Surface Functionalization of Metallic Nanowires

Laura Ann Bauer and Gerald J. Meyer
Department of Chemistry, Johns Hopkins University
3400 N. Charles Street, Baltimore, MD 21218

The objective of this work is to study surface chemistry of metallic nanowires. The metallic nanowires are fabricated via electrodeposition in nanoporous templates and vary from 10 to 350 nm in diameter and up to 50 microns in length. The fabrication method allows a wide variety of metal nanowires to be prepared. In fact, metals can be deposited sequentially to form nanowires comprised of different segments whose composition varies along the length of the wire. By exploiting the chemical properties of specific segments of these nanowires, it has been possible to rationally fabricate 'multifunctional nanowires' that have two desired functional groups spatially arranged along the wire. To increase the number and types of functional groups in a single nanowire, it is necessary to quantify the affinity and stability of different functional groups for specific wire segments under a wide variety of experimental conditions. This will be the focus of this presentation.

An example of a nickel wire functionalized with a single molecule is shown in Figure 1. The wire has been made fluorescent by reacting it with Hematoporphyrin IX, which has two carboxylic acid functional groups for binding to the nickel oxide surface. A functionalized wire 22 microns in length and 350 nm in diameter was deposited on a glass over slip for characterization under a fluorescence imaging microscope. Figure 1 shows the visible and fluorescent image of this wire. The surface linkage is stable over the course of many days in ethanol as determined spectroscopically.[1]

The affinity of the Hematoporphyrin IX for nickel is very high. Figure 2 shows the surface coverage as a function of solution concentration in ethanol. The data is well described by the Langmuir absorption isotherm model. The surface coverage approaches saturation when the wires were placed in a micromolar solution of Hematoporphyrin IX. Double reciprocal plots, shown as an inset, are linear and allow the adduct formation constants to be quantified.

Figure 3 shows a 350 nm diameter wire comprised of a 12 micron nickel segment and an 8 micron gold segment. The dual functionalization of this wire was accomplished by a "one pot" method. The nickel/gold wire was placed in a solution containing both the fluorescent Hematoporphyrin IX, for binding to the nickel surface, and a non-fluorescent octane thiol ligand for binding to gold. The intense fluorescence of the nickel segment of the wire shows the presence of Hematoporphyrin IX, while the non-fluorescence in the gold segment indicates negligible Hematoporphyrin IX on this segment.

In this presentation, the functionalization of metallic nanowires, including nickel and gold, will be discussed in more detail. The selective binding of ligands to specific nanowires and/or segments of nanowires demonstrate how surface binding varies with the type of ligand and metal. It will be show that the functionalization of metallic wires can be done selectively, such that each segment of the wire can be independently manipulated to produce desired properties. Assembly of functionalized wires into ordered arrays will also be discussed. [1]

[1.] Tanase, M.; Bauer, L.A.; Hultgren, A.; Silevitch, D.M.; Sun, L.; Reich, D.H.; Searson, P.C.; Meyer, G.J. *NanoLett* **2001**, *1*, 155-158.

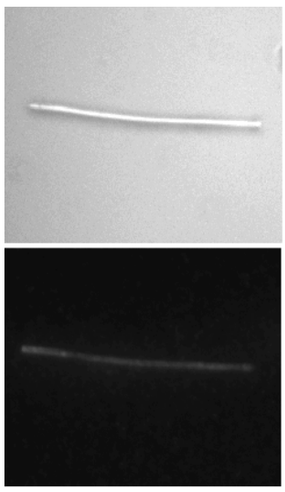

Fig. 1. a) Visible image of a functionalized nickel wire, and b) fluorescence image of same nickel nanowire.

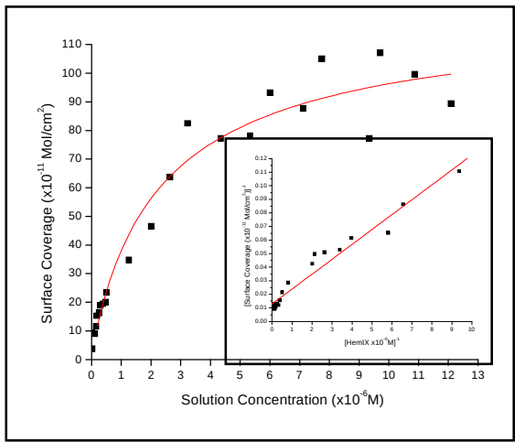

Fig. 2. Langmuir absorption isotherm for absorption of Hematoporphyrin IX in the surface of nickel wires. The inset shows a double reciprocal plot of this same data.

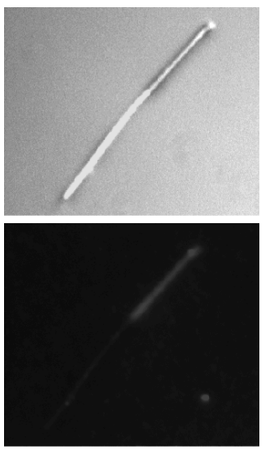

Fig. 3. a) Visible picture of a bimetallic wire, with the dull nickel segment at the top right and the gold segment at bottom left. b) Fluorescence image of the same wire, showing the strongly fluorescent nickel segment and the non-fluorescent gold segment.