Lee Smith, A. In *The Analytical Chemistry of Silicones*; John Wiley & Sons: New York, 1991; Chapter 12.

Table 1. Properties of Oligomer III Used and Amounts of $Pd(OAc)_2$ Added

	functional groups in polymer (mmol)						
sample[a]	−CN[b]	Si−H	Si−OH[c]	$Pd(OAc)_2$ added	Pd loading (wt %)	CN/Pd	diameter (nm)
1	1.1	3.8	3.9	0.1	0.9	11	1.3 ± 0.41
2	2.9	3.4	2.5	0.3	1.5	9.7	1.3 ± 0.42
3	5.9	2.0	0.8	0.6	2.5	9.8	1.3 ± 0.44
4	5.2	2.1	1.4	1	5.0	5.2	1.3 ± 0.42
5	0	9.2	0	0.6	3.3	0	3.0 ± 0.80
6	0.6	2.5	5.7	0.6	3.0	1	2.4 ± 0.80
7	2.0	2.5	4.3	0.6	2.4	3	1.6 ± 0.48
8[d]	6.0	9.2	0	0.6	3.0	10	2.2 ± 0.63
9[e]				0.6	2.5		2.8 ± 0.58

[a] Every sample started with 10 mmol Si as PMHS, or 9.2 mmol Si−H units. ^1H NMR of these modified polysiloxane are shown in Figures S1 and S2 in the Supporting Information. [b] The quantity of −CN was assumed to be the same as $-CH_2(\alpha)$, which was estimated from the $CH_2(\alpha)$ and the CH_3 resonances in ^1H NMR of **III** (see Figure S2 in the Supporting Information). [c] Difference between mmoles of H_2 collected and of −CN. [d] Prepared with butanenitrile and PMHS in THF instead of engineered siloxane polymer. [e] Obtained by calcining sample 3 at 500 °C in air and then 400 °C in H_2.

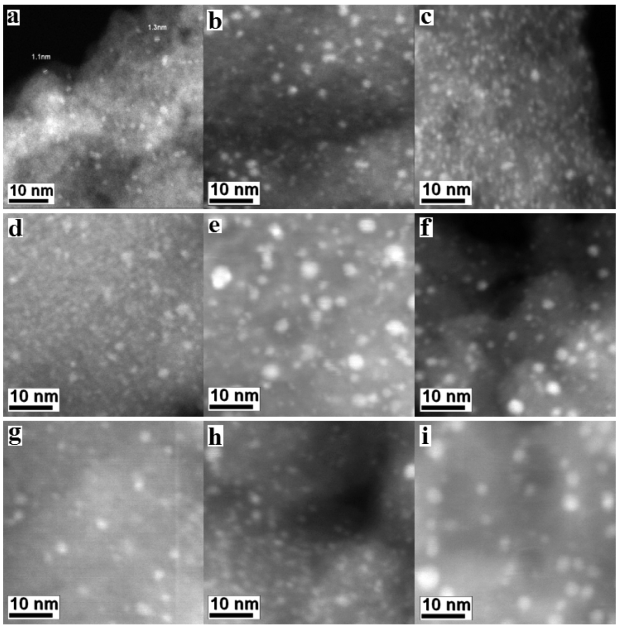

Figure 2. TEM images of samples in Table 1: sample (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, and (i) 9.

the Pd particles are easily accessible even after treatment at as low as 200 °C.

The FTIR spectra of samples heated to 150 °C showed retention of −CN at 2260 cm^{-1} (C≡N stretch) and 580 cm^{-1} (C≡N bending) (Figure S7A for sample 4). Peaks at 2170 cm^{-1} (Si−H stretch), 840 cm^{-1} (Si−H bending), 2980 cm^{-1} (C−H stretch), 1470 cm^{-1} (C−H bending), 1000−1160 cm^{-1} (Si−O−Si vibrations), 1260 cm^{-1} (Si−C−H vibration), and 3100−3600 cm^{-1} (O−H stretches) were also detected.[17] Calcination at 500 °C removed practically all peaks due to the Si−H and C−H bonds (Figure S7B). Peaks due to silica−alumina framework vibration remained.

CO chemisorptions on Samples 3 and 5 (with and without nitrile stabilization, respectively), heated to 120 °C (Figure S8) or 500 °C (see Figure S9 in the Supporting Information) were investigated by diffuse reflectance FTIR. Linearly adsorbed CO on Pd atoms at corners and edges (2077−2080 cm^{-1}) and $\mu2$ bridge-bonded CO and $\mu3$ CO on 3-fold hollow sites (1950−1850 cm^{-1}) were observed on all samples.[18] The relative intensities of the linear to bridging CO were higher for sample 3 than for sample 5 when compared at the same pretreatment temperature, consistent with its smaller Pd particle size. After 500 °C calcination and then reduction, the linear CO peak was split into a peak at 2086 cm^{-1} (linear CO on corner sites) and another at 2055 cm^{-1} (linear CO on (111/(111)) and (111/(100)) edge sites[17]). The relative intensities of the linear to bridged bonded CO peaks remained higher for sample 3 than for sample 5, suggesting retention of a higher metal dispersion in the former sample.

In conclusion, we have devised a general, easy-to-apply method to prepare metal nanoparticles that permit independent control of metal particle size at the nanometer scale and loading. The method makes use of a designer oligomer that is derived from the readily available polymethylhydrosiloxane to contain reducing and anchoring functionalities in close proximity. The inclusion of a third functional group (Si−OH) in the designer molecule further permits connecting the polymer, and consequently the metal particles, to a variety of oxidic supports. This versatile method should be applicable to different metals and for different support oxides.

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Supporting Information Available: Details on preparation procedure and characterization, NMR spectra, particle size distribution, IR and H_2 dispersion, and CO chemisorption (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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