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Fabrication and Characterization of Self-Assembled Spherical Gold Ultramicroelectrodes

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Spherical ultramicroelectrodes with diameters of 1−30 μm have been prepared by self-assembly of Au nanoparticles and 1,9-nonanedithiol molecules at the tip end of glass micropipets. The electrodes were characterized by optical and scanning electron microscopy, cyclic voltammetry in aqueous and acetonitrile solution, and scanning electrochemical microscopy approach curves. A modified theory for hemispherical electrodes was used to compute the approach curves, which agreed with the experimental results. The construction strategy represents a bottom-up approach to the fabrication of microspherical electrodes.

Ultramicroelectrodes (UMEs) have been widely used for the study of fast kinetics, high-resolution electrochemical imaging, and electrochemical sensing in spatially restricted environments such as biological cells.[1,2] These applications generally require knowledge of the electrode geometry to interpret the electrochemical response correctly. Disk-shaped electrodes produced by sealing a conductive wire (e.g., Pt or C) in an insulating layer (e.g., glass or epoxy) followed by polishing are the most frequently used UMEs, although cylindrical and band structures have also been employed.[1,2] However, spherical UMEs are also possible and have the advantage of simpler theoretical behavior, because the electrode surface is uniformly accessible and hence the current density is uniform across the surface (neglecting any possible shielding at the small fraction of the surface in contact with the sphere support).[3] Moreover, in the micrometer and nanometer range, it is technically difficult to control the disk electrode shape precisely. A further complication is that these electrodes are often recessed within their insulating sheath, which makes them unsuitable as tips for scanning electrochemical microscopy (SECM), both for kinetic studies and for high-resolution imaging.[4,5] A recessed electrode cannot approach a surface very closely, because its protruding glass rim collides with the substrate. While there are several reports on the preparation and properties of these very small UMEs[6,7] and even smaller nanodes,[8] the preparation of a suitable SECM tip in this size range still depends on the skill and patience of the experimenter. Indeed, knowledge of the UME configuration and geometry is important in drawing kinetic conclusions from measurements at UMEs.[5,9] From these considerations a method allowing the routine fabrication of UMEs with well-defined geometry, like a sphere, is highly desirable.

We report here the first colloid chemical approach to the preparation of UMEs. It leads to perfectly spherical electrodes, in the size range of 1−30 μm, by self-assembly from solution. This technique is based on the work of Schiffrin and co-workers, who found that nanometer-sized Au particles can be self-assembled to electronically conductive bulk materials[10] and multilayer thin films,[11] by the use of dithiol cross-linking agents. Their method involves either the addition of dithiol to a solution of Au particles, which leads to the precipitation of the conductive material, or layer-by-layer growth of thin-film structures by alternate immersion of a suitably functionalized substrate in solutions of Au particles and dithiol linking agent.

The approach presented here is a modification of this method, where the dithiol linking agent is confined to the tip lumen of a micropipet, which is then immersed in a solution of Au particles. Well-developed spheres with a golden metallic luster grow at the end of the tip. If a conductive carbon coating is applied to the inside wall of the micropipet prior to the preparation of the self-assembled electrode, the microspheres can be electrically contacted. The electrodes prepared in this way have been characterized by optical and scanning electron microscopy, cyclic voltammetry in aqueous and acetonitrile solution, and SECM approach curves. The theoretical treatment of the approach of a hemispherical electrode was adapted to fit the experimental approach curves.

The self-assembly of nanometer-sized constituents into a predetermined geometry of micrometer dimensions, as observed here, is relevant in the general area of nanofabrication and

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(1) Wightman, R. M.; Wipf, D. O. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1989; Vol. 15, p 267.

(2) *Microelectrodes: Theory and Applications*; Montenegro, M. I.; Queiros, M. A.; Daschbach, J. L., Eds.; NATO ASI Series E; Kluwer: Boston, 1991; Vol. 197.

(3) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications;* Wiley: New York, 1980.

(4) Bard, A. J.; Fan, F.-R. F.; Mirkin, M. V. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1994; Vol. 18, p 243.

(5) Bard. A. J.; Fan, F.-R. F. *Proceedings of the Robert A. Welch Foundation Conference on Chemical Research. 40: Chemistry on the Nanometer Scale*; in press.

(6) (a) Strein, T. G.; Ewing, A. G. *Anal. Chem.* **1992**, *64*, 1368. (b) Strein, T. G.; Ewing, A. G. *Anal. Chem.* **1993**, *65*, 1203.

(7) (a) Wong, D. K. Y.; Xu, L. Y. F. *Anal. Chem.* **1995**, *67*, 4086. (b) Zhang, X.; Zhang, W.; Zhou, X.; Ogorevc, B. *Anal. Chem.* **1996**, *68*, 3338.

(8) Penner, R. M.; Heben, M. J.; Longin, T. L.; Lewis, N. S. *Science* **1990**, *250*, 1118.

(9) (a) Baranski, A. S. *J. Electroanal. Chem.* **1991**, *307*, 287. (b) Oldham, K. B. *Anal. Chem.* **1992**, *64*, 646.

(10) Brust, M.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. *Adv. Mater.* **1995**, *7*, 795.

(11) Bethell, D.; Brust, M.; Schiffrin, D. J.; Kiely, C. *J. Electroanal. Chem.* **1996**, *409*, 137.

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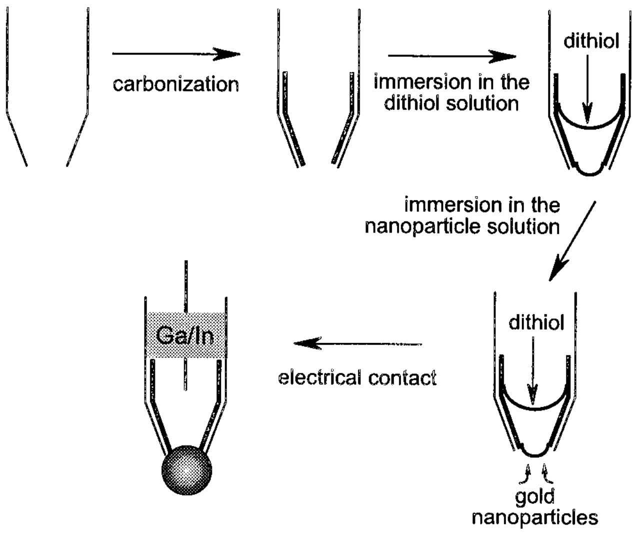

Figure 1. Schematic for the preparation of self-assembled spherical UMEs.

represents a novel construction strategy with a controlled bottom-up approach to the formation of microstructures.

EXPERIMENTAL SECTION

Preparation of Au Sols. Solutions containing Au particles of ~8 nm diameter in toluene were prepared as described by Schiffrin et al.[10] Briefly, 30 mL of a 30 mM aqueous solution of hydrogen tetrachloroaurate was mixed with 80 mL of a 50 mM solution of tetraoctylammonium bromide in toluene and stirred vigorously. After quantitative transfer of the tetrachloroaurate to the organic phase, 25 mL of a freshly prepared 0.5 M aqueous solution of sodium borohydride was added with vigorous stirring. After further stirring for 2 h, the ruby organic phase was separated, washed once with 0.1 M sulfuric acid, twice with 1 M sodium carbonate solution, and five times with water, and dried over anhydrous sodium sulfate. Before use the solution was diluted with toluene to give a gold content of ~125 mg/L.

UME Fabrication. The procedure of UME manufacture is outlined schematically in Figure 1. Glass micropipets having a tip orifice of 0.1−1-μm diameter were pulled using a Sutter Instruments (Novato, CA) laser pipet puller Model P2000. The glass capillaries (Sutter) used were of 1-mm outer and 0.5-mm inner diameters. The inner walls of the pipets were coated with an electrically conductive layer of amorphous carbon, generally following the method described by Wong and Xu.[7a] Briefly, the micropipets were filled with methane and immersed under a constant pressure of 16 bar in a He-flooded quartz tube, which had been heated to 1000 °C with a heating coil. To prevent cracking of the carbon film, immersion and withdrawal of the pipets were carried out slowly, over a period of ~5 min, and as a continuous process, i.e., without letting the pipets rest inside the heated quartz tube. This procedure causes a carbon film to deposit on the inside wall of the pipet without closing the tip. Micropipets carbonized in this way were then immersed in a 5 mM solution of 1,9-nonanedithiol in 2-propanol for at least 1 h to fill the tip ends with a small amount of this solution. The same results were obtained with toluene as solvent for the cross-linking agent. Subsequently, the outside walls of the pipets were thoroughly rinsed with toluene to remove excess dithiol from the glass. The pipets were then immersed in Au sol. Self-assembled spheres were formed in 2 h. They had a golden metallic luster under the optical microscope and diameters ranging from 1 to 30 μm, depending on the micropipet tip size and the concentration of the dithiol solution. In some cases, a conductive layer of the material was also deposited on the external surface of the glass adjacent to the self-assembled sphere. This layer could easily be removed by briefly dipping the tip in a dilute solution of aqua regia ($HNO_3/HCl/H_2O$ 1:3:10) and subsequent rinsing with water. The final electrical contact was made by inserting a thin Ni wire after filling the pipet from the top with liquid Ga/In eutectic, which touched the carbon film but not the self-assembled microsphere at the end of the tip.

Microscopy. Self-assembled UMEs were inspected by optical and scanning electron microscopy using an Olympus BH-2 optical microscope and a JEOL JSM 35 C scanning microscope.

Electrochemistry. Cyclic voltammetry was carried out using a CH Instruments (Memphis, TN) Model 660 electrochemical work station and a standard three-electrode cell with a Pt wire auxiliary electrode, a saturated calomel reference electrode (SCE) in aqueous solution, and a Pt quasi-reference in acetonitrile. SECM approach curves were recorded in aqueous solution using a 0.5-mm-diameter Pt disk, which had been polished to mirror finish, as a conductive substrate and a glass microscope slide as an insulating substrate. The method and instrumentation employed has been described elsewhere.[12,13] All potentials are quoted with respect to SCE.

Materials. All chemicals used were of highest available purity grade and were used as received from Aldrich and Fluka.

RESULTS AND DISCUSSION

Self-Assembly of Microspheres. A representative selection of self-assembled spherical UMEs is shown in the micrographs in Figure 2. The most striking feature of the new preparation technique is that the electrodes in the size range investigated so far are near perfect smooth spheres. This finding is important for their applications in electrochemistry, but it also raises a number of questions regarding their growth mechanism and structure, which we discuss below. A number of parameters could be chosen as possible variables to control the size of the microspheres, which will ultimately depend on the total amount of dithiol initially present in the tip. It should be possible to adjust the size simply by altering the concentration of the dithiol solution while using a standard tip size. Unfortunately, the tip size cannot be controlled very precisely in the required size range, and the thickness of the conductive carbon film at the inner wall of the pipet is somewhat variable. For these reasons, only very preliminary studies were conducted aimed at achieving precise size control. Tip orifices of ~0.5-μm diameter gave microspheres of 2−10-μm diameter with a 5 mM solution of 1,9-nonanedithiol. Smaller tips (~0.1 μm) under the same conditions produced spheres of 1−3-μm diameter, while spheres with a diameter up to 30 μm were obtained using a tip orifice of ~1 μm. The smallest tips that can be pulled typically have an orifice of a diameter between 20 and 50 nm, but the carbon coating at the inside wall of these generally closes the tip. Self-assembly of microspheres can still be achieved, if the tip end is etched open electrochemically by cycling the potential into the region of anodic decomposition of the carbon film, until a pronounced thin-layer cell behavior of

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(12) Bard, A. J.; Fan, F.-R. F.; Kwak, J.; Lev, O. *Anal. Chem.* **1989**, *61*, 1794.
(13) Wipf, D. O.; Bard, A. J. *J. Electrochem. Soc.* **1991**, *138*, 489.

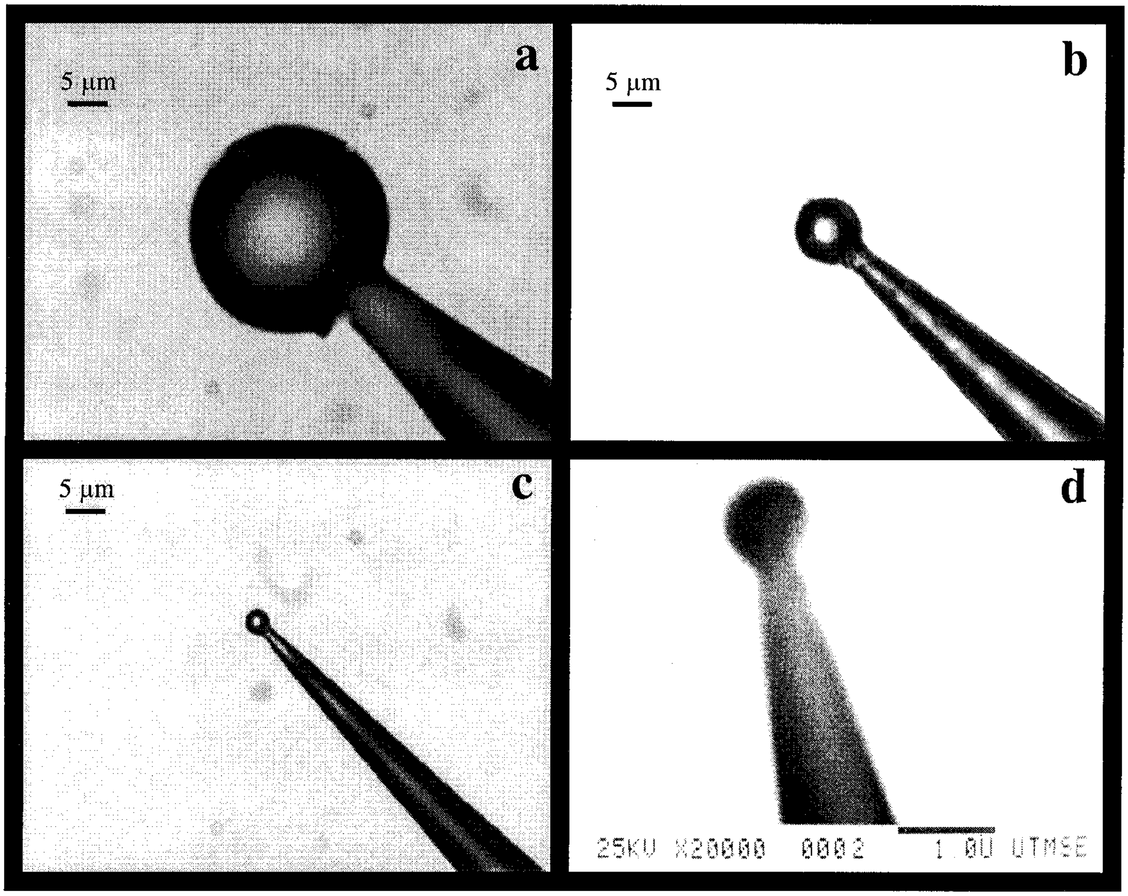

Figure 2. Optical (a−c) and SEM (d) micrographs of self-assembled UMEs. The horizontal bar at the lower corner of (d) represents 1 µm. Electrode diameter, (a) 26, (b) 8, (c) 3, and (d) 0.9 µm.

a suitable redox couple in solution is observed. This way, submicrometer spheres should be obtainable. These are currently being investigated.

Previous TEM observations have shown that solutions of Au particles (on the order of 8-nm diameter) like those used here react with dithiols to form globular aggregates on the 100-nm scale, as well as strings of such aggregates, rather than dendritic random structures which would be expected for merely diffusion-limited growth.[10] These aggregates exhibit a remarkable degree of long-range ordering among the particles, and similar preparations lead to the formation of two-dimensional superlattices of Au particles.[14,15] TEM and studies of the temperature dependence of the electronic conductivity also showed that the Au particles maintain their individual character within the material and do not fuse to larger units.[10] Our preparations differ from those described in ref 10 only in that the mixing region of dithiols and Au particles is confined to the tip end of the micropipet, which restricts the aggregation of particles to this region. On the basis of previous studies, the self-assembled microspheres reported here probably also comprise individual Au particles of ~8 nm diameter, which are cross-linked by 1,9-nonanedithiol molecules and possibly even show formation of three-dimensional superlattices of the nanoparticles. Obviously, further characterization of the material is required to substantiate this model. The spherical shape is indicative of a certain mobility of the individual particles within the aggregates and supports the notion that the self-assembly process is not simply a deposition of bulk gold from a colloidal solution for which dendritic growth would be expected. In the absence of dithiol, no deposition of material is observed, which demonstrates the importance of the cross-linking agent for the self-assembly process. The microspheres grow while the tip containing the dithiol solution is already closed by aggregated particles and hence isolated from the Au particle solution. Therefore the dithiol molecules must be able to penetrate the growing spherical assemblies, possibly by space replacement reactions. This is consistent with the findings of Murray and co-workers,[16] who prepared functionalized Au clusters by replacing their surface-bound thiol ligands with bifunctional thiols simply by equilibrium place exchange reactions. It is unclear to what extent the dithiol molecules might be attached to only one gold particle in a looped mode. Recent STM studies by Nakamura et al. suggest that even longer chain dithiols (C_{12}) are predominately attached to planar gold surfaces via only one thiol group.[17] Thus, from these results, looped dithiols, if present at all, probably constitute a minority species in our system. A further interesting question is whether any ions or solvent molecules are incorporated in the spherical assemblies. Preliminary XPS studies indicate the presence of nitrogen from the quarternary ammonium ions but show no evidence for the entrapment of bromide within the

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(14) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428.

(15) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690.

(16) Hostetler, M. J.; Green, S. J.; Stokes, J. J.; Murray, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 4212.

(17) Nakamura, T.; Kondoh, H.; Matsumoto, M.; Nozoye, H. *Langmuir* **1996**, *12*, 5977.

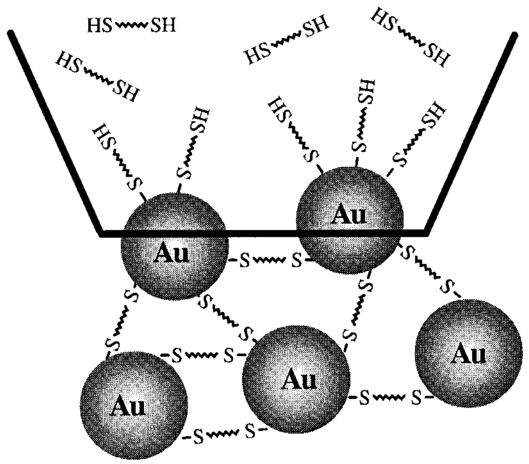

Figure 3. Schematic picture of the self-assembly process leading to the formation of microspheres at the end of the micropipet tip. Such a diffusion-limited growth mechanism normally leads to dendritic structures. The formation of energetically favored spheres indicates mobility of the Au particles within the assemblies.

structure. We thus have a preliminary qualitative picture of the formation of microspheres via spatially confined self-assembly of Au nanoparticles from solution which is illustrated in Figure 3. The particles diffuse to the tip and react immediately with dithiol molecules until the initial aggregate forms a blockage at the end of the tip. Dithiol molecules are able to permeate the nanostructure and further particles are attached until all of the dithiol is consumed. The particles maintain sufficient mobility within the assembly to accommodate themselves into a sphere, which is the most favorable geometry to minimize the surface energy.

Cyclic Voltammetry. Although the microspheres are probably composed of individual Au nanoparticles, their electrochemical behavior is very similar to that of bulk Au electrodes. Presumably only the surface layer of the Au particles is involved in heterogeneous electron transfer, and although the electronic resistivity of the material is high compared to bulk Au, it is still negligibly small with respect to the currents that flow at UMEs. The observed electrochemical behavior is consistent with previous reports on electrochemically addressable monolayers[11,18–20] and multilayer thin films[11] of small Au particles. Figure 4 shows the cyclic voltammogram of a 10-μm electrode in 0.5 M sulfuric acid. In the anodic region, the onset of oxide formation is not as sharp as observed for clean bulk Au electrodes, probably because of the oxidation of some dithiols present at the surface of the sphere. Otherwise, the observed voltammogram is typical for gold. Repeated cycling does not lead to significant changes in the cyclic voltammogram. The surface area estimated from the oxide reduction peak[21] is 3×10^{-6} cm^2, which is in good agreement with the diameter determined by optical microscopy. Figure 5 shows a series of cyclic voltammograms obtained with five electrodes of different size in a 7.5 mM aqueous solution of hexaammineruthenium(III) chloride and 1 M KCl base electrolyte. The electrochemically determined surface area agrees very well

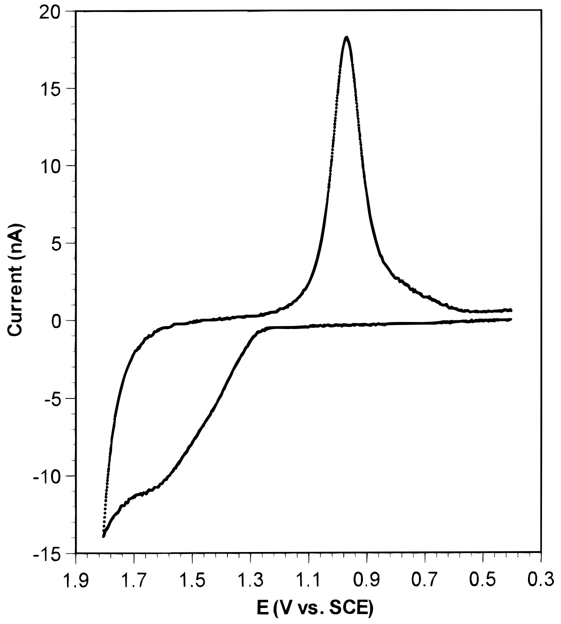

Figure 4. Cyclic voltammogram of a self-assembled UME in 0.5 M H_2SO_4. Scan rate, 1 V/s.

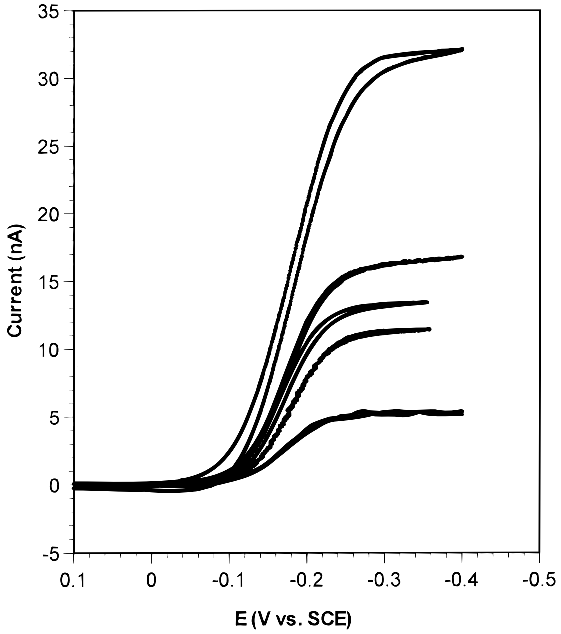

Figure 5. Cyclic voltammograms of self-assembled UMEs of different sizes recorded in a 7.5 mM aqueous solution of hexaammineruthenium(III) chloride and 1 M KCl electrolyte. Electrode diameters, from top to bottom, 10, 5, 4, 3, and 1.7 μm. Scan rate, 0.1 V/s.

with the size measured by optical microscopy, which confirms the notion of surface smoothness and absence of porosity. The contact area between the glass capillary and the microsphere is negligibly small for these considerations (less than 15% of the electrode area). None of the electrodes showed thin-layer cell behavior at high sweep rates (10 V/s), which is sometimes observed for microelectrodes that do not form a good seal with the glass capillary. This problem is often absent in aqueous solution but can still be very pronounced in acetonitrile because of its lower surface tension. For this reason the electrodes were also tested in acetonitrile (Figure 6) where they showed the same near-ideal UME behavior as in aqueous solution.

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(18) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

(19) Doron, A.; Katz, E.; Willner, I. *Langmuir* **1995**, *11*, 1313.

(20) Grabar, K. C.; Allison, K. J.; Baker, B. E.; Bright, R. M.; Brown, K. R.; Freeman, R. G.; Fox, A. P.; Keating, C. D.; Musick, M. D.; Natan, M. J. *Langmuir* **1996**, *12*, 2353.

(21) Rand, D. A. J.; Woods, R. *J. Electroanal. Chem.* **1971**, *31*, 29.

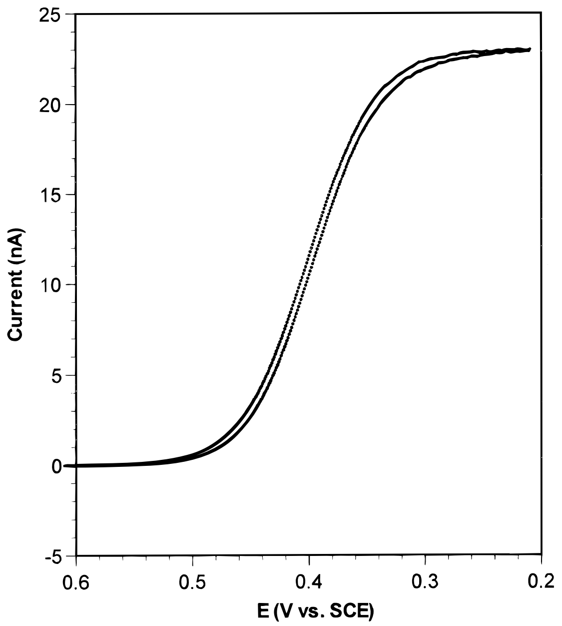

Figure 6. Cyclic voltammogram of tetracyanoquinodimethane (6.5 mM) at a 6-μm-diameter self-assembled UME in acetonitrile. Supporting electrolyte, tetrabutylammonium tetrafluoroborate (0.1 M). Scan rate, 0.1 V/s.

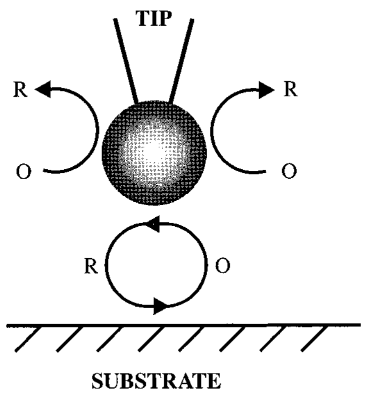

Figure 7. Illustration of how positive feedback occurs at the lower hemisphere while the contribution of the upper hemisphere to the tip current remains constant.

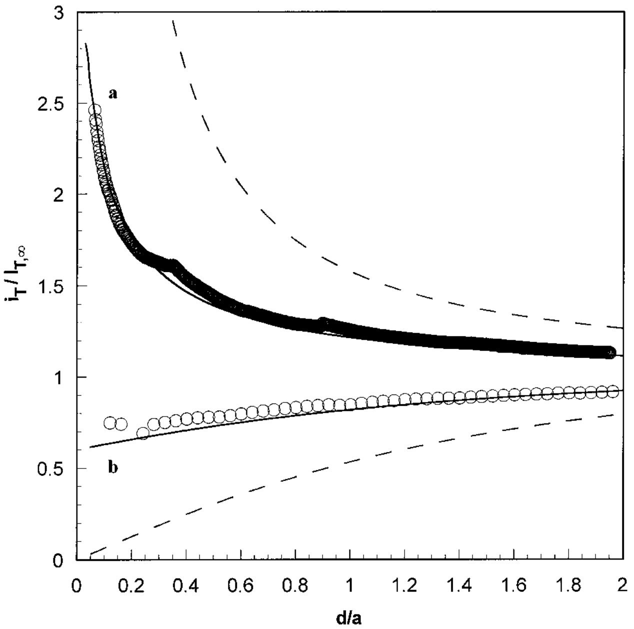

Figure 8. Experimental approach curve obtained with a 4-μm-diameter spherical self-assembled UME in an aqueous solution of hexaammineruthenium(III) chloride (5 mM) and 1 M KCl electrolyte. (—) Theoretical approach curve for a spherical electrode calculated as described in the text. (- - -) Theoretical approach curve for a disk electrode. The small experimental deviations with the conductive substrate represent clicks in the inchworm driver of the SECM. (a) Conductive platinum substrate. (b) Insulating glass substrate.

Scanning Electrochemical Microscopy Approach Curves. The SECM curve involves the movement of the UME tip toward a smooth substrate and recording the tip current, i_T, as a function of distance, d, usually with the potential maintained in the limiting current region of the voltammogram (where the current far from the substrate is $i_{T,\infty}$).[4] The current decreases with decreasing d with an insulating substrate because of blockage of the diffusion path. With a conductive substrate, reconversion of the tip-generated species causes the current to increase with a decrease in d (positive feedback). Previous theoretical treatments[22] have shown that the shape of the normalized approach curve ($i_T/i_{T,\infty}$ vs d/a, where a is the radius of the electrode) depends on the electrode shape. For example, a hemispherical electrode shows a less pronounced decrease above an insulator than a disk UME. No previous experimental studies were reported for a spherical or hemispherical electrode. The theoretical approach curve for a spherical electrode at a conductive substrate was obtained by modifying the numerical solution for a hemispherical electrode,[22] assuming that the upper hemisphere does not receive any feedback from the substrate and therefore contributes to the total tip current with a constant current at all tip separations (Figure 7). This modification is simply given by $I_s = (I_h + 1)/2$, where I_s and I_h are the normalized currents for spherical and hemispherical electrodes, respectively. Experimental SECM approach curves with a conducting and insulating substrate are given in Figure 8. To prevent damage to the tip, the approach was stopped before the sphere made contact with the substrate and an offset d/a of 0.05 was used to approximate the contact point. As can be seen from Figure 8, the experimental data for a conducting substrate are in excellent agreement with the theoretically expected approach curve, while the data for an insulating substrate only agree moderately well with theory. This is because the original model for a hemispherical electrode includes an insulating sheath, whose influence is negligibly small for positive feedback but not for negative feedback. A better model to calculate approach curves with spherical electrodes at insulating substrates is not available at present. In comparison with disk electrodes, the maximal feedback of spherical electrodes is expectedly lower. However, for practical applications, such as studies of fast kinetics and high-resolution imaging, the feedback obtained is sufficient. Particularly for kinetic studies, we believe that these spherical tips could prove superior to disk electrodes. Because they can approach the surface at least 4 times closer, extremely short-lived species generated at the tip can be collected at the substrate. For a 1-μm sphere, a first-order rate constant of up to $\sim 10^6\ s^{-1}$ could be determined in this way. Disk electrodes cannot be approached that closely, because their glass sheath tends to collide with roughness features of the substrate or simply touches the substrate first, due to slight deviations from perpendicular tip

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(22) Mirkin, M. V.; Fan, F.-R. F.; Bard, A. J. *J. Electroanal. Chem.* **1992**, *328*, 47.

alignment. Spherical electrodes are not sensitive to such minute alignment errors.

CONCLUSIONS

Spherical ultramicroelectrodes in the size range of 1−30 μm have been prepared by a simple self-assembly process of nanometer-sized Au particles. Unlike all other methods for the fabrication of ultramicroelectrodes of comparable size, the electrode geometry is perfectly controlled and reproducible. The simplicity of the method makes routine fabrication possible. The electrodes have the electrochemical properties of metallic Au and show ideal microelectrode behavior both in aqueous and in acetonitrile electrolyte solutions. They can be used as SECM tips giving approach curves that are in excellent agreement with theory for conductive substrates. The construction strategy via self-assembly represents a bottom-up approach and implies that a lower size limit at least 1 order of magnitude below the size range of electrodes produced in the present work can be made.

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