the center of one of the two cyclopentadienyl rings (0.124 Å). The C_g-Ln-C_g angles of the less constrained five-atom-bridged bis(indenyl)lanthanocenes $[\{O(CH_2CH_2C_9H_6)_2\}LnCl(thf)]$[12] (131.4° Ln = Nd, 132.3° Gd, 132.6° Ho) are larger and show little dependence on the size of the central metal cation.

It is expected that **1** and **2** will be useful as reducing agents due to the presence of minor quantities of uncoupled acene radical anionic species in solution, detected by ESR spectroscopy. Reactiviy studies of both complexes are in progress.

Experimental Section

All manipulations were performed under nitrogen atmosphere or in vacuum. Elemental analyses were obtained by using a Perkin-Elmer Series II CHNS/O 2400 Analyzer, NMR spectra were recorded on a Bruker ARX 200 instrument. The commercially available acenaphthylene (Aldrich; purity 75%) was purified further to 85% (10 to 15% acenaphthene as impurity) by sublimation (80/10^{-1} Torr). The given quantities of acenaphthylene and the yields of the products refer to pure acenaphthylene.

1: A mixture of ytterbium metal (7.8 g, 45 mmol) and iodine (1.85 g, 14.6 mmol) in THF (30 mL) was stirred for 1 h at 50 °C, and the resulting suspension of YbI_2 was decanted off. The residual activated metal was washed with warm THF (2 × 30 mL), and then a solution of acenaphthylene (1.23 g, 6.37 mmol) in THF (50 mL) was added. The mixture was stirred for 1 h at reflux. The warm, dark red-brown solution was filtered and then concentrated to 15 mL which yielded **1** as dark red almost black crystals. Yield: 2.34 g (93%); m.p. > 180 °C (decomp); ^{1}H NMR (200 MHz, [D$_8$]THF, 20 °C, TMS): δ = 6.87 (d, ^3J(H,H) = 8.26 Hz, 2H; CH, H^3), 6.65 (dd, ^3J(H,H) = 9.7, 2.0 Hz, 2H; CH, H^6), 6.45 (dd, ^3J(H,H) = 8.24, 8.26 Hz, 2H; CH, H^4), 6.29 (s, 2H; CH, H^1), 6.26 (d, ^3J(H,H) = 4.54 Hz, 2H; CH, H^5), 6.02 (dd, ^3J(H,H) = 9.7, 3.56 Hz, 2H; CH, H^7), 5.59 (d, ^3J(H,H) = 3.14 Hz, 2H; CH, H^2), 4.45 (s, 2H; CH, H^8), 3.71 (m, 8H; CH_2), 1.59 (m, 8H; CH_2); elemental analysis (%): calcd for $C_{32}H_{32}O_2Yb$ (621.62): C 61.83, H 5.19; found: C 60.79, H 4.25.

2: The dark brown crystalline compound **2** was prepared as described for **1** using samarium (4.2 g, 28 mmol), iodine (1.3 g, 10.24 mmol), and acenaphthylene (0.76 g, 5 mmol) in THF (50 mL). Yield: 1.34 g (90%); m.p. > 180 °C (decomp); ^{1}H NMR (200 MHz, [D$_8$]THF, 20 °C, TMS): δ = 17.67 (s, 2H; CH, H^3), 15.52 (s, 2H; CH, H^1), 12.84 (s, 2H; CH, H^6), 12.01 (s, 2H; CH, H^4), 6.89 (s, 2H; CH, H^2), 5.12 (s, 2H; CH, H^5), 3.6 (s, 8H; CH_2), 1.73 (s, 8H; CH_2), 0.72 (s, 2H; CH, H^7), −9,88 (s, 2H; CH, H^8); elemental analysis (%): calcd for $C_{32}H_{32}O_2Sm$ (598.93): C 64.17, H 5.38; found: C 63.37, H 5.42.

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Fabrication and Properties of Gold Single-Crystal Ultramicroelectrodes**

Vladimir Komanicky and W. Ronald Fawcett*

Ultramicroelectrodes (UMEs) are important in electrochemistry and electroanalysis because of the special mass transfer conditions observed with respect to those at electrodes of normal dimensions.[1] This property has been used to facilitate the measurement of very fast electron transfer kinetics, a well-known example being the electrooxidation of ferrocene.[2] On the other hand UMEs made from metals in the usual way are necessarily polycrystalline in nature. As a

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result, the crystallinity of the electrode and therefore its double-layer properties can vary from electrode to electrode. This fact prevents assessment of the role of interfacial properties in the kinetics of very fast electron transfer processes.

Electrochemical methods for determining slow electron transfer kinetics at gold single-crystal electrodes with well-defined surface properties are now well established.[3] Gold single-crystals are usually prepared by the Czochralski method or by zone melting and cut with the aid of an X-ray goniometer to expose a face of known crystallographic orientation.[4] On the other hand it is well known that gold single crystals of nano- and microdimensions can be prepared by techniques involving the use of silicate gels.[5] An important example is the method described by Kratochvil et al.[6] which yields thin platelike gold crystals with a (111) orientation on the face. The microcrystals have hexagonal or triangular shapes with effective disc diameters d_{eff}[7] between 5 and 200 μm, and a thickness between 0.05 and 0.1 μm. We have fabricated single-crystal UMEs (SCUMEs) using these microcrystals but their thinness makes them fragile and difficult to work with.

Herein we outline a new electrochemical technique for preparing robust Au crystals with mainly (100) and (111) facets in a silicate gel. The gel is formed at low pH with HCl and $HAuCl_4$ as components. When a small current is passed through the gel between two gold electrodes, Au metal is deposited at the cathode and Cl_2 gas is formed at the anode. Surprisingly, Au crystals are observed in the vicinity of the anode after 24 h. Cl_2 reacts with the Au of the anode to form a metastable Au^I complex [Eq. (1)],[8] which disproportionates further from the anode [Eq. (2)].[9] The conditions for nucleation and growth of the gold crystals are established by the gel and its pH value.[5]

$$2\,Au + Cl_2 + 2\,Cl^- \rightarrow 2\,[AuCl_2]^- \quad (1)$$

$$3\,[AuCl_2]^- \rightarrow [AuCl_4]^- + 2\,Au + 2\,Cl^- \quad (2)$$

A representative sample of microcrystals harvested from the electrochemical cell is shown in Figure 1. The crystals are mainly triangular (b, e) or hexagonal plates (a) with a (111) orientation on the main plane. Rectangular faces (d) correspond to a (100) orientation. The crystals can be further characterized by using an atlas of crystal forms.[10] The surfaces were smooth on an atomic level without visible terraces or steps when examined with a scanning electron microscope. The density of the gel plays an important role in determining crystal quality.

A selected microcrystal was first attached to a gold microwire using a gold paint which can be converted to metallic gold on heating. It was then aligned under a microscope using a specially designed micromanipulator (Figure 2) with which the operating face of the crystal was set parallel to the microscope table. The crystal and connecting wire were then insulated with epoxy cement so that only the working face was exposed. Figure 3 shows a hexagonal microcrystal with a d_{eff} close to 10 μm mounted for use as a SCUME on a 10 μm wire.

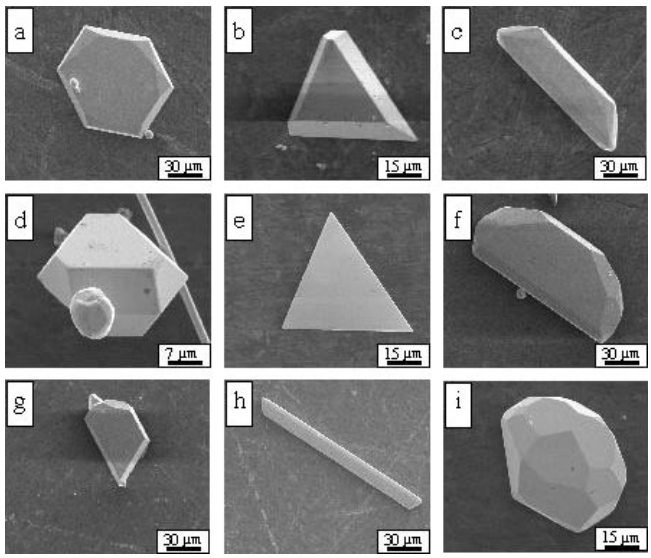

Figure 1. Scanning electron microscope images showing the variety of microcrystals grown in an electrochemical cell containing the silica gel.

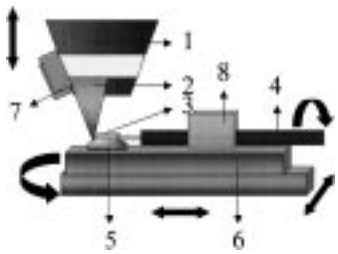

Figure 2. Schematic diagram of the micromanipulator used to attach, align and insulate the SCUME: 1) microscope lens; 2) metal tip used with the epoxy resin; 3) Au microcrystal; 4) copper wire; 5) epoxy resin; 6) stand which is fixed to the microscope table; 7, 8) holders for the copper wire. Two positioning screws were used to achieve exact horizonal orientation of the working face of the Au microcrystal before it was surrounded by insulating epoxy resin.

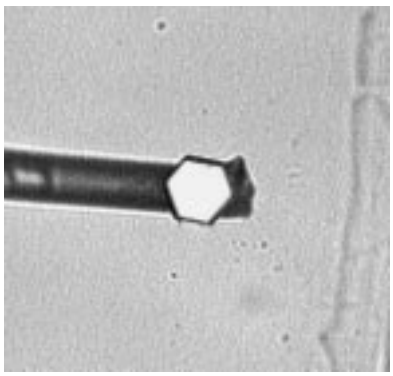

Figure 3. Optical microscope image of a hexagonal Au (111) microcrystal with $d_{eff} \approx 10$ μm. The crystal has been attached to a 10 μm Au microwire clearly visible in the background and surrounded from all sides by insulating epoxy resin to a level equal to the height of the crystal.

The electrochemical behavior of the SCUMEs having a (111) orientation was compared with that of a gold (111) single-crystal electrode of usual dimensions ($d_{eff} = 0.145$ cm). The current–voltage curve has a characteristic shape in the positive region which is used to identify the orientation of the

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surface and confirm that single-crystal quality has been maintained during the surface preparation steps. In the case of a (111) crystal face three anodic peaks are observed in the positive-going sweep, and a large reduction peak corresponding to reduction of gold oxide on the negative sweep (Figure 4a). The corresponding results for a SCUME with a

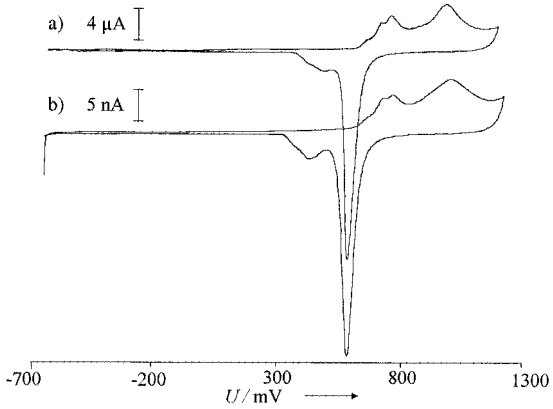

Figure 4. a) Cyclic voltammogram at a Au(111) single crystal with an area of 0.066 cm^2 recorded in 0.093 M $HClO_4$ at 20 $mV\,s^{-1}$; b) cyclic voltammogram at a Au (111) SCUME with an area of 3500 μm^2 recorded in 0.01 M $HClO_4$ at 50 $mV\,s^{-1}$.

d_{eff} of 33 μm are shown in Figure 4b. The current is approximately 1000 times smaller than that at the macroelectrode but the features of the current–voltage curve are essentially the same. In the case of the SCUME the electrode must be cycled into the hydrogen evolution region to ensure that the gold oxide is completely reduced in subsequent cycles. On the first cycle for the SCUME, only one oxide formation peak was observed at +1.1 V; on subsequent cycles this peak diminished and shifted in the positive direction. Eventually three oxide formation peaks were observed at +0.65, +0.70, and +0.76 V, just as with the macroelectrode. The double-layer region remains flat indicating that leakage of electrolyte around the microcrystal is not a problem.

Figure 5 shows cyclic voltammograms at an electrode with a d_{eff} of 5 μm for scan rates of 50, 100, and 150 $mV\,s^{-1}$. The characteristic features in the oxide formation region only develop clearly at higher scan rates with only two current peaks observed in the positive-going sweep. Otherwise the current–voltage characteristics are the same as those at the SCUME with a d_{eff} of 33 μm, but with currents below 1 nA.

Thus we have produced SCUMEs which are sufficiently small that they could be used to study the kinetics of very fast electron transfer reactions. Work has been carried out with both Au(111) and Au(100) crystal faces. Much more will be done to characterize these systems using established methods,[11] for example to study the surface properties using scanning tunneling microscopy and impedance spectroscopy. This will allow a more detailed assessment of surface imperfections such as steps. The method is also being extended to other coinage metals, specifically, silver.

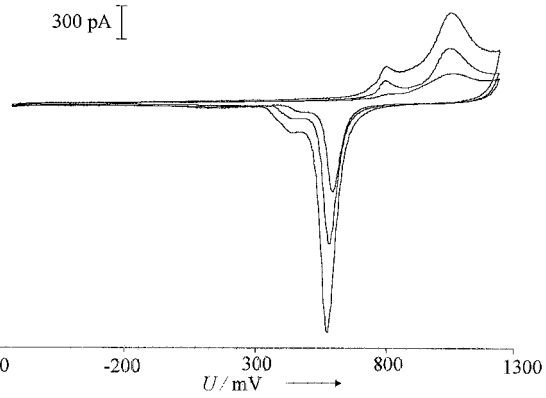

Figure 5. Cyclic voltammograms at a Au (111) SCUME with an area of 80 μm^2 recorded in 0.01 M $HClO_4$ at 50, 100, and 150 $mV\,s^{-1}$. The current increases with increasing scan rate.

Experimental Section

An excess of pure gold wire (99.99%) was dissolved in hot aqua regia (90 °C). The resulting solution of $HAuCl_4$ was filtered to remove the undissolved gold after cooling to room temperature. The resulting saturated solution of $HAuCl_4$ was added dropwise to a solution of sodium metasilicate (Aldrich, $\rho = 1.05\,g\,cm^{-3}$) until the $HAuCl_4$ concentration reached 0.2 M. Then 1 M HCl was added dropwise until the pH value reached 1.0. The solution was then poured into a 2 mL glass test tube which had a gold wire sealed into its bottom. The high HCl concentration in the gel provided the best conditions for microcrystal formation but the gel was formed only after a rather long time (~3 weeks) during which ~35% of the water evaporated.[12] After the gel was formed a second gold electrode was placed at the top of the glass tube and a current of 14 μA was passed through the cell for three weeks using a 1.5 V battery with a 107 kΩ resistor in series with the cell. The current density at the anode was typically 90 $\mu A\,cm^{-2}$. Gold crystallites were observed in the vicinity of the anode after one day, but they were harvested after operating the cell for two weeks, that is, after they had reached the optimum size for the present experiments. The gel was then dissolved in 5 M KOH to free the microcrystals which were then thoroughly washed with ultrapure water. They were pipetted as a suspension in the ultrapure water onto a glass slide and the water was allowed to evaporate. After sorting under a microscope, a microcrystal having the desired facet without visible steps or deformations was selected for incorporation in a SCUME.

Attachment of the microcrystal to a gold microwire and alignment were performed in the micromanipulator (Figure 2). Initially a 1 cm length of the gold microwire (10 μm diameter, JMC Puratronic) was soldered to a longer length of copper wire (1 mm diameter). The copper wire was then placed in the holder (7) of the micromanipulator such that the tip of the microwire was exactly in the focus of the microscope. Then the tip was dipped into an organometallic gold paint (Glassgold, Engelhardt) and the selected microcrystal sitting on the glass slide was attached to the painted tip by applying gold paint on one face. Contact between the painted tip and the painted face was achieved by lowering the microscope lens (1). The electrode system was then carefully annealed above a small gas-oxygen flame until all the paint was converted to metallic gold, thereby establishing an all-gold contact between the wire and the crystal. The copper wire was then placed in the holder (8) of the micromanipulator until the desired working crystal face was perfectly aligned in a horizontal position. This was confirmed by reflection of the microscope light source on the working face of the microcrystal.

The final step in the fabrication process was to insulate the conducting parts of the system using epoxy cement so that only the working face was exposed. In the case of the flat trigonal and hexagonal crystal with a (111) face, a drop of epoxy (Devcon, 2-Ton) was placed under the crystal and allowed to harden sufficiently such that the crystal would float on its surface. In this way the back and sides were completely covered and the exposed face was embedded in a smooth epoxy resin background which was the same height as the crystal to within less than 1 μm. After the epoxy

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resin had hardened completely the remainder of the uninsulated gold microwire was covered with a thin layer of epoxy resin so that only the (111) face was left exposed. This procedure was successful for microcrystals with $d_{eff} = 10-35$ μm. In the case of smaller SCUMEs, for example with a d_{eff} of 5 μm, a slightly different procedure was used to minimize the capacitative current.[13] In this case a 100 μm length of a gold microwire with a diameter of 3 μm was first fixed to the larger 10 μm wire using the gold paint. The small microcrystal was then fixed to the 3 μm wire using the same procedure described above. Slightly different procedures were used to fabricate SCUMEs with exposed (100) faces.

All electrochemical experiments were carried out in a water-jacketed glass cell with the SCUME, a Pt counterelectrode, and a calomel reference electrode containing 0.05 M KCl. The cell was placed in a Faraday cage and coaxial cables were used to connect the electrodes to the potentiostat. Electrolyte solutions were prepared from $HClO_4$ (Aldrich, 99.999 % pure) diluted to 0.01 M in nanopure water. The solution was purged with argon for 10 min and kept under argon during the measurements. The reference electrode was connected to the body of the cell using a Luggin capillary containing the 0.01 M $HClO_4$ solution. Cyclic voltammograms were recorded by using a EG&G 283 potentiostat connected to a PC minicomputer by a GPIB IEEE-488.2 interface. The current-potential data were acquired digitally.

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$Ga_9(CMe_3)_9$, an Important New Building Block in the Structural Chemistry of the Alkylelement(I) Compounds E_nR_n (E = B – In)**

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Numerous organoelement cluster compounds of the elements boron, aluminum, gallium, and indium have been published in recent literature. Most of them are difficult to prepare and were isolated in only very poor yield. They often contain cluster anions such as $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ or $[Ga_9\{Si(SiMe_3)_3\}_6]^-$.[1] Beside these ionic derivatives a few neutral cluster compounds such as In_8Ar_4 (Ar = 2,6-dimesitylphenyl) or $In_{12}\{Si(CMe_3)_3\}_8$[2] were synthesized in which the number of the cluster atoms exceeds the number of the substituents. To the best of our knowledge there is no systematic approach to the description of their formation and of their fascinating structural chemistry. Element(I) compounds E_nR_n were isolated and structurally characterized before only as monomers ER or as tetrahedral clusters of the type E_4R_4,[3] in which R denotes very bulky substituents. A neopentylgallium(I) compound was reported in literature,[4] however, it was not isolated in a pure form. For many years we have tried to control the size of E^I clusters by the systematic variation of the steric demand of their substituents. Smaller groups should lead to the formation of larger clusters, which are of particular interest owing to their bonding and broad preparative application in secondary reactions. However, the tendency to disproportionate as a consequence of insufficient steric shielding prevented the isolation of such derivatives.

The reaction of *tert*-butyllithium with gallium trihalides affords tri(*tert*-butyl)gallium[5] in a good yield as well as a small quantity of elemental gallium by a redox reaction. By systematically changing the reaction conditions we attempted to stop the partial reduction of trivalent gallium at an intermediate oxidation state. Finally, we obtained a green solution from which black-green crystals of **1** were isolated in 4 % yield after separation of the alkylgallium(III) compound [Eq. (1)]. Owing to the easy availability of compound **1** a complete characterization was possible despite its low yield. The crystal structure determination[6] revealed a tricapped

$$GaCl_3 + 3\,LiCMe_3 \xrightarrow[-LiCl]{} Ga(CMe_3)_3 + \underset{\mathbf{1}}{Ga_9(CMe_3)_9} \qquad (1)$$

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