

Electrochemical Preparation of Nanostructured Bimetallic Clusters

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Interest in nanostructured transition-metal clusters arises for fundamental and practical reasons.¹ Examples of applications in catalysis, photocatalysis, and electrocatalysis are already known.^{1,2} The preparation of these materials is generally based on the reduction of transition-metal salts by a variety of reducing agents such as hydrogen, hydrazine, formaldehyde, ethanol, or boron hydrides. To prevent undesired agglomeration, these processes are usually carried out in the presence of stabilizers such as ligands, polymers, or surfactants.³ Nevertheless, such problems as clean preparation, high yield, easy isolation, size-selectivity, and unambiguous characterization may arise.¹

Recently we reported an electrochemical method¹ for the size-selective preparation of tetraalkylammonium salt-stabilized transition-metal clusters in the size range of 1–6 nm.⁴ In this procedure, a sacrificial anode such as a palladium or nickel sheet is electrochemically oxidized with the formation of the corresponding metal ions which are reduced back to the zero oxidation state thereby forming metal clusters which are stabilized by the ammonium salts (which also functions as the electrolyte). The advantages include high yield, easy isolation, and simple control of particle size by adjustment of the current density.⁴ A combined TEM/STM study showed that the clusters are surrounded by a monomolecular layer of tetraalkylammonium salt.⁵ Electrochemically prepared cobalt clusters of this type have been shown to be superparamagnetic.⁶

Since *bimetallic* clusters are of great interest in catalysis and electrocatalysis,^{1,2} the question arose as

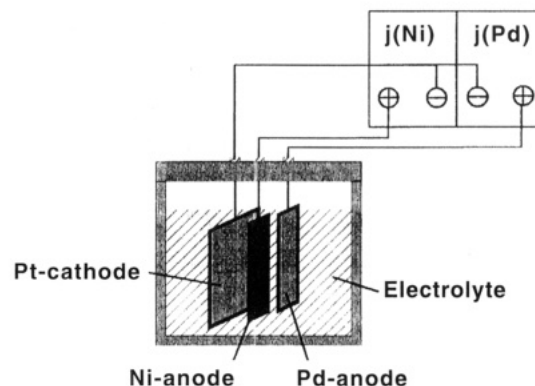


Figure 1. Schematic picture of the electrolysis cell.

Table 1. Electrochemical Preparation of $(n\text{Oct})_4\text{N}^+\text{Br}^-$ -Stabilized Bimetallic Clusters

metal pair M_1/M_2	current density $j(M_1)/j(M_2)$ [mA/cm ²]	cluster size by TEM [nm]	metal content ^a (elemental analysis) %M ₁ /%M ₂	ratio %M ₁ :%M ₂
Ni/Pd	5/30	2.5–3.5	11.3/45.6	20:80
Ni/Pd	20/20	2.5–3.5	13.6/43.9	24:76
Ni/Pd	25/5	2.5–3.5	38.8/7.3	84:16
Fe/Co	5/5	2.5–3.0	22.9/8.8	74:26
Fe/Ni	5/5	2.5–3.0	21.1/8.8	72:28

^a The rest corresponds to the protective layer.

to whether electrochemistry can be used to produce such materials. Here we describe the first examples of the use of two sacrificial metal anodes in a single electrolysis cell for the formation of nanometer-sized bimetallic clusters.

In all cases a commercially available electrolysis cell (Metrohm AG, Switzerland) designed for solution volumes of about 80 mL was used in which the two anodes are positioned in such a way that they lie in a common plane facing the cathode (about 10 mm away), the latter having about twice the surface area relative to one of the anodes. The current densities at the two anodes can be controlled independently of each other (Figure 1).⁷

In a typical procedure, the above electrolysis vessel having a nickel anode (2 × 5 cm commercial sheet), a palladium anode (2 × 5 cm), and an inert cathode (5 × 5 cm commercial Pt sheet) was employed in the preparation of Ni/Pd bimetallic clusters. The supporting electrolyte consisted of a 0.1 M solution of $(n\text{Oct})_4\text{N}^+\text{Br}^-$ in dry THF. After a charge flow of about 500 C/anode, during which rapid mixing was ensured by magnetic stirring (or sonification) at room temperature, a black solution was obtained. The current yield amounted to 60–80%. The electrolysis and the workup were generally performed under argon. The solvent was removed and the resulting black material was washed with pentane/ethanol (1:1) and dried in vacuo. The material can be redispersed in THF (up to 1 M). Data concerning metal content as determined by elemental analysis and metal cluster size as observed by transmission electron microscopy are summarized in Table 1. It can be seen that the Ni-to-Pd ratio depends upon the applied current densities at the two anodes. However, the observed compositions do not completely correspond to the theo-

(1) (a) Davis, S. C.; Klabunde, K. *J. Chem. Rev.* **1982**, *82*, 153. (b) Gates, B. C.; Guzzi, L.; Knözinger, H. *Metal Cluster in Catalysis*; Elsevier: Amsterdam, 1986. (c) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709. (d) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693. (e) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457. (f) *Clusters and Colloids*; Schmid, G., Ed.; VCH: Weinheim, 1994. (g) Schön, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 101.

(2) (a) Conway, B.; Tilak, B. In *Adv. Catalysis*; Eley, D., Pines, H., Weisz, P., Eds.; Academic Press: New York, 1992; Vol. 38. (b) Wendt, H. *Electrochemical Hydrogen Technology*; Elsevier: Amsterdam, 1990.

(3) (a) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214. (b) Blum, J.; Sasson, Y.; Zoran, A. *J. Mol. Catal.* **1981**, *11*, 293. (c) Boutonnet, M.; Kizling, J.; Stenius, P.; Maire, G. *Colloids Surf.* **1982**, *5*, 209. (d) Toshima, N.; Takahashi, T.; Hirai, H. *Chem. Lett.* **1985**, 1245. (e) Boutonnet, M.; Kizling, J.; Touroude, R.; Maire, G.; Stenius, P. *Appl. Catal.* **1986**, *20*, 163. (f) Meguro, K.; Toriyuka, M.; Esumi, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 341. (g) Wiesner, J.; Wokaun, A.; Hoffmann, H. *Prog. Colloid Polym. Sci.* **1988**, *76*, 271. (h) Satoh, N.; Kimura, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1758. (i) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Dinjus, E.; Jousen, T.; Korall, B. *Angew. Chem.* **1991**, *103*, 1344; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1312. (j) Toshima, N.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 400.

(4) Reetz, M. T.; Helbig, W. *J. Am. Chem. Soc.* **1994**, *116*, 7401.

(5) Reetz, M. T.; Helbig, W.; Quaiser, S. A.; Stimming, U.; Breuer, N.; Vogel, R. *Science* **1995**, *267*, 367.

(6) Becker, J. A.; Schäfer, R.; Festag, R.; Ruland, W.; Wendorff, J. H.; Pebler, J.; Quaiser, S. A.; Helbig, W.; Reetz, M. T. *J. Chem. Phys.* **1995**, *103*, 2520.

(7) (a) Helbig, W. Dissertation, Ruhr-Universität Bochum, 1994. (b) Reetz, M. T.; Helbig, W.; Quaiser, S. A., patent applied for, 1994.

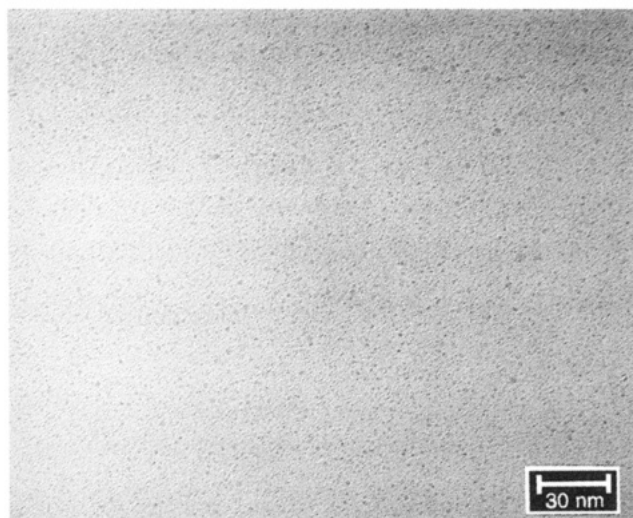


Figure 2. Transmission electron micrograph of Ni/Pd bimetallic clusters (Ni:Pd = 1:4).

retically expected values, particularly in the case in which the applied current density is the same as each anode (20 mA/cm^2). This may well be due to differences in the reduction potential of the two metals, i.e., in the relative behavior of the two metal cations at the cathode. Transmission electron micrographs showed the particles to be in the 2.5–3.5 nm size range (Figure 2). According to energy-dispersive X-ray spot analysis (EDX) of single particles, they are true bimetallic clusters.⁷ As Table 1 shows, other metal combinations can also be chosen, e.g., iron/cobalt or iron/nickel. In these cases dark brown solutions were obtained which were transferred into a Schlenk tube where they were slowly treated with ether/ethanol (10:1), resulting in the formation of gray-black precipitates. Following decantation after 3 h, the solid materials were dried in vacuo. They are also fully redispersible in THF.

The role of the surfactant as the stabilizing mantle⁵ can be pictured in the case of the present bimetallic

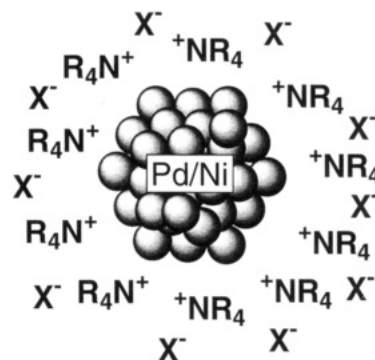


Figure 3. Representation of a $\text{R}_4\text{N}^+\text{X}^-$ -stabilized bimetallic cluster.

clusters as illustrated in Figure 3. Several factors contribute to the stabilization, including electrostatic and steric effects.^{3,4,5,7}

In summary, we have developed a simple electrochemical method for the production of tetraalkylammonium salt-stabilized bimetallic clusters in the nanometer size range. Ammonium salt-stabilized³ bimetallic clusters involving Pd/Ni, Fe/Co, and Fe/Ni have not been described previously. The mechanism involves formation of adatoms in the vicinity of the cathode, followed by cluster formation and efficient stabilization by the ammonium salt. The self-organization of the ammonium salt around the metal core is essential in preventing undesired metal powder formation. As demonstrated for the case of Ni/Pd clusters, the relative composition of the two metals can be controlled conveniently by the proper choice of the current densities. More work is necessary to see if the actual cluster size can be adjusted in a defined manner as previously described in the formation of monometallic clusters.^{4,8}

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(8) Reetz, M. T.; Quaiser, S. A. *Angew. Chem.* **1995**, *107*, 2461; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, XXX.