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Deon T. Miles

*Mississippi State University*

Andrew Knedlik

*Mississippi State University*

David O. Wipf

*Mississippi State University, dow1@msstate.edu*

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# Construction of Gold Micro-Bead Ultramicroelectrodes

Deon T. Miles, Andrew Knedlik, and David O. Wipf\*

Department of Chemistry, BOX 9573

Mississippi State, MS 39762

(601) 325-3584, (601) 325-1618 [FAX]

*wipf@ra.msstate.edu*

## Abstract

A new way to construct small electrodes by the use of metal micro-beads is described. Gold beads of 1.5 to 3.0  $\mu\text{m}$  diameter were used to construct inexpensive and disposable microelectrodes with overall structural diameters of  $\leq 6 \mu\text{m}$  and electrode diameters of  $\leq 5 \mu\text{m}$ . The voltammetric response of these electrodes is consistent with existing theory and the electrodes exhibited the sigmoidal waves expected at ultramicroelectrodes.

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ORCID IDS:

DOW <https://orcid.org/0000-0003-2365-1175>

DTM <https://orcid.org/0000-0002-9017-1406>

Structurally small ultramicroelectrodes are of interest for their use as either microscopic analytical probes or in fundamental studies of transport at electrode surfaces. As such, methods for their preparation are an ongoing concern.<sup>1-11</sup> A common construction approach is the use of metal micro-wires embedded in an insulating material. Although electrodes constructed in this way are rugged and have excellent electrochemical behavior,<sup>12</sup> these electrodes are ultimately limited by the available size of the micro-wire. In addition, expense becomes critical for the thinnest of the micro-wires. A popular method to make structurally small electrodes is to use either etched metal wires<sup>4, 7</sup> or carbon fibers,<sup>5, 8</sup> which are then usually insulated with a thin layer of polymer. Alternately, small ring- or disk-shaped electrodes can be made by deposition of silver<sup>10</sup> or carbon<sup>1, 9, 11</sup> on the inner walls of micropipette tips or gold on a glass fiber.<sup>13</sup> Pendley has described an interesting method in which a Pt wire in a capillary is pulled to a small diameter on a pipette puller, thus making a micro-sized electrode.<sup>6</sup>

In this paper we demonstrate a method for preparation of small gold ultramicroelectrodes using microscopic gold beads as starting material. An advantage to the use of microscopic metal particles to make electrodes compared to electrodes constructed from micro-wires or etched wires is that they are inexpensive and particles are available in smaller dimension than metal micro-wires. In addition, metal particles are easy to handle as suspensions in water and thus avoid the fragility of the etched wires or the micro-wires.

## Experimental

**Chemicals** Hexaammineruthenium(III) chloride (Strem Chemicals) was used as received. All other chemicals were reagent grade and were used as received. Solutions were prepared with 18 M $\Omega$  distilled-deionized water. The gold beads were purchased from Aldrich Chemical Co. and were specified to have a diameter of 1.5-3.0  $\mu\text{m}$ . EPON 828 epoxy resin and triethylenetetramine (TETA) hardener were purchased from Miller-Stephenson Chemical Co., (Danbury CT).

**Electrodes and Instrumentation** Micropipette blanks were pulled from 1.5 mm o.d., 0.86 mm i.d., filament-containing borosilicate tubing (Sutter Instrument Co., Novato, CA) with the use of a Model P-87 (Sutter) puller. The electrodes were polished with the use of a micromanipulator and a glass micropipette

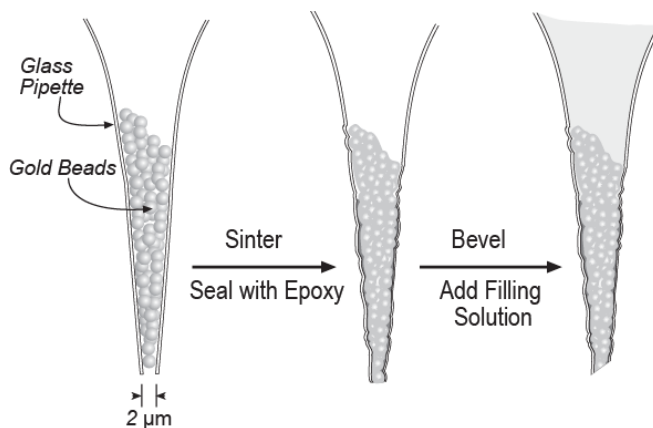
beveler (World Precision Instruments). The beveler used a diamond impregnated abrasive polishing plate (extra fine, Sutter). Further construction details are given below.

All potentials are referred to a Ag/AgCl (3 M NaCl) reference electrode. The auxiliary electrode was a Pt wire.

The electrochemical experiments were performed with the BAS 100B/W electrochemical workstation (BAS, West Lafayette, IN). The microphone apparatus for use in the polishing step was home built. An inexpensive battery powered amplifier (Radio Shack) provided audible output.

## Results and Discussion

**Construction of the Ultramicroelectrodes** The basic steps used in construction of the micro-bead gold electrodes are shown in Figure 1. A micropipette puller is used to pull capillaries with a tip opening of 2  $\mu\text{m}$ . The pipette puller uses a preprogrammed series of heating, pulling, and stretching steps to produce pipettes that are very uniform in shape and opening dimension. It is important to use capillaries that have an internal glass filament, which greatly aids in filling the pipettes.



**Figure 1.** Cartoon of the micro-bead ultramicroelectrode electrode construction process.

Gold beads of 1.5 to 3.0  $\mu\text{m}$  diameter are injected as a suspension (2 mg/mL in distilled-deionized water) into the non-tapered end of the pipette. Holding the pipette tip down allows the beads to settle into a cone shape collection at the tip. The remaining water is evaporated by heating in a 120° C oven for 60 min.

The pipette tip and beads are then reheated (using the pipette puller heating filament) to a temperature of about 580° C for 1 to 2 s to sinter the gold beads into a solid mass.

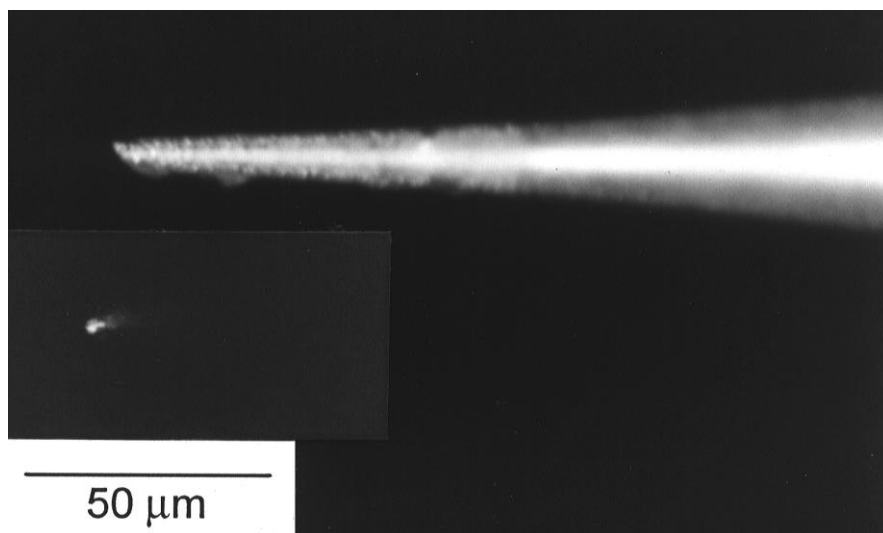
After sintering, epoxy is used to provide a leak-proof seal of the gold beads in the pipette tip. A mixture of EPON 828 resin (100 parts) and TETA hardener (13 parts) is heated slightly to reduce its viscosity to a water-like consistency. The tip is dipped into the warm resin mixture for 30 seconds while applying a vacuum from a water aspirator to the open end of the electrode. Any epoxy remaining on the outside of the tip after dipping is removed by an acetone rinse. The epoxy is then cured for a minimum of 3 hours in a 120° C oven. By making batches of 10 to 20 electrodes at a time, the average preparation time for the unpolished electrodes is less than 5 min., excluding the evaporation and epoxy curing times.

After sealing, the electrodes are polished as they are needed by the use of a micropipette beveling apparatus. Because of the fragile nature of the tips, some care is required in the polishing step. A micromanipulator is used to lower the electrode tip to a rotating diamond abrasive plate. Observation, by use of a low-power microscope, of the shadow cast by the electrode onto the plate assisted in the approach. A small lamp, shining perpendicular to the electrode, was used to increase the definition of the shadow line. However, an indispensable aid in the polishing step is the use of a microphone and amplifier. By mounting the microphone on the microelectrode holder the vibration caused by contact of the electrode with the polishing plate is transmitted through the electrode and the electrode mount to the microphone body. Using earphones, the moment at which the tip touched the polishing plate can be heard. Once contact is made, complete polishing requires about five seconds.

Electrical contact between the gold beads and external circuits is made with an electrolyte filling solution consisting of 4 M potassium acetate, 0.1 M potassium ferricyanide, 0.1 M potassium ferrocyanide, and 0.15 M KCl. A Pt wire is inserted to complete the connection. Other reports suggest that either a 4 M potassium acetate/0.15 M KCl or a 3 M NaCl solution give good results for contact to carbon-fiber electrodes.<sup>14, 15</sup> However, use of these solutions produced waves with up to 200 mV of hysteresis and irreproducible half-wave potentials at the gold-bead electrodes. Adding the ferri/ferrocyanide salts to the 4 M potassium acetate solution removes the hysteresis and shifts the waves to the expected position. Note that the use of traditional electrode contact materials such as silver-filled epoxy or carbon powder were not used due to difficulty in placing the contact material into the small tip.

The success rate for construction of these electrodes was about 46%, (55 of 121 electrodes). This number includes early attempts so future success rates will likely improve. A success was defined as an electrode that gave a sigmoidal wave for the reduction of  $\text{Fe}(\text{CN})_6^{3-}$  or  $\text{Ru}(\text{NH}_3)_6^{3+}$ . A common failure mode is tip breakage and, more so in early experiments, leakage. Leaky electrodes give interesting results because application of a potential causes a large iontophoretic current to flow as filling solution ions are ejected from the tip.

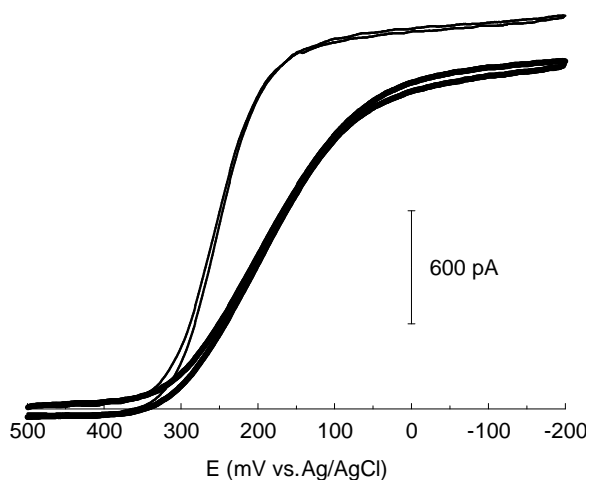
An optical micrograph of a completed electrode is shown in Figure 2. Visible in the photograph is the bevel formed during polishing and the sintered gold particles inside the pipette. A demarcation line about  $90\ \mu\text{m}$  from the tip shows the extent of the epoxy seal. To the right of that is the conducting electrolyte solution in contact with the gold. Below the lateral view, an end-on view shows the exposed electrode. The resolution of the photograph is not sufficient to fully resolve the electrode shape but the larger gold spot to the left is the exposed electrode. To the right, the smaller gold spot is not actually exposed but is visible looking through the transparent epoxy.



**Figure 2.** An optical micrograph of the tip of a gold-microbead ultramicroelectrode. Below the lateral view is an inset showing an end-on view of the tip.

**Voltammetry at the Ultramicroelectrodes** Electrodes constructed using the above methods were tested by cyclic voltammetry in a solution of  $\text{Fe}(\text{CN})_6^{3-}$  ion in 1 M KCl or  $\text{Ru}(\text{NH}_3)_6^{3+}$  ion in pH 4.0 phosphate/citrate buffer. Two example voltammograms are shown in Figure 3. These two voltammograms,

of 2 mM  $\text{Fe}(\text{CN})_6^{3-}$  in 1 M KCl, are obtained at two different electrodes (electrodes A and B in Table 1) constructed on the same day. Notice that one of the voltammetric waves (electrode A) is more drawn out than the other. This illustrates an occasional problem of a high resistance contact due to the electrolyte filling solution and is most likely due to a small bubble in the filling solution near the tip end. Although objectionable, the higher resistance of the contact may not be critical for amperometric measurements. In addition, simply waiting or gentle tapping can remove or reduce the bubble size to provide a lower resistance contact. The data for voltammograms of the  $\text{Ru}(\text{NH}_3)_6^{3+}$  ion shows this. These voltammograms, taken shortly after the  $\text{Fe}(\text{CN})_6^{3-}$  data, have uniform and correct half-wave positions (cf. Table 1).



**Figure 3.** Cyclic voltammograms at gold micro-bead electrodes for the reduction of 2 mM  $\text{Fe}(\text{CN})_6^{3-}$  in 1 M KCl at 100 mV/s. (thick line) Electrode #A from Table 1. (thin line) Electrode #B from Table 1.

An estimate for the diameter of the micro-bead electrodes can be made by using the following equation, which gives the steady-state limiting current,  $i_l$ , at an embedded disk electrode:<sup>12</sup>

$$i_l = 4rnFDC \quad (1)$$

where  $r$  is the electrode radius,  $n$  is the number of electrons involved in the transfer,  $F$  is the Faraday constant, and  $D$  and  $C$  are the diffusion coefficient and the concentration of the electroactive species, respectively. Table 1 shows electrochemical data collected for three electrodes, the calculated electrode diameter from equation 1, and the external diameter of the tip measured by optical microscopy. Note that the diameter is measured perpendicular to the electrode's long axis and not along the beveled edge.

Interestingly, electrodes A and B have measured tip diameters equal to or smaller than the estimated electrode diameter. Obviously, the electrode diameters estimated using equation 1 are inaccurate. In a larger sample of 33 electrodes, the average electrode diameter estimated from equation 1 was  $5.2 \pm 3.2 \mu\text{m}$  while the measured tip diameter was  $5.7 \pm 1.9 \mu\text{m}$ .

**Table 1. Cyclic Voltammetric and Microscopic Data for Three Gold Micro-Bead Electrodes**

Electrode	Measured Tip Diameter ( $\mu\text{m}$ )	2 mM $\text{Fe}(\text{CN})_6^{3-}$			1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$		
		$i_l$ (nA)	Estimated Electrode Diameter ( $\mu\text{m}$ ) <sup>a</sup>	$E_{1/2}$ (mV vs. Ag/AgCl)	$i_l$ (nA)	Estimated Electrode Diameter ( $\mu\text{m}$ ) <sup>b</sup>	$E_{1/2}$ (mV vs. Ag/AgCl)
A	5	1.62	6.0	192	0.63	4.7	-139
B	6	1.93	7.1	254	0.94	8.8	-138
C	5	0.72	2.6	184	0.27	2.5	-143

<sup>a</sup>Calculated from equation 1,  $C = 2.0 \times 10^{-6} \text{ mol cm}^{-3}$ ,  $D = 7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (obtained from ref. 16).

<sup>b</sup>Calculated from equation 1,  $C = 1.0 \times 10^{-6} \text{ mol cm}^{-3}$ ,  $D = 5.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (obtained from ref. 16).

Scanning electron microscope images of the micro-bead electrodes did not show sufficient contrast between the gold and the insulating glass or epoxy to allow a direct measurement of the electrode diameter. However, the SEM images did show that the electrodes were smoothly polished with no evidence that the electrode was either recessed or protruding from the surface. And also, that the thickness of the glass insulator was between 0.7 to 1  $\mu\text{m}$  at the tip end.

There are two reasonable explanations for the poor electrode size estimate. One is that equation 1 assumes a disk embedded in an *infinite* insulating plane. In this case the insulator size is quite finite. Shoup and Szabo considered this problem and showed that in the case of a finite insulator, the current is increased due to a spherical diffusion contribution (as opposed to only hemispherical or convergent diffusion).<sup>17</sup> The relevant parameter,  $\rho$ , is the ratio of the electrode diameter over the insulator diameter. For  $\rho$  of about 0.8, an enhancement of about 22% over the prediction of equation 1 is calculated. The enhancement drops to less than 10% at  $\rho$  equal to 0.5



A second reason for the poor estimate is that the electrodes are not always disk shaped. A disk-shaped electrode will be formed from the cross section of a single bead. However, if the exposed electrode is larger and composed of two or more beads, the electrode would be roughly elliptical in shape. An elliptical, rather than a disk, shape would give a 41% increase in apparent electrode area at a 45° bevel angle. Thus, the diameter calculated from equation 1 would be 19% larger. Another aspect is that electrodes with more than one exposed gold bead have 2, 3, or more lobes and so the perimeter of these electrodes is larger than a disk or ellipse of equivalent area. The increased perimeter would also tend to increase the amount of current observed.

Given these two effects, consider Figure 4. The bottom panel plots the measured tip diameter versus the apparent electrode diameter (from equation 1). There is little correlation, but this plot does show that the apparent electrode diameter is often larger than the measured tip diameter. The top panel shows a clearer picture. In this case a ratio  $Z$ , defined as:

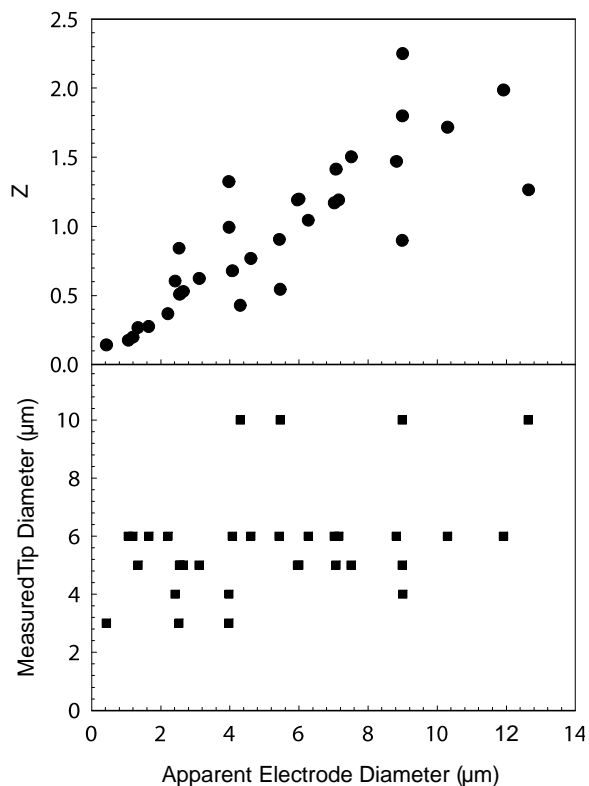
$$Z = \text{Apparent Electrode Diameter/Measured Tip Diameter} \quad (2)$$

is plotted versus the apparent electrode diameter. At apparent electrode diameters of 2.5  $\mu\text{m}$  or less,  $Z$  is less than about 0.5. This is consistent with the above presumptions. The electrode is likely disk-shaped, not elliptical, and the thickness of the glass and epoxy insulator is sufficient to diminish the enhancement due to a finite insulator radius. At larger apparent electrode diameters the ratio rises to a value of around 1.5. As the electrode becomes larger, the current enhancement effect of the finite insulator thickness causes the apparent electrode diameter to increase by about 22% (for a 6  $\mu\text{m}$  diameter tip the maximum electrode size is about 4.6  $\mu\text{m}$  due to the insulator thickness,  $\rho = 0.8$ ). The effect of the elliptical electrode shape could cause an additional 19% increase to give a total increase of about 45%. There are a few data points at larger ratios in Figure 4. An irregular electrode shape or a non-smooth surface (perhaps due to partially broken or chipped tip) may account for the larger ratios.

The above analysis suggests that the current response is not abnormal. Better estimates of the electrode diameter are not possible without additional information. If the actual electrode diameter is required, it could be determined from a combination of the transient and steady-state electrode response.<sup>18</sup> In most cases the tip diameter was measured as less than 6  $\mu\text{m}$ , suggesting that the actual electrode diameter was about 4  $\mu\text{m}$  or less.

## Conclusions

Significantly smaller electrodes can be constructed with the use of micro-beads than with the use of micro-wires. These micro-bead electrodes may be useful for in-vivo electrochemical measurements<sup>5, 11, 15</sup> or in any restricted volume measurement. These electrodes can be used as tips for the scanning electrochemical microscope and a satisfactory SECM image has been acquired with a gold micro-bead electrode.<sup>19</sup> In addition, gold micro-bead electrodes can be constructed at a much lower material cost than electrodes constructed from gold micro-wire. Over 20 micro-bead electrodes can be made for the cost of a single 5  $\mu\text{m}$  gold micro-wire electrode, with the majority of the cost for the micro-bead electrode due to the cost of the capillary tube.



**Figure 4.** (Bottom) Plot of the measured tip diameter for a number of different gold micro-bead electrodes versus the apparent electrode diameter as calculated from equation 1. (Top) Plot of the ratio of the apparent electrode diameter/measured tip diameter ( $Z$ ) versus the apparent electrode diameter.

Further improvements in the construction of these types of electrodes is needed in making electrical contact to the metal particles and in the polishing process. One method that can be used to improve the

polishing process is measurement of the electrical impedance between the electrode and an electrolyte covered polishing disk. These types of impedance measurements are commonly used in polishing of micro-pipettes<sup>20</sup> and have been used in polishing of etched carbon-fiber microelectrodes.<sup>5</sup> Polishing to a set electrode impedance should provide more reproducible electrode diameters. Improvement in polishing techniques will also allow smaller metal particles or beads to be used, perhaps permitting nanometer-dimension electrodes to be constructed. For example, Pt particles of less than 500 nm size are available as well as colloidal gold particles.

Alternately, beads can be used to make microelectrodes from non-ductile metals. Iridium has been used as a non-alloying base at which to deposit small mercury electrodes.<sup>21</sup> In this report, the iridium disk electrode was constrained by the wire size to 127  $\mu\text{m}$  in diameter. However, iridium particles are available in sizes less than 38  $\mu\text{m}$  in diameter, which could allow construction of significantly smaller iridium-mercury electrodes.

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