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Synthesis of Metal Nanoparticles Stabilized by Metal−Carbon Bonds

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Covalent attachment of different functionalities to semiconductors, carbon, and metal surfaces using diazonium derivatives of aromatic compounds has been extensively reported.[1] The covalent bonds that are formed by reduction grafting of diazonium compounds to the corresponding radical are stronger than those obtained for surface modification by self-assembly and has been employed for the modification of electrode surfaces for a variety of applications[2] and, importantly, for a wide range of transition and noble metal surfaces.[1c−f]

For the coinage metals, thiol chemistry has been successfully employed for the attachment of different functionalities as capping ligands and for the synthesis of nanoparticles with a narrow size distribution.[3] The range of metals for which nanoparticles can be prepared is limited, however, by the stability of the metal−sulfur bond. It is, therefore, of great practical interest to have a general synthetic approach that is less reliant on the chemisorption of stabilizing ligand containing soft atoms (S, N, or P), and alternative methods for the preparation of metal and alloy nanoparticles in organic solutions would be advantageous.[4]

A new synthetic route that avoids the use of quaternary ammonium salts as a phase transfer reagent and uses surface grafting techniques is described below. The synthesis is based on the formation of carbon−metal bonds by the reduction of the diazonium salt of a derivative of a long chain alkyl benzene that acts both as a phase transfer reagent and as a stabilizing ligand.

The synthetic strategy followed was similar to that used for thiol-stabilized nanoparticles, except that no phase transfer reagent was required. Briefly, 4-diazonium decylbenzene fluoroborate (DDB) was synthesized by the diazotization of 4-amino decylbenzene. All reagents used were from Aldrich. 4-decylbenzene diazonium fluoroborate was prepared by suspending 4-decylaniline (2.3 g, 10 mmol) in a 50/50 by volume acetic and propionic acid and then adding 12 mL of 48% fluoroboric acid. The mixture was cooled to 3 °C in an ice bath, and then 1 g of sodium nitrite was slowly added in five portions. The mixture was stirred for 2 h and allowed to warm gently to ~10 °C, and 10 mL of water was added. The product was filtered, washed four times with water, and dried in vacuum over $CaCl_2$. Yield 2.6 g; calcd C 59.29%, H 5.28%, N 8.64%; found C 59.18%, H 5.34%, N 8.48%. Mp 57.7 °C; dec. temp > 108 °C. A mixture of 5 mmol (80 mL) solution of hydrogen tetracholoroaurate (Aldrich) or hydrogen hexacholoroplatinate (Aldrich) in deionized water and 10 mmol (150 mL) of the diazonium compound in toluene was vigorously stirred until the gold or platinum ions were transferred to the organic phase according to

$$\mathrm{AuCl_4^-\,(aq) + N_2Ar^+\,(tol) \rightarrow AuCl_4^-N_2Ar^+\,(tol)} \qquad (1)$$

where the hydrophobic diazonium salt cation acts as the phase transfer reagent. A similar reaction occurs with the chloroplatinate anion. After further stirring for 2 h, the organic phase was separated and washed twice with water. The metal ions and the diazonium compound were simultaneously reduced by the dropwise addition with vigorous stirring of 40 mL of 0.3 M aqueous $NaBH_4$ during 2 h. The color of the organic phase turned to deep ruby red in the case of gold and green for platinum. The aqueous phase was separated, and the organic phase was washed first with 0.5 M H_2SO_4, then with 0.5 M Na_2CO_3, and finally with water; the solution was dried over magnesium sulfate. The individual reduction reactions taking place can be schematically described by

$$n\mathrm{Au(III)(tol)} \xrightarrow{\text{red}} \mathrm{Au}_n\mathrm{(tol)} \qquad (2)$$

$$m\mathrm{N_2Ar^+\,(tol)} \xrightarrow{\text{red}} m\mathrm{Ar^\bullet(tol) + N_2\,(g)} \qquad (3)$$

followed by bond formation according to

$$\mathrm{Au}_n\mathrm{(tol)} + m\mathrm{Ar^\bullet(tol)} \rightarrow \mathrm{Au}_n\mathrm{Ar}_m\mathrm{(tol)} \qquad (4)$$

The order in which these reactions occur and mechanistic details are not known. It is reasonable to assume, however, that the attachment of the −Ar group results in the inhibition of the growth of the metal clusters in a manner similar to that in the thiol−gold system; that is, the metal core growth is arrested by the binding of the stabilizing ligand. It is proposed that the presence of a large hydrophobic ligand on the surface of the nanoparticles would result not only in the arrested growth of the metal cores but also in the decrease of the likelihood of polymerization of the attached ligands by radicals formed in the solution, as suggested by Laforgue et al. for the formation of self-assembled monolayers on bulk metals.[1f] This would be a consequence of steric crowding of the nanoparticle surface.[5]

The toluene solutions of these nanoparticles were stable for weeks. The nanoparticle solutions were purified using a silica chromatographic column, and the impurities were eluted by toluene. The metal particles were strongly retained by the silica. The column was eluted first with toluene to eliminate impurities, and then, the nanoparticle band was eluted using 1-butanol. The solvent was evaporated in a vacuum rotary evaporator, and the residue was dissolved in a suitable solvent for spectroscopic measurements. Panels a and b of Figure 1 show TEM images of the gold and platinum nanoparticles prepared. A particle size of 8.1 ± 0.8 nm for gold and 3 ± 1 nm for platinum was obtained. The average close contact interparticle separation of the gold clusters was 2.8 ± 0.3 nm. The length of the fully extended capping ligand was estimated at 1.6 nm (Spartan software), showing that some degree of interdigitation between the capping molecules takes place. Similar effects have been observed with other nanoparticles.[6] A similar analysis could not be carried out for the Pt particles because the sizes were too small to lead to a regular packing on the TEM supporting grid. The observed preservation of the integrity of the nanoparticles on solvent evaporation is a clear indication of stable bond formation between the ligand and the metal core in both cases studied.

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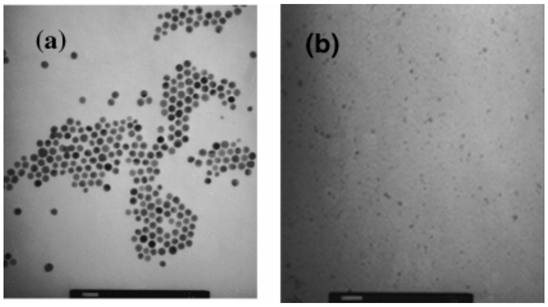

Figure 1. TEM images of (a) gold and (b) platinum nanoparticles. The bars correspond to a distance of 20 nm.

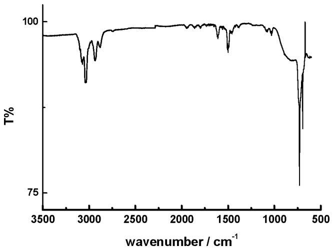

Figure 2. FT-IR spectrum of Au nanoparticles; toluene solution evaporated on a NaCl disk.

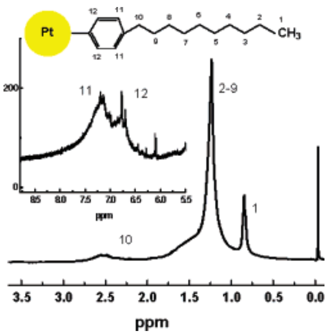

Figure 3. ^{1}H NMR spectrum of Pt nanoparticles in CD_2Cl_2 solution.

FT-IR spectra of the nanoparticles showed the presence of C−H aromatic bands at 686, 729 and 810−870, 1500, and 1608 in the ring breathing region (C═C). Methylene C−H stretching modes at $\nu_s = 2880$, $\nu_{as} = 2939$ and aromatic C−H vibrations at $\nu_s = 3036$ and $\nu_{as} = 3079$ cm^{-1} are observed. The lack of a diazonium band at 2250 cm^{-1} and the aromatic C−N band between 1180 and 1360 cm^{-1} support the complete removal of the diazonium group on reduction (Figure 2, compare with DDB spectrum see S1). Carbon and ^{1}H NMR spectra of nanoparticles show the aliphatic and aromatic carbon and hydrogen similar to those of the free ligand (see Supporting Information). An interesting feature of the NMR spectra, which has been discussed, is the broadening of NMR peaks for atoms close to the nanoparticle core center[3c−e] as is also observed in the solid state.[5b] Figure 3 shows the ^{1}H NMR spectrum of Pt nanoparticles. The relatively sharp peak at 0.8 ppm corresponds to the methyl terminal group with an integrated band intensity that corresponds to three hydrogen atoms. The strong peak at 1.3 ppm corresponds to 16H related to the methylene chain. The methylene linked to the benzene ring shows a broad peak at 2.6 ppm with integration of 2H. The aromatic region shows two broad peaks at 6.8 and 7.3 ppm, corresponding to four H, representing two types of aromatic hydrogens as expected for a 1,4-substituted ring. No other peaks corresponding to DDB or other impurities were observed. Broadening of NMR peaks due to the fast spin−spin relaxation of atoms close to a metal core, different chemical shifts for different binding sites, or size-dependent spin−spin relaxation are a clear indication of the core−shell linkage.[3d] Similar broadening was also observed in ^{13}C NMR for carbon atoms close to the metal core, and the peaks corresponding to the aromatic carbons were broadened so that they could not be distinguished from the background (see Figure S3). It can be concluded that the NMR spectra provide strong additional evidence that the DDB ligand is indeed chemically bonded to the metal core at the para position.

Elemental and thermogravimetric (TG) analysis of the Pt particles showed 29.2% C, 3.7% H, and 54% Pt, and a carbon-to-hydrogen ratio of 7.9 close to the theoretical value for the capping molecule of 7.68 was found. The number of Pt atoms per DDB molecule was approximately 2, slightly lower than that for the core sizes measured. Preliminary experiments have shown that the choice of ligand-to-metal ratio, reducing agent, and reduction conditions are important to control the reaction and thus particle size.

In conclusion, these results show a simple and efficient method for the preparation of monolayer-protected metal nanoparticles by metal−carbon bond formation. This is stronger than that of metal−sulfur or metal−nitrogen bonds and provides enhanced chemical stability as observed for metal functionalization.[1,2] The method proposed thus appears to be an alternative for the preparation of nanoparticles when the metal−sulfur bond should be avoided and would enlarge the range of materials from which monolayer-protected clusters can be synthesized.

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Supporting Information Available: Additional supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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