Bipolar Electrochemistry of Inorganic Objects: Synthesis and Applications

Christopher Barile Literature Seminar October 2, 2012

There has been increasing interest in the manipulation of inorganic objects at the micrometer and submicrometer scale. Although bipolar electrochemistry has been used in a few niche industrial applications since the 1960's,[1,2] it has only recently been recognized as a powerful tool for modifying inorganic objects in novel ways.[3,4]

The concept of bipolar electrochemistry is very different from the traditional three-electrode electrochemical cell which utilizes a working, counter, and reference electrode.[5] In bipolar electrochemistry, objects in solution are placed in a static electric field which is generated by two feeder electrodes, typically composed of an inert metal such as platinum.[6] If the objects placed in this electric field are conducting, they will respond by generating their own electric field with a polarity opposite to that of the electric field of the feeder electrodes. Furthermore, if the electric field generated by the objects is large enough, it can be harnessed to drive electrochemical reactions. The objects then become so-called bipolar electrodes with anodic and cathodic poles (Figure 1).

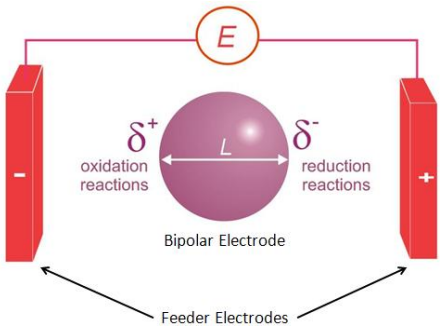

Figure 1. Schematic of bipolar electrochemistry.

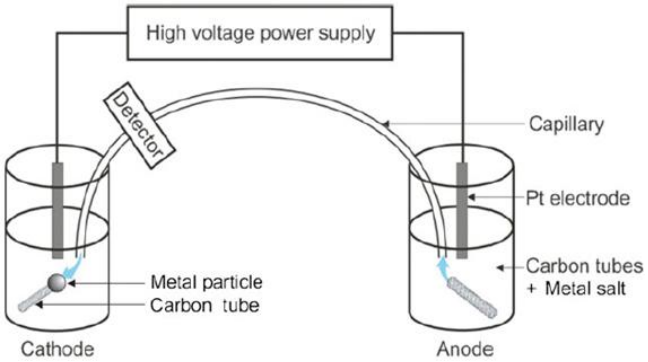

Figure 2. Schematic of capillary-assisted bipolar electrodeposition as used to modify carbon microtubes.

The potential difference across the two poles of a bipolar electrode is approximately proportional to the electrode length. This means that in order to achieve a modest potential difference across a 1 μm-long bipolar electrode (~100 mV) in a typical cell, an electric field on the order of 10 kV must be generated by the feeder electrodes.[7] Although these potentials are large, cells used in capillary electrophoresis routinely employ these voltages. Hence, capillary-assisted bipolar electrodeposition (CABED) has been developed in which objects of interest are modified while they travel through a capillary in the direction of the electroosmotic flow (Figure 2).[4] A detector may be used to monitor the flow of species through the capillary, and the objects are collected at the source electrode.

Kuhn and coworkers have used CABED to deposit various metals including gold, platinum, nickel, and copper on the ends of carbon microtubes.[8] In a typical preparation, an aqueous solution containing carbon microtubes and the salt of the appropriate metal is

used. Upon application of an electric field by the feeder electrodes, the carbon microtubes align with their primary axes parallel to the electric field. The metal salt in solution is reduced to the metal at the cathodic pole of the carbon microtubes. Concurrently, water is oxidized to oxygen gas at the anodic pole. The concentration of the metal salt is kept in the low millimolar range to ensure that the majority of the current passing through the cell also passes through the carbon microtubes. Kuhn *et al*. were also able to deposit metals on both ends of the carbon microtubes by pulsing the electric field of the feeder electrodes. After an initial deposition on one end of the carbon microtubes, the electric field is turned off causing the microtubes to relax and rotate freely. Upon the second pulse, half of the carbon microtubes will have flipped so that what was the anodic pole becomes the cathodic pole. With enough pulses, it is ensured that all of the carbon microtubes have metal deposits on both ends.

Janus particles, spherical particles with two compositionally distinct hemispheres, have also been synthesized using bipolar electrodeposition.[9] Traditionally, these particles have been made by taking advantage of interfacial phenomena.[10] For example, particles at the interface between a biphasic mixture of solvents can be selectively modified at one hemisphere by performing modification chemistry in only one of the solvents. However, these interfacial techniques are not easily scalable since they only produce monolayers of particles at a time. The synthesis of Janus particles via bipolar electrodeposition is advantageous because it is a bulk technique. Unlike carbon microtubes, spherical particles are isotropic and thus do not have any preferential orientation in an electric field. Therefore, bipolar electrodeposition performed in a typical aqueous solution containing a metal salt results in uniform deposition across the surface of the spheres, not in Janus particles. In order to circumvent this problem, gelling agents are added to increase the viscosity of the solution, thus limiting the rotation of the particles over the time course of the deposition. By adjusting the length of the deposition time or the size of the particles, carbon microspheres with metal deposits of various sizes, ranging from full hemispheres to small nodules, can be synthesized (Figure 3).[11]

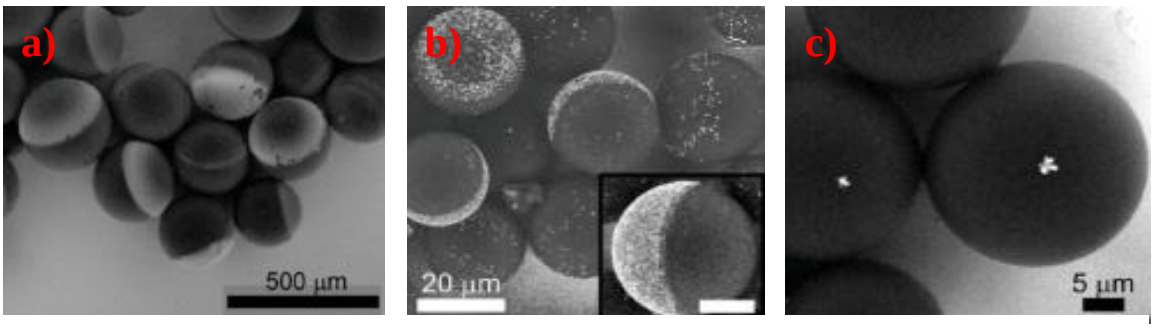

Figure 3. SEM images of carbon Janus particles modified with a) a hemisphere, b) less than a hemisphere, and c) a small nodule of deposited gold.

Some of the objects synthesized by bipolar electrodeposition have been used to generate chemical locomotion.[12-14] For instance, a carbon microtube modified with a platinum deposit will propel itself when placed in a solution of hydrogen peroxide. The platinum catalyzes the decomposition of hydrogen peroxide, and the resulting oxygen evolution generates either translational or rotational motion depending upon the alignment of the platinum deposit with respect to the axis of the carbon microtube.[15]

In conclusion, bipolar electrochemistry offers a unique and fairly simple tool for chemists seeking to modify objects at the micrometer and submicrometer scale. The use

of bipolar electrochemistry at this small length scale is still very much in its infancy, and it is likely that the technique will be a focal point of future research.

References

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