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Electrodeposition of Conductors and Semiconductors  
with Controlled Stoichiometries and Morphologies.

by

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13. ABSTRACT (Maximum 200 words)  <b>In an attempt to electrodeposit carbon from CCl<sub>4</sub> in nonaqueous solvents, we observed growth of several unusual morphologies. Fibers with diameters on the order of 0.1-5 microns were synthesized by cathodic galvanostatic electrodeposition from nonaqueous solvents (CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub>) and an electrolyte containing CCl<sub>4</sub> and tetrabutylammonium salts. The fibrous morphology forms without the help of a structural template. Production of fibers can be observed on Ni, Fe, or Cu substrates, with the morphology being very dependent on current density, CCl<sub>4</sub> concentration, and electrode surface preparation. The materials apparently consist of carbon or a carbon nitride compound. The aspect ratio of the fibers ranges from about 2:1 to &gt;100:1, depending upon deposition conditions. Growth of the unusual morphology is presumed to be driven by directional covalent bonding in a graphitic material, analogous to buckminsterfullerene-derived nanotubes.</b>			
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**Electrodeposition of Conductors and Semiconductors with Controlled Stoichiometries and Morphologies.**

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Experiments directed at the electrochemical synthesis of CdSe, CdTe, carbon, and SiC will be discussed. In an attempt to electrodeposit carbon from  $CCl_4$  in nonaqueous solvents, we observed growth of several unusual morphologies. Fibers with diameters on the order of 0.1-5 microns were synthesized by cathodic galvanostatic electrodeposition from nonaqueous solvents ( $CH_3CN$  or  $CH_2Cl_2$ ) and an electrolyte containing  $CCl_4$  and tetrabutylammonium salts. The fibrous morphology forms without the help of a structural template. Production of fibers can be observed on Ni, Fe, or Cu substrates, with the morphology being very dependent on current density,  $CCl_4$  concentration, and electrode surface preparation. The materials apparently consist of carbon or a carbon nitride compound. The aspect ratio of the fibers ranges from about 2:1 to >100:1, depending upon deposition conditions. Growth of the unusual morphology is presumed to be driven by directional covalent bonding in a graphitic material, analogous to buckminsterfullerene-derived nanotubes.

**Preparation**

For the semiconductor fibers, working electrodes were cut from 99.5% purity metal foils (Johnson Matthey Electronics). Wires were attached to the backside with conductive Ag paint and the contacts covered with epoxy (Hysol 1C Epoxy Patch Kit). Electrolytic solutions were distilled under nitrogen from the appropriate drying agent, and  $CCl_4$  was vacuum distilled before use. The electrolytic deposition solutions typically consisted of 30 mL of solvent ( $CH_3CN$  or  $CH_2Cl_2$ ), 1 mL of  $CCl_4$ , and 1 g of tetrabutylammonium tetrafluoroborate. All electrodeposition experiments were carried out under argon atmosphere. Current density for deposition was typically 3-5 mA/cm<sup>2</sup> and the depositions were carried out for 30-60 min.

**Results**

Figure 1 shows an electron micrograph of the fibers formed on a Ni substrate, from  $CH_3CN$ . The fibers in this image are approximately 5 microns in diameter, and have pronounced striations running parallel to the long axis. The image is not representative of the entire surface. In many places, patches of what appear to be bundles of these fibers are apparent, and in other areas, amorphous chunks of material without any discernible shape are seen.

Figure 2 shows an electron micrograph of fibers formed on a Cu substrate. Coiled structures such as the one in the center of this image were occasionally observed. Many of the fibers that we have observed in this system appear to have more of a square, rectangular, or T-shaped cross section, as opposed to the circular cross sections apparent in figure 1.

The diffuse reflectance infrared spectrum of the material scraped from the electrode surface of several deposition runs (from  $CH_3CN$  solutions) displays a sharp, strong absorption band at 2203 cm<sup>-1</sup>, indicative of an isonitrile species. Presumably this isonitrile is incorporated into the material as a result of  $CH_3CN$  solvent decomposition. Separate measurement of the working electrode potential during the course of the depositions showed that it often exceeded the solvent decomposition potential (measured in the absence of  $CCl_4$ ). However, fiber formation has also been observed in  $CH_2Cl_2$  solution, and so the codecomposition of  $CH_3CN$  is not necessary for the production of fibers.

More complete characterization of these materials by X-ray diffraction, X-ray photoelectron, infrared, and Raman spectroscopy, and transmission electron microscopy is in progress.



Figure 1: Scanning electron micrograph (secondary electron image, 20 kV) of fibers formed on Ni from cathodic decomposition of  $CCl_4$  in  $CH_3CN$ .



Figure 2: Scanning electron micrograph (secondary electron image, 20 kV) of fibers formed on Cu from cathodic decomposition of  $CCl_4$  in  $CH_3CN$ .

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