J. Am. Chem. Soc. 1994, 116, 7401–7402

# Size-Selective Synthesis of Nanostructured Transition Metal Clusters

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*Received May 2, 1994*

Current interest in transition metal clusters and colloids in the nanometer size range is driven by fundamental and practical reasons.[1] Particles in the range 1-10 nm have been predicted to have unusual electronic properties which may lead to new technologies based on advanced materials, e.g., quantum dots in the miniaturization of electronic devices.[1,2] Furthermore, some of these particles have already been shown to have novel catalytic properties,[1–7] and more applications in the general area of catalysis, photocatalysis, and electrocatalysis are likely. The preparation of these materials involves such techniques as metal vaporization or reduction of metal salts by a wide variety of reducing agents.[1,3] In order to prevent agglomeration, these processes are often performed in the presence of stabilizing ligands,[4] polymers,[5] or surfactants such as tetraalkylammonium salts;[6,7] metal particles have also been immobilized on metal oxide supports[1] and in zeolite cages.[8] Although some progress in the control of particle size of nanostructured metal clusters has been made by varying the temperature, concentration, reducing agent, and solvent,[1] it has recently been stated that "true control of particle size remains the most attractive goal for the synthetic chemist in this field".[9] In this communication we demonstrate for the first time that electrochemical methods[10] can be used to produce certain transition metal colloids in the nanometer region, and that the particle size can be controlled in a simple manner by adjustment of the current density.

The process makes use of an inexpensive two-electrode setup for 50–250-mL electrolyte solutions in which the sacrificial anode consists of the bulk metal to be transformed into metal clusters.

**Scheme 1.** Electrochemical Synthesis of Stabilized Metal Clusters[a]

$$\text{Anode:}\quad \text{Met}_{\text{bulk}} \longrightarrow \text{Met}^{n+} + ne^-$$

$$\text{Cathode:}\quad \text{Met}^{n+} + ne^- + \text{stabilizer} \longrightarrow \text{Met}_{\text{coll}}/\text{stabilizer}$$

$$\text{Sum:}\quad \text{Met}_{\text{bulk}} + \text{stabilizer} \longrightarrow \text{Met}_{\text{coll}}/\text{stabilizer}$$

[a] $\text{Met}_{\text{bulk}}$ = bulk metal sheet; $\text{Met}_{\text{coll}}/\text{stabilizer}$ = ammonium salt stabilized colloidal metal cluster.

Dry oxygen-free solvents are used under an argon atmosphere. Potentiostatic control is not necessary. The supporting electrolyte consists of tetraalkylammonium salts, which also serve as stabilizers for the metal clusters. Thus, in the overall process the bulk metal is oxidized at the anode, the metal cations migrate to the cathode, and rereduction takes place with formation of metal in the zero oxidation state. Agglomeration with formation of undesired metal powders is prevented by the presence of the ammonium stabilizers (Scheme 1).

In the initial experiment we employed a palladium sheet (2 cm × 5 cm) as the anode and a platinum sheet (2 cm × 5 cm) as the cathode, the two being 5 mm apart. Tetraoctylammonium bromide (0.1 M) in acetonitrile/tetrahydrofuran (4:1) served as the supporting electrolyte. Upon applying a current density of 0.1 mA/cm$^2$ and an applied voltage of 1 V (vs counter electrode), we obtained >95% of a palladium cluster stabilized by tetraoctylammonium bromide, the current yield being >95%. In the present context current yield is the fraction of the total charge used for the observed amount of dissolution ($Pd \rightarrow Pd^{2+} + 2e^-$). Since the material is essentially insoluble in the solvent mixture used, workup turned out to be particularly simple (decantation and drying in vacuo). The solid black material is stable in air and can be fully redispersed in THF or toluene in concentrations of up to 1 M. Elemental analysis of the solid material consisting of the metal and tetraoctylammonium bromide points to a palladium content of 72.8% (C, 19.1%; H, 3.27%; N, 0.6%; Br, 3.98%). Since the elemental analysis is correct within ±0.5%, there is little, if any, oxidized form of Pd present. NMR and MS studies are in accord with the presence of tetraoctylammonium bromide. Analysis by transmission electron microscopy (TEM) shows a mean particle size of 4.8 nm (Figure 1c).

In order to see if the current density has any effect upon particle size, we repeated the process using current densities of 0.8 and 5.0 mA/cm$^2$, respectively, under otherwise identical conditions. Significantly, we obtained in a fully analogous manner materials having a mean particle size of 3.1 and 1.4 nm, respectively (Figure 1b,a). The palladium content as determined by elemental analyses turned out to be 71–72%. Solubility in various solvents is similar in all three cases.

The results clearly show that the particle size of the Pd clusters can be controlled by variation of the current density, which directly influences the reduction potential at the cathode. The higher the current density, the higher the overpotential, which is defined as the deviation of the reduction potential from the equilibrium potential.[11] With increasing current density and therefore overpotential, the particle size of the colloid decreases (Figure 2). A typical size distribution diagram is shown in Figure 3.

The precipitation of the clusters not only makes simple isolation possible. It also means that the electrolyte solution does not contain particles which could change the electrochemical properties of the system during electrolysis.

Although the precise mechanism of colloid formation is difficult to determine, the gross features can be described as follows. The reduction of the palladium ions affords so-called adatoms[11] in the

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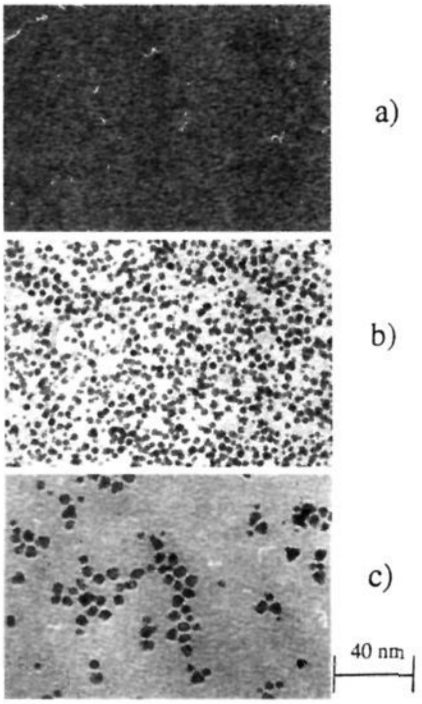

**Figure 1.** Transmission electron micrographs of Pd clusters prepared at current densities of (a) 5.0, (b) 0.8, and (c) 0.1 mA/cm$^2$; in all cases magnification of 250 000.

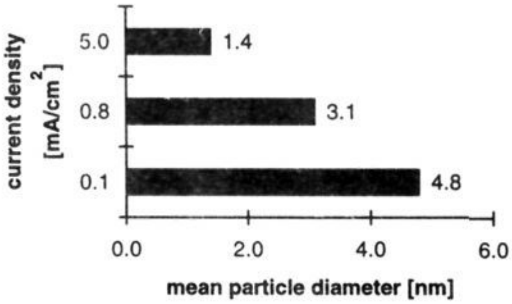

**Figure 2.** Dependence of average particle size of Pd clusters on the current density during electrolysis; averaged over 200 particles.

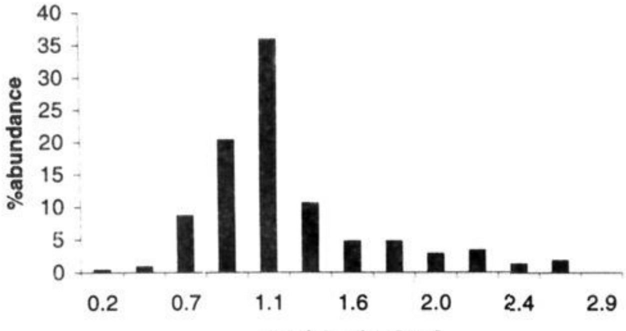

**Figure 3.** Size distribution diagram of the Pd particles in Figure 1a.

vicinity of ammonium ions near the surface of the cathode. The Pd adatoms then form clusters which are stabilized by the ammonium ions (Figure 4). If solvents are chosen in which the stabilized clusters are insoluble, they precipitate out as solid materials which can be dissolved in proper solvents.

It is known from the literature on electrochemistry that the critical radius $r_{\text{crit}}$ of clusters of adatoms (prior to powder formation) at the cathode interface is given by the equation[11]

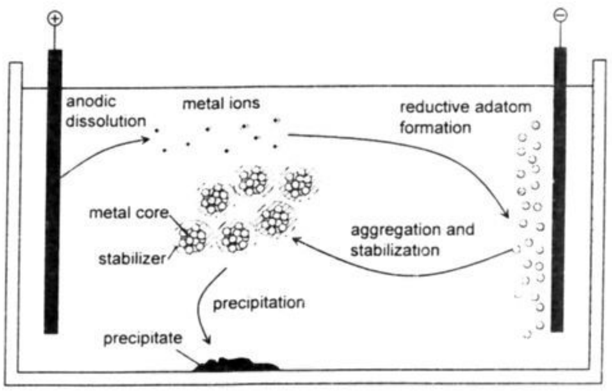

**Figure 4.** Formation of electrochemically produced tetraalkylammonium-stabilized metal clusters.

$$r_{\text{crit}} = \frac{2M\gamma}{nF\eta\rho}$$

where $M$ = molecular weight, $\gamma$ = surface tension, $F$ = Faraday constant, $\eta$ = overpotential, $\rho$ = density of the cluster, and $n$ = valency. Accordingly, $r_{\text{crit}}$ is inversely dependent on the overpotential $\eta$, which in turn is directly related to the current density. Indeed, the cluster sizes observed are in the predicted range.[12] This means that the ammonium ions are highly effective stabilizers which prevent metal agglomeration with formation of undesired powders.

The method is effective using a wide variety of tetraalkylammonium and phosphonium salts (e.g., tributylhexadecylphosphonium bromide). A precipitate consisting of, e.g., 3.8-nm Pd particles soluble in DMF can be obtained by employing tetrabutylammonium bromide in THF as the electrolyte. The use of longer chain alkylammonium salts (e.g., tetraoctadecylammonium bromide) leads to precipitates soluble even in nonpolar solvents like pentane. On the other hand, water solubility can be achieved by using the sulfobetaine 3-(dimethyldodecylammonio)propanesulfonate·LiCl (e.g., 8-nm Pd clusters).

It is also of interest to note that the Pd clusters can be immobilized by carrying out the electrolysis in the presence of a solid support. For example, if the solvent contains a slurry of carbon black in addition to tetraoctylammonium bromide, electrolysis at a current density of 3 mA/cm$^2$ affords immobilized clusters (5.5% Pd content on carbon black). Importantly, TEM analysis shows that the cluster size (2 nm) is essentially the same as in the absence of the solid support. This is significant for two reasons. Firstly, it allows for the controlled "treatment" of surfaces, a process of potential importance in the generation of quantum dots. Secondly, control of metal particle size in heterogenized (supported) materials may have applications in heterogeneous catalysis.[1,3]

Finally, the present method can be applied to the quantitative preparation of tetraalkylammonium-stabilized nickel clusters in a completely analogous manner. For example, using tetraoctylammonium bromide, Ni clusters of 2.2 and 4.5 nm were obtained having Ni contents of 42–46%.

In conclusion, we have demonstrated that the size-selective synthesis of tetraalkylammonium-stabilized Pd and Ni clusters is possible by a simple electrochemical process. The most salient features include high yield, absence of undesired side products such as metal hydrides or boron impurities, easy isolation, and simple control of particle size by variation of the current density.

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(12) For example, choosing $M = 106.4$; $n = 2$; $\rho = 12$ g/cm$^2$, $\gamma = 2 \pm 1$ N/m, and $\eta = 50$–$1000$ mV, one obtains $r_{\text{crit}} = 36$–$1.8$ nm.