Heterogeneous Seeded Growth: A Potentially General Synthesis of Monodisperse Metallic Nanoparticles

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We report growth of nearly monodisperse Bi, Sn, and In nanoparticles of various sizes upon 1.5-nm Au seeds.

The mechanisms by which monodisperse colloid or nanoparticle samples may form are currently under debate. Two proposed mechanisms assert that the rates of nanoparticle nucleation and growth must be widely separated: the classic LaMer mechanism,[1] which features fast, supersaturated-burst nucleation and slow growth, and the Finke mechanism,[2] which features slow, continuous nucleation and fast, autocatalytic surface growth. A third, aggregative mechanism proposed by Zukoski[3] and others[4] does not neatly distinguish the time scales for nucleation and growth. Unfortunately, all three mechanisms appear to require circumstances that are not easily extended to the general case, and none provides a simple rationale for controlling nanoparticle mean size.

We propose a fourth mechanism, seeded growth, which is known (see below), but largely unrecognized potential. In seeded growth, preformed seeds provide the nuclei for subsequent growth of metallic nanoparticles. The seeds (nuclei) need not have the same composition as the material deposited upon them. We show that seeded growth fulfills the criterion of widely separated nucleation and growth kinetics and may offer a general strategy for the formation of a wide variety of monodisperse metallic nanoparticles of specified size.

Seeded growth has been employed in a few cases for the growth of large metallic nanoparticles on seeds of the same metal (homogeneous seeded growth).[5–9] Seeded growth has also been used to prepare core–shell bimetallic nanoparticles in which the cores constitute a substantial volume fraction of the nanoparticles (heterogeneous seeded growth).[10] Watzky and Finke demonstrated the potential of *homogeneous* seeded growth to control the sizes and dispersities of metallic nanoparticles and suggested a similar potential for *heterogeneous* seeded growth.[2,11] Here we demonstrate experimentally, with three types of metallic nanoparticles, that heterogeneous seeded growth affords rational size control, while maintaining narrow size distributions.

Metallic nanoparticles are of current interest as optical probes,[12] nanoscale ferromagnets,[13] catalysts for organic reactions,[2,14] and catalysts for VLS[15,16] and SLS[17,18] growth of nanowires. We are attempting to prepare monodisperse semiconductor quantum wires over a range of controlled diameters (2–20 nm) by the low-temperature SLS mechanism,[18] and have therefore sought monodisperse catalyst nanoparticles of low-melting metals such as Bi, Sn, and In having similar, selected sizes. Chaudret and co-workers (Sn,[19] In[20]), and Foos and co-workers (Bi[21]) have synthesized nanoparticles of these metals but not over the range of specific sizes we desire.

We use the $Au_{101}(PPh_3)_{21}Cl_5$ clusters reported by Hutchison and co-workers,[22] which have 1.5-nm diameter Au cores, as the heterogeneous nucleants or seeds. Deposition of Bi, Sn, or In at sufficiently low temperatures and precursor concentrations should avoid homogeneous (self) nucleation. Thus, all deposition should occur upon the Au seeds, leading to narrow size dispersions. Knowledge of the number of seeds used, seed size, amount of Bi, Sn, or In precursor used, and the metal densities then allows simple stoichiometric calculation of the expected nanoparticle mean size. We compare our observed nanoparticle mean sizes to such theoretical sizes below.

The resulting nanoparticles are not pure, because of the Au contamination. However, the amount of Au in the nanoparticles becomes vanishingly small upon a modest extent of growth. For example, stoichiometric calculations show that Bi nanoparticles grown to 6.6-nm final diameters on 1.5-nm Au seeds should contain only 2.5 mol % Au.

Growth was accomplished by decomposing the precursors $Bi[N(SiMe_3)_2]_3$,[23] $Sn(NMe_2)_2$,[24] or $In(C_5H_5)$[25] in solutions containing the Au seeds, with polymers added to stabilize the nanoparticles. The synthetic methods, described in the Supporting Information, were derived from those previously employed by Chaudret and co-workers.[19,20] The Bi and Sn precursors were thermally decomposed at 150 and 140 °C, respectively, in the presence of poly(styrene$_{0.86}$-*co*-vinyl-pyrrolidinone$_{0.14}$). The In precursor was decomposed at room temperature by addition of methanol, in the presence of poly(vinylpyrrolidinone). The resulting nanoparticles formed black dispersions that were stable for weeks, from which the nanoparticles could be precipitated as black solids upon addition of appropriate cosolvents.

The nanoparticles were characterized by transmission electron microscopy (TEM), electron diffraction, energy-dispersive X-ray spectroscopy (EDS), and X-ray powder diffraction (XRD). Representative TEM images are shown in Figure 1. The Bi and Sn samples consisted of apparently spherical nanoparticles with smooth surfaces. The In nanoparticles were also essentially

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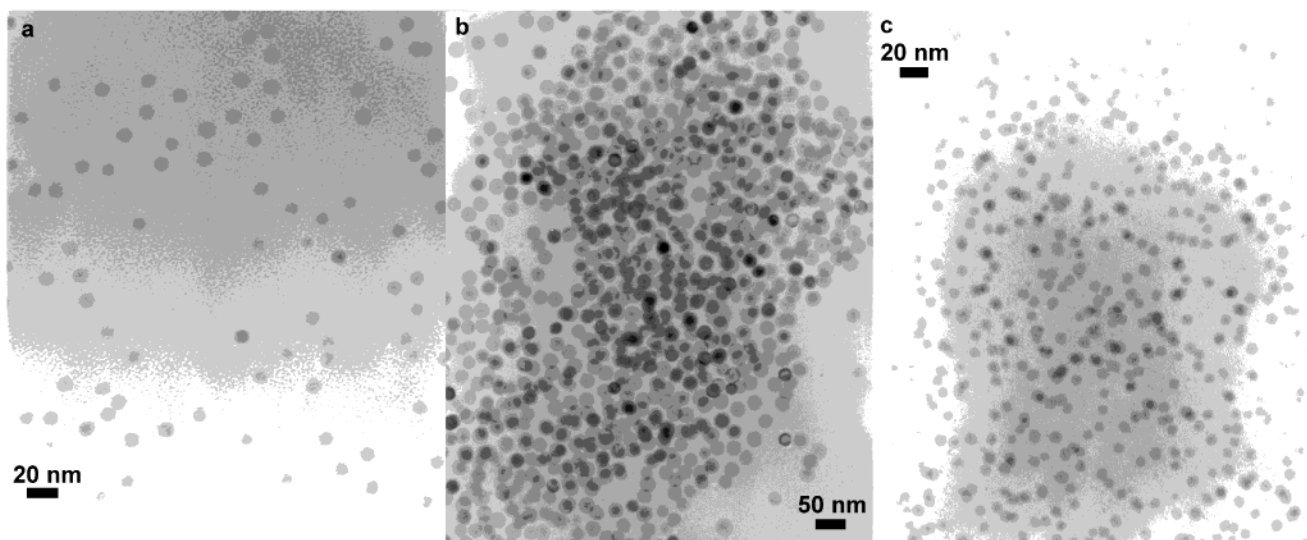(6) Shirtcliffe, N.; Nickel, U.; Schneider, S. *J. Colloid Interface Sci.* **1999**, *211*, 122–129.
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Figure 1. Representative TEM images: (a) 9.3-nm Bi (Bi/2), (b) 25.4-nm Sn (Sn/1), and (c) 7.1-nm In (In/3) nanoparticles.

Table 1. Theoretical and Observed Nanoparticle Diameters

M/trial	d_{theor} (nm)	d_{obs} (nm)[a]	d_{obs}/d_{theor}
Bi/1	10.1	12.4 ± 0.9 (± 7.2%)	1.2
Bi/2	6.6	9.3 ± 0.7 (± 7.3%)	1.4
Bi/3	6.0	8.6 ± 0.5 (± 5.6%)	1.4
Sn/1	16.7	25.4 ± 1.8 (± 7.1%)	1.5
Sn/2	14.5	17.3 ± 1.2 (± 6.7%)	1.2
Sn/3	9.7	10.5 ± 1.4 (± 13.2%)	1.1
In/1	22.7	15.7 ± 1.5 (± 9.6%)	0.69
In/2	8.7	9.1 ± 0.9 (± 10.2%)	1.0
In/3	7.0	7.1 ± 0.5 (± 7.0%)	1.0

[a] Mean diameter ± one standard deviation.

spherical, but often contained surface features or deposits of an unknown nature. Rough surfaces were particularly evident in the largest (15.7-nm) In nanoparticles. Electron diffraction and XRD established the conventional crystal structures and normal lattice parameters of the as-grown Bi, Sn, and In nanoparticles (see the Supporting Information). EDS confirmed the presence of Au in the samples. However, our characterization did not distinguish if the Au remained at the cores, or became otherwise distributed throughout the nanoparticles.

As shown in Figure 1, the nanoparticle samples grown upon the Au seeds approached monodispersity. Particle-size distributions for each sample were determined by manual measurement using enlarged TEM images. The results, summarized in Table 1, confirmed narrow size distributions, with standard deviations generally within 7−10% of the nanoparticle mean diameters. In contrast, nanoparticle syntheses conducted as control experiments *without* the Au seeds typically gave extremely broad size distributions.

Table 1 reveals several of the observed nanoparticle mean diameters (d_{obs}) to be either smaller or larger than predicted by stoichiometric calculations (d_{theor}). We propose that these differences are consistent with the two primary complications to size control by seeded growth.

Note that two of the In samples exhibited the predicted sizes ($d_{obs}/d_{theor} = 1$). The third In sample (In/1 in Table 1) exhibited a smaller mean size ($d_{obs}/d_{theor} < 1$). This sample was grown with a drastically smaller number of Au seeds, which should increase the probability for *homogeneous* nucleation, that is, for the formation of and subsequent growth upon In nuclei (seeds), co-occurring with growth upon the Au seeds. We surmise that homogeneous nucleation of In seeds became favorable because the In nutrient was generated from the precursor at a rate faster than the smaller number of Au seeds could consume. The additional (In) seeds increased the number of growing particles competing for the available In nutrient, resulting in a nanoparticle mean size that was smaller than predicted for growth occurring exclusively upon the Au seeds.

In contrast, the observed mean diameters for the Bi and Sn nanoparticles were larger than predicted (Table 1). Aiken and Finke have found that surface growth (comparable to seeded growth) and nanoparticle aggregation (coalescence) are always in competition.[26] The Bi and Sn nanoparticles were grown at elevated temperatures (140−150 °C), which should favor nanoparticle aggregation. Thermal coalescence of either the Au seeds or the metal nanoparticles would decrease the number of growing particles and shift the size distributions to larger-than-predicted diameters, as observed. Such aggregation could presumably be diminished by better polymer or ligand stabilization of nanoparticles and seeds, or by improved precursors and decreased growth temperatures.

Therefore, both homogeneous nucleation and nanoparticle aggregation can interfere with the seeded-growth rationale for size control. Even so, by comparison to the other synthetic methods that we know of, the seeded-growth strategy and results reported here come closest to providing monodisperse metallic nanoparticles of pre-specified sizes. The 1.5-nm Au clusters[22] appear to be potent heterogeneous nucleants for growth of metallic nanoparticles and may support development of seeded growth as a general method. Further work should extend the range of metallic nanoparticles available and improve the size-control afforded.

Supporting Information Available: Experimental procedures, a complete set of particle-size histograms, associated TEM images, and XRD and electron-diffraction patterns (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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