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Nanoscale Metal Particles by Homogeneous Reduction with Alkalides or Electrides

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Abstract: A new method for the preparation of small metal/oxidized metal particles is described that utilizes homogeneous reduction of dissolved alkalides or electrides in an aprotic solvent such as dimethyl ether or tetrahydrofuran. Salts of Au, Pt, Cu, and Te form metallic particles with little or no oxidation even when washed with methanol. Reduction of salts of Ni, Fe, Zn, Ga, Si, Mo, W, In, Sn, and Sb yields surface oxidation over a metallic core, while only oxidized Ti was observed. Mixtures of salts of Au–Cu, Au–Zn, Cu–Te, Zn–Te formed particles that contained the intermetallic compounds rather than mixtures of the separate metals. The method should also be applicable to the formation of finely divided metals on oxide supports and to the synthesis of organometallic compounds.

Introduction

The preparation of nanoscale particles (1–20-nm diameter) as colloids or aggregates is a well-developed field that involves a variety of chemical and physical techniques.(1) Small noble-metal particles are commonly made by mild reduction.(2–4) Rieke and co-workers(5–7) and others(8) have reduced salts of more active metals in ethereal or hydrocarbon solvents, either heterogeneously with alkali metals (slow) or homogeneously with aromatic radical anions such as naphthalide (fast). The products of such reactions are highly active metal powders. Other methods such as pyrolysis of precursors,(9) evaporation of metals,(10) matrix isolation(11) (solvated metal atom disperson), and sol–gel processes(12) have also been used to prepare small particles.

The solvated electron (e_s^-) is thermodynamically the most powerful reducing agent possible in a given solvent. It also usually reacts rapidly with metal ions and with simple compounds that contain a metal in a positive oxidation state. Alkali-metal anions (M^-) are nearly as effective and can provide two electrons in a single encounter. Side reactions with the solvent can arise, however, when a protic solvent such as ammonia or a primary or secondary amine is used.(13)

A solution that contains e_s^- or M^- in an aprotic solvent is an attractive reducing medium. The alkali metals can be solubilized in aprotic solvents(14–16) such as dimethyl ether (Me_2O) or tetrahydrofuran (THF) with use of a suitable cation complexant such as a crown ether(17) or cryptand.(18) The resulting homogeneous solutions contain either e_s^- or M^-, depending on the metal/complexant ratio.(19) Identical solutions can be prepared by dissolving presynthesized electrides or alkalides(20–22) in the solvent. When a metal salt or complex can be dissolved in the same solvent, rapid reduction to the metal can occur upon mixing the two solutions.(23)

Homogeneous reduction of various metal salts with alkalides or electrides in Me_2O or THF at −50 °C or below produces 2–15-nm diameter particles of metals, alloys, or oxidized products. Reactions are rapid, complete, and applicable to a wide range of elements from Ti to Te. Mixtures of salts can produce alloys or compounds rather than mixture of the pure metals. Metallic particles dispersed on high surface area oxides can also be prepared in this way. We report here a feasibility study that demonstrates the generality of this method.

Experimental Section

All the metal salts were purchased from Aldrich or AESAR in the highest available purity. Liquid samples were $TiCl_4$ (99.995+%), $GeCl_4$ (99.999%), $SiCl_4$ (99.999%), $SbCl_5$ (99%), and $SnCl_4$ (99.999%). Solid samples were $CuCl_2$ (99.9999%), $GaCl_3$ (99.99+%), ZnI_2 (99.99%), $MoCl_5$ (99.99%), $FeCl_3$ (98%), H_2PtCl_6 (99.9%), $InCl_3$ (99.999%), $TeBr_4$ (99%), WCl_6 (99.9+%), $AlCl_3$ (99.99%), VCl_3, and $AuCl_3$. The oxide support was 150-mesh neutral activated Al_2O_3 with a specific surface area of 155 m^2/g. A 0.25-mm-thick 99.99+% indium foil or a 0.5-mm-thick 99.99% lead foil was used to mount the samples for X-ray photoelectron spectroscopy (XPS) studies.

A few milligrams of the desired compound were added to an evacuated H-cell(24) with a medium frit in the He-filled drybox. An excess of alkalide or electride was added to the other side of the H-cell in a nitrogen-filled glovebag. A liquid nitrogen bath was used to cool the cell to prevent decomposition of the alkalide or electride. About 20 mL of either prepurified Me_2O or THF was distilled into both sides after evacuation to about 10^{-5} Torr while the cell was kept in a −50 °C isopropyl alcohol bath.

The blue solution of either the alkalide or electride was poured through the frit to react with the solution of the metal salt to be reduced after both solids had been completely dissolved in the solvent. Reaction occurred immediately upon addition of the alkalide or electride as indicated by the fading of the blue color. A slight excess of alkalide or electride was added until the blue color no longer disappeared to make sure that the reaction was complete. Different colors of various colloids were formed at the same time. Then the solvent was distilled out under vacuum.

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III B	IV B	V B	VI B	VII B	VIII B			I B	II B	III A	IV A	V A	VI A
										B	C	N	O
										Al 5	Si 2	P	S
Sc	Ti 4	V 5	Cr	Mn 5	Fe 3	Co	Ni 3	Cu 1	Zn 2	Ga 2	Ge 5	As	Se
Y	Zr	Nb	Mo 3	Tc	Ru	Rh	Pd	Ag	Cd	In 2	Sn 2	Sb 2	Te 1
La	Hf	Ta	W 3	Re	Os	Ir	Pt 1	Au 1	Hg	Tl	Pb	Bi	Po

Figure 1. Part of the periodic table showing the elements studied to date. Identification: 1, washable metals; 2, surface-oxidized; 3, nonwashable; 4, reoxidized; 5, not identified. See the text for more detailed definitions.

The products were removed from the walls of the H-cell and mounted on the indium or lead foil in the He-filled drybox. A vacuum-transfer vessel was used to carry the sample from the drybox to the XPS transfer chamber without exposing the sample to the air. The pressure of the main chamber of the XPS instrument was kept below 3×10^{-8} Torr during measurement. In some cases, deionized and degassed distilled water or prepurified methanol was used to wash away the byproducts in a glovebag. Washing was performed by centrifugation to separate the undissolved metal particles from the water- or methanol-soluble byproducts. X-ray diffraction (XRD) patterns were recorded by placing the precipitate on a glass slide either with or without washing. A drop of washed suspension was put on the transmission electron microscope (TEM) carbon-coated grid and allowed to dry in the air, after which TEM micrographs, energy-dispersive spectra (EDS), and selective-area electron diffraction (SAD) patterns were obtained.

Results and Discussion

Typical reaction stoichiometries such as[25]

$$CuCl_2 + 2K^+(15\text{-crown-}5)_2e^- \xrightarrow{Me_2O} Cu + 2K^+(15\text{-crown-}5)_2Cl^-$$

or

$$CuCl_2 + K^+(15\text{-crown-}5)_2K^- \xrightarrow{Me_2O} Cu + K^+(15\text{-crown-}5)_2Cl^- + K^+Cl^-$$

were verified by XRD studies of reaction products after solvent removal by distillation. For crystalline particles, average diameters larger than 3 nm could be determined by applying Scherrer's equation[26] to the XRD line widths. TEM micrographs were also used to determine particle sizes and size distributions. EDS permitted analysis, and SAD was used to identify the bulk structure of the particles. XPS (photoelectron and AUGER peaks) identified the surface composition (metallic or oxidized), and argon ion sputtering removed surface layers to verify the presence of subsurface metal.

The reduction products are displayed in Figure 1 and may be classified as follows.

(1) Washable metals: Metal particles could be washed with little or no surface oxidation. Compounds reduced include $AuCl_3$, H_2PtCl_6 (hydrated), $TeBr_4$, and $CuCl_2$.

(2) Surface-oxidized: Partial or complete surface oxidation occurs with or without washing, but the subsurface material is metallic. Compounds include $SbCl_5$, ZnI_2, $GaCl_3$, $SnCl_4$, $InCl_3$, and $SiCl_4$.

(3) Nonwashable: Metal was observed with the unwashed product only. Oxidation occurs upon washing with methanol. Included are $NiBr_2$ + triethylphosphine, $MoCl_5$, $FeCl_3$, WCl_6.

(4) Reoxidized: No metal was observed (with or without washing), although initial reduction occurs as indicated by fading of the blue color of the alkalide solution. This includes only $TiCl_4$ so far.

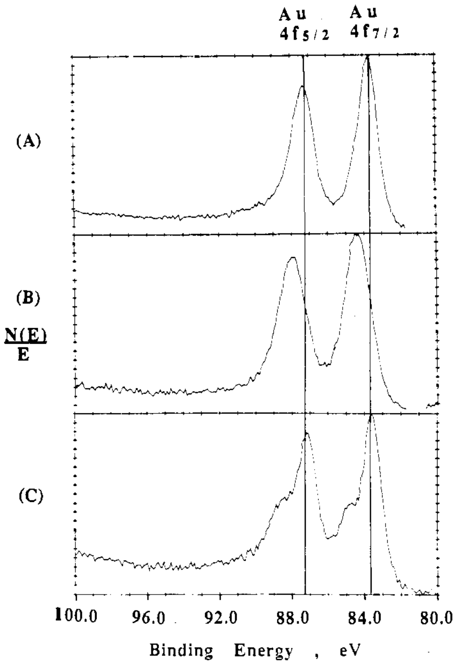

Figure 2. XPS spectrum for the $4f_{5/2}$ and $4f_{7/2}$ levels of Au: (A) gold particles from reduction of $AuCl_3$ showing only the metal XPS peaks; (B) AuZn particles formed from reduction of a mixture of $AuCl_3$ and excess ZnI_2; (C) AuZn + Au particles formed from reduction of a mixture of $AuCl_3$ and ZnI_2 with the former in excess.

(5) Not identified: Reduction occurs, but the reaction products have not yet been identified. This class includes $AlCl_3$, VCl_3, $GeCl_4$, and MnI_2.

Other elements in the periodic table have not yet been tested. Six alkalides and two electrides were used as reducing reagents with identical results. Individual or clustered particles with a distribution of sizes and average diameters from <3 to ~15 nm always formed.

The most remarkable aspect of this method may well be the preparation of alloys or compounds by simultaneous reduction of two or more metal salts. All systems tested (Au-Zn, Au-Cu, Cu-Te, and Zn-Te) yielded binary alloys or compounds. For example, Figure 2a shows the XPS spectrum of Au ($4f_{7/2}$ and $4f_{5/2}$) from the product of reduction of $AuCl_3$. The binding energy of both the Au $4f_{7/2}$ state at 83.70 eV and the $4f_{5/2}$ state at 87.30 eV shows that the product is pure metallic gold.[27] Figure 2b is the Au $4f_{7/2}$ and $4f_{5/2}$ XPS spectrum from the product of reduction of a mixture of $AuCl_3$ and ZnI_2 with excess ZnI_2. These peaks are shifted to 84.45 and 88.00 eV, respectively. The splitting of the 4f energy levels (3.55 eV) is narrower than that (3.60 eV) of pure gold, and the levels are shifted to higher binding energies with respect to the Fermi level. This indicates that an alloy is formed from the reduction of the mixtures. This result is in agreement with the XPS work of Al-Au alloy by Fuggle and co-workers.[28] Figure 2c is the spectrum from the mixtures of $AuCl_3$ and ZnI_2 with excess $AuCl_3$. This spectrum shows clearly that both pure metallic gold and the alloy are formed. The compound was later identified as AuZn by its SAD pattern.[29]

The Au-Cu system has been the subject of many investigations, and its phase diagram has been extensively studied.[30] The most nearly ideal structure at the stoichiometry of AuCu consists of

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(25) IUPAC name: 15-crown-5; 1,4,7,10,13-pentaoxacyclopentadecane.

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alternate layers of Au and Cu atoms parallel to a cube face. The symmetry is slightly distorted to tetragonal with $c/a = 0.93$. This structure transforms to orthorhombic with $b/a = 10.03$ at about 380 °C.[30] The particles produced by reduction of stoichiometric mixtures of $AuCl_3$ and $CuCl_2$ at −50 °C have an SAD pattern that corresponds to a simple cubic pattern with each Au atom at the center of a cube of Cu atoms and vice versa.

The method may be used to prepare highly dispersed metals on oxide surfaces as previously done by other methods.[5] To verify this, $AuCl_3$ adsorbed on neutral activated Al_2O_3 (155 m^2/g) was reduced with $K^+(15\text{-crown-}5)_2K^-$ in Me_2O. Au particles (~6-nm average diameter) were randomly dispersed on the surface. One might be able to prepare a large surface area metal oxide catalyst by coreduction of a noble metal and an active metal, followed by oxidation of the latter. It should also be possible to prepare organometallic compounds by reaction of suitable precursors with freshly prepared active metals.[5,8,31]

The objective of this study was to test the generality of homogeneous reductions of soluble metal salts by solvated electrons and/or alkali-metal anions in aprotic solvents. Although many of the metals studied can be prepared as small particles by other methods, the procedure described here has the advantage of being rapid and quantitative and of requiring only low temperatures for all steps. The initial reduction products must consist of very small, reactive particles as binary alloy formation is observed rather than mixtures of metals when two metal salts are simultaneously reduced.

The XRD patterns of the unwashed products and the absence of significant carbon signals in the XPS data of washed samples show that most of the crown ether complexant is not destroyed in the process and could be recovered if desired. This would be important in the utilization of the method because of the relatively high costs of the complexants.

Studies of reductions of other salts, binary mixtures, and mixtures of salts of active and inactive metals are continuing. Also, the factors that determine the distribution of particle sizes and the stabilities of colloidal solutions are being investigated.

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Picosecond Studies of Quinone-Substituted Monometalated Porphyrin Dimers: Evidence for Superexchange-Mediated Electron Transfer in a Photosynthetic Model System

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Abstract: Time-resolved studies are reported for a series of quinone-substituted porphyrin monomers and monometalated phenyl-linked dimers. Irradiation of the simple porphyrin monomer systems Ph–Zn–Q, Ph–H_2–Q, and H_2–Q in toluene at 295 K elicits charge separation to produce the oxidized free-base (H_2) or zinc (Zn) porphyrin and the reduced quinone (Q) within the 350-fs excitation flash. (Ph is the phenyl spacer utilized in the porphyrin dimers.) Charge recombination occurs with a time constant of 3–6 ps, returning the system to the electronic ground state but in an excited nuclear configuration that takes ~10 ps to relax. Somewhat more complex behavior is observed for the two regioisomeric monometalated porphyrin dimers $Zn\frown H_2$–Q (gable) and Zn–H_2–Q (flat), although complete recovery is again observed within ~15 ps of excitation and ascribed to charge separation/recombination between the quinone and the adjacent H_2 subunit. In contrast, very different photodynamic behavior is found for the regioisomeric monometalated dimers $H_2\frown Zn$–Q and H_2–Zn–Q, in which the central Zn porphyrin forms a built-in energy barrier between the H_2 subunit and the quinone acceptor. In particular, a slow step having a time constant of 55–75 ps is observed at 295 K, in addition to the fast (<15 ps) charge separation/recombination process involving the quinone and adjacent Zn subunit. From the absorption changes accompanying the 55–75-ps process in the $H_2\frown Zn$–Q and H_2–Zn–Q systems, and their absence in the other complexes, it is concluded that the slower process involves a quinone-induced deactivation of the lowest $^1(\pi,\pi^*)$ state of the free-base subunit to the ground state. The time constant for this slower process is only weakly dependent on temperature (and solvent), increasing for $H_2\frown Zn$–Q in 2-MTHF from 55 ps at 295 K to 106 ps at 77 K. This observation, coupled with an energetic analysis, indicates that net H_2^* to Q electron transfer does not involve a thermally activated step. Rather, the results suggest that it takes place by a direct Zn porphyrin mediated superexchange mechanism. Additionally, the results suggest that in all complexes charge separation/recombination between the porphyrin and adjacent quinone involve vibrationally excited states.

The three-dimensional structure of the bacterial reaction center has provided an important structural basis for understanding the primary charge separation process in photosynthesis.[1] One of the more intriguing unresolved issues is the role of the bacteriochlorophyll (BChl) monomer in mediating the rapid (~3 ps) electron transfer (ET) from the excited primary electron donor (P*), a dimer of BChls, to a bacteriopheophytin (BPh). Recent subpicosecond transient absorption and other studies have generally

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