Improved Synthesis of Small ($d_{CORE} \approx 1.5$ nm) Phosphine-Stabilized Gold Nanoparticles

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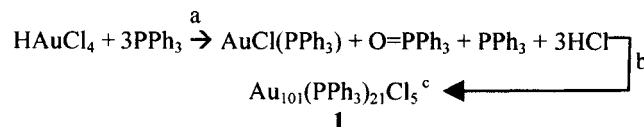*University of Oregon, Eugene, Oregon 97403-1253*

Phosphine-stabilized gold nanoparticles, originally formulated as $Au_{55}(PPh_3)_{12}Cl_6$ by Schmid et al.[1] in 1981, have been widely investigated as models for metallic catalysts[2] and as building blocks for nanoscale electronic devices.[3,4] Although the original formulation has been disputed,[5−8] the small size and narrow dispersity (1.4 ± 0.4 nm)[7] of the as-synthesized material is unparalleled, largely eliminating the need for fractional crystallization or chromatographic size selection.[9] The synthesis is cumbersome, however, requiring rigorously anaerobic conditions and diborane gas as a reducing agent. As a result, phosphine-stabilized gold nanoparticles have lost favor since the development of a more convenient, scalable synthesis of thiol-stabilized gold nanoparticles by the method of Brust et al.[10] To fully develop the rich chemistry of phosphine-stabilized nanoparticles improved syntheses are needed.

Phosphine-stabilized nanoparticles are excellent precursors to other functionalized nanoparticle building blocks possessing well-defined metallic cores.[3] From this common precursor we have recently prepared a wide variety of ligand-stabilized nanoparticles where nearly any functional group can be introduced into the ligand shell, and the metal core size can be tuned from 1.4 to 10 nm in diameter through ligand exchange reactions.[11,12] The small size, narrow dispersity, and enhanced stability of the 1.4-nm alkanethiol-stabilized nanoparticles have been exploited in numerous studies of nanoparticle-based nanoelectronic materials.[4,13,14]

A more convenient synthesis of phosphine-stabilized gold nanoparticles would provide the opportunity to fully explore the use of these unique building blocks.[15] Here we describe a safer,

Scheme 1. Reaction Pathway to Nanoparticle **1**

$$HAuCl_4 + 3PPh_3 \xrightarrow{a} AuCl(PPh_3) + O=PPh_3 + PPh_3 + 3HCl$$

$$Au_{101}(PPh_3)_{21}Cl_5^c \xleftarrow{b}$$

1

[a] Toluene, water, tetraoctylammonium bromide, 5 min, room temperature. [b] 10 equiv of sodium borohydride, 3 h, room temperature. [c] Average empirical formula based on atomic composition measurements by XPS and an assumed 101 gold atom core. See text for details.

more convenient, and more versatile synthesis of phosphine-stabilized nanoparticles analogous to those originally reported by Schmid.[1] The synthesis eliminates the use of diborane or borane, can be carried out quickly under ambient conditions, permits the use of a variety of phosphines as passivating ligands, and provides control over particle core size.

The convenient biphasic reaction conditions (Scheme 1) produce 1.5-nm nanoparticles that can be easily prepared from commercially available materials. Hydrogen tetrachloroaurate trihydrate (1.00 g, 2.54 mmol) and tetraoctylammonium bromide (1.60 g, 2.93 mmol) were dissolved in a nitrogen[16] sparged water/toluene mixture (50 mL/65 mL). When the golden color had transferred into the organic phase, triphenylphosphine (2.32 g, 8.85 mmol) was added and the solution was stirred vigorously for at least 10 min until the organic phase was white and cloudy. Aqueous sodium borohydride (1.41 g, 37.3 mmol, dissolved in 10 mL of water immediately prior to use) was rapidly added (this addition results in vigorous bubbling and should be performed cautiously). The organic phase immediately turned dark purple after which it was stirred for 3 h under nitrogen. The toluene layer was separated and washed with water (2×100 mL). The solvent was removed in vacuo or with a stream of nitrogen[17] to yield a black solid.

The resulting solid was washed with a series of solvents (hexanes, saturated aqueous sodium nitrite, and a 2:3 methanol:water mixture) to remove the phase transfer catalyst, byproducts, and unreacted starting materials.[18] Further purification by precipitation from chloroform upon slow addition of pentane (typically 2−3 precipitations) removed Au salts such as AuCl(PPh₃). After purification, the yield is 170 mg of purified nanoparticle **1** from 1 g of $HAuCl_4$.

Direct evidence of nanoparticle size and dispersity is provided by transmission electron microscopy (TEM).[18] A representative TEM (Figure 1a) shows narrowly disperse nanoparticles 1.5 nm $\pm$ 0.4 nm in diameter, comparable to material produced by the traditional synthesis[19] (1.4 nm $\pm$ 0.4 nm).[7] UV−vis spectroscopy confirmed the size determined by TEM. A representative UV−vis spectrum of **1** (Figure 1b) shows no significant plasmon resonance at 520 nm, indicative of gold nanoparticles that are <2 nm in diameter.[20]

The atomic composition of **1** was determined by using the complementary techniques of X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA).[18] XPS spectra indicate an atomic ratio of 19.1 Au to 4 P to 1 Cl for the nanoparticles and show that 3.7 mass percent of the sample is

(1) Schmid, G.; Pfeil, R.; Boese, R.; Bandermann, F.; Meyer, S.; Calis, G. H. M.; van der Velden, J. W. A. *Chem. Ber.* **1981**, *114*, 3634.

(2) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709.

(3) (a) Schön, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 101. (b) Averin, D. V.; Likharev, K. K. J. *Low Temp. Phys.* **1986**, *62*, 345. (c) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger, R. *Science* **1996**, *272*, 1323. (d) Janes, D. B.; Kolagunta, V. R.; Osifchin, R. G.; Bielefeld, J. D.; Andres, R. P.; Henderson, J. I.; Kubiak, C. P. *Superlattices Microstruct.* **1995**, *18*, 275. (e) Feldheim, D. L.; Grabar, K. C.; Natan, M. J.; Mallouk, T. E. *J. Am. Chem. Soc.* **1996**, *118*, 7640.

(4) Clarke, L.; Wybourne, M. N.; Brown, L. O.; Hutchison, J. E.; Yan, M.; Cai, S. X.; Keana, J. F. W. *Semicond. Sci. Technol.* **1998**, *13*, A111.

(5) Gutiérrez, E.; Powell, R. D.; Furuya, F. R.; Hainfels, J. F.; Schaaff, T. G.; Shafigullin, M. N.; Stephens, P. W.; Whetten, R. L. *Eur. Phys. J. D* **1999**, *9*, 647.

(6) (a) McNeal, C. J.; Winpenny, R. E. P.; Hughes, J. M.; Macfarlane, R. D.; Pignolet, L. H.; Nelson, L. T. J.; Gardner, T. G.; Irgens, L. H.; Vigh, G.; Fackler, J. P., Jr. *Inorg. Chem.* **1993**, *32*, 5582. (b) Fackler, J. P., Jr.; McNeal C. J.; Winpenny, R. E. P.; Pignolet, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 6434.

(7) Rapoport, D. H.; Vogel, W.; Cölfen, H.; Schlögl, R. *J. Phys. Chem. B* **1997**, *101*, 4175.

(8) Vogel, W.; Rosner, B.; Tesche, B. *J. Phys. Chem.* **1993**, *97*, 11611.

(9) (a) Monolayer samples prepared by electrostatic assembly of phosphine-stabilized nanoparticles on a surface have shown narrower dispersities than bulk samples.[9b] (b) Schmid, G.; Bäumle, M.; Beyer, N. *Angew. Chem., Int. Ed.* **2000**, *39*, 181.

(10) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801.

(11) Brown, L. O.; Hutchison, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 12384.

(12) Brown, L. O.; Hutchison, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 882.

(13) Clarke, L.; Wybourne, M. N.; Yan, M.; Cai, S. X.; Brown, L. O.; Hutchison, J. E.; Keana, J. F. W. *J. Vac. Sci. Technol. B* **1997**, *15*, 2925.

(14) Wybourne, M. N.; Hutchison, J. E.; Clarke, L.; Brown, L. O.; Mooster, J. L. *Microelectron. Eng.* **1999**, *47*, 55.

(15) Although phosphine-stabilized gold nanoparticles are commercially available as biological taggants for electron microscopy, they are too expensive for most applications. Nonreactive 1.4-nm gold particles (Nanogold) are available from Nanoprobes, Inc. (http://nanoprobes.com). The current price (as of 7/00) is $152/30 nmol or around $338000/g.
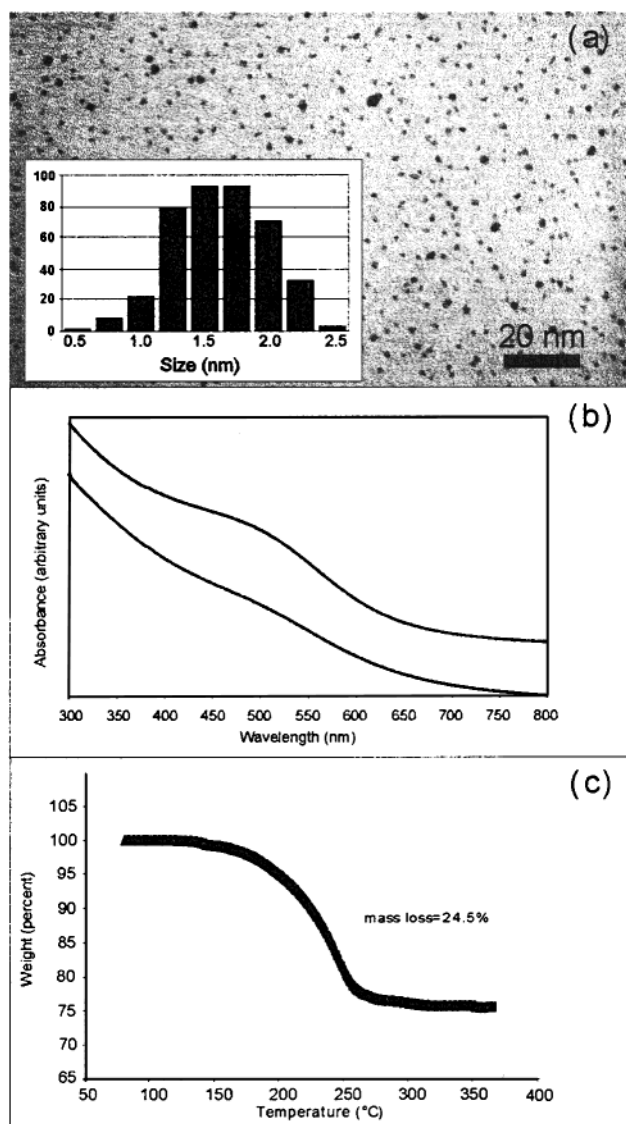
(16) The synthesis is also successful using unsparged solvents in air.

(17) Excessive heating causes decomposition of the nanoparticles.

(18) See Supporting Information.

(19) Schmid, G. *Inorg. Synth.* **1990**, *27*, 214.

(20) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M. N.; Vezmar, I.; Whetten R. L. *J. Phys. Chem. B* **1997**, *101*, 3706.

Figure 1. (a) TEM of **1**, $d_{\text{CORE}} = 1.5$ nm $\pm$ 0.4 nm ($N = 408$). (b) UV−vis spectra (CH$_2$Cl$_2$) of **1** (lower trace). The lack of a significant plasmon resonance at 520 nm indicates $d_{\text{CORE}} < 2$ nm. Shown for comparison is the spectrum of larger tricyclohexylphosphine-stabilized gold nanoparticles (upper trace). (c) TGA of **1**, indicating that 75.5% of the sample is gold.

the impurity AuCl(PPh$_3$). Taking into account this impurity, the mass percent of gold calculated by quantification of the XPS data is 75.8%. TGA indicates that 75.5% of the sample is gold by mass (Figure 1c), independently confirming the ratio determined by XPS. To calculate an average molecular formula for **1** it is necessary to know the number of gold atoms in the metal core. Given the average particle size (1.5 nm) this number is estimated to be ∼101 by the method of Whetten et al.[21] and leads to an estimated formula of Au$_{101}$(PPh$_3$)$_{21}$Cl$_5$.

The ligand exchange reactivity of nanoparticle **1** with thiols is indistinguishable from that of the Schmid nanoparticles. Using previously reported methods we have exchanged a number of *n*-alkanethiol[11] and water-soluble *ω*-functionalized-alkanethiol[22]

ligands onto the two types of nanoparticles. In all cases the materials produced with the phosphine-stabilized particle **1** displayed the same properties (e.g., size, solubility, and stability) as those derived from the Schmid preparation. These results suggest that the newly synthesized nanoparticles are functionally the same as the nanoparticles prepared by Schmid's method.

This synthesis provides a general approach to tuning the molecular composition and metal core size within the class of phosphine-stabilized nanoparticles. For example, we have successfully synthesized trioctylphosphine- and tricyclohexylphosphine-stabilized gold nanoparticles under the same conditions used to prepare **1**. We found that the core size of these nanoparticles is larger as evidenced by the increased plasmon absorbance in the UV−vis spectrum (see Figure 1b, upper trace). Based upon these initial results we expect that control of ligand shell composition and nanoparticle core size similar to that widely exploited for alkanethiol-stabilized gold nanoparticles[23] will be possible.

We now turn our attention to the reaction conditions that yield nanoparticle **1**. The reaction occurs in two steps (Scheme 1), analogous to the popular method of Brust et al.[10] In the first step the gold precursor is transferred to the organic layer where, we hypothesize, it reacts with triphenylphosphine to yield 1 equiv each of AuCl(PPh$_3$), triphenylphosphine, and triphenylphosphine oxide and 3 equiv of HCl.[24] In the second step, the mixture is reduced by NaBH$_4$. When this mixture (AuCl(PPh$_3$)/O=PPh$_3$/PPh$_3$/3HCl) was prepared separately and reduced with NaBH$_4$ under phase transfer conditions, the crude product (as analyzed by UV−vis spectroscopy) was similar to a crude preparation of **1**. Reduction of AuCl(PPh$_3$) alone with sodium borohydride results in smaller cluster compounds (such as undecagold),[25] suggesting that the composition of the mixture affects nanoparticle formation. We are investigating the role of each reactant in hopes of elucidating the function of each in nanoparticle formation and enabling further tuning of nanoparticle properties.

This new, simple synthesis coupled with an improved understanding of the properties of phosphine-stabilized nanoparticles presents the opportunity to reinvigorate the study and use of these materials. The ability to easily prepare larger amounts of phosphine-stabilized nanoparticles in a single step with sodium borohydride in place of diborane should permit the use of this material in a wider range of applications. In addition, the synthesis allows size control and is tolerant of a variety of phosphine ligands, providing access to previously unknown phosphine-stabilized nanoparticles.

Supporting Information Available: Synthetic methods with a detailed description of purification of **1** including information regarding characterization by ^{1}H NMR, XPS, TEM, UV−vis, and TGA (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA002673N

(21) Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L.; Cullen, W. G.; First, P. N.; Gutiérrez-Wing C.; Ascensio, J.; Jose-Yacamán M. J. *J. Phys. Chem. B* **1997**, *101*, 7885.

(22) Warner, M. G.; Reed, S. M.; Hutchison, J. E. *Chem. Mat*. **2000**, *12*, 3316.

(23) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17.

(24) Braunstein, P.; Lehner, H.; Matt, D. *Inorg. Synth*. **1990**, *27*, 218.

(25) (a) Cariati, F.; Naldini, L. *Inorg. Chim. Acta* **1971**, *5*, 172. (b) Bartlett, P. A.; Bauer, B.; Singer, S. J. *J. Am. Chem. Soc*. **1978**, *100*, 5085.