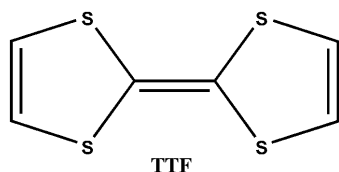


Electrochemical Growth of Organic Conducting Microcrystals of Tetrathiafulvalene Bromide**

Marta Mas-Torrent* and Peter Hadley

A new trend in electronics research is to increasingly employ chemical synthesis techniques in order to fabricate device components exhibiting physical properties addressed to specific applications. Examples of this approach are circuits made from carbon nanotubes and semiconducting nanowires.^[1] These nanostructures can be used, for instance, as chemical or biological sensors.^[2] In addition, chemical synthesis can be scaled up easily, which could give rise to cheaper devices. In this respect, it is interesting to consider nanowires or microwires of conducting organic salts as an appealing alternative route for the fabrication of nanoscale devices. In this paper, we describe the preparation of very good quality microcrystals of the metallic organic charge-transfer salt, tetrathiafulvalene bromide ((TTF)Br_x).^[3] The methodology employed here allows for the controlled synthesis of large quantities of microcrystals and could also be extendable to the fabrication of a multitude of charge-transfer salts with different physical properties.

In the field of organic conductors, the development of new organic charge-transfer salts based on tetrathiafulvalene (TTF) derivatives has remained at the forefront of re-



search since the discovery of the first organic metal tetrathiafulvalene-7,7',8,8'-tetracyanoquinodimethane (TTF-TCNQ) over thirty years ago.^[4] Since then, a wide range of TTF salts, typically synthesized by electrocrystallization means and showing an extensive variety of electrical properties (e.g. semiconducting, metallic, and superconducting), has been prepared.^[5] An additional attractive feature of these salts is the possibility of preparing materials in which electrical, magnetic, and optical properties can coexist.^[6]

Despite the intense work focused on preparing a large range of TTF salts, little attention has been paid to obtaining microcrystals of these salts. Films of metallic and semi-

conductor microcrystals embedded in polymeric matrices have been prepared by treating a film containing the TTF derivative with vapors of an oxidant reagent.^[7,8] Jeszka et al. have reported different methods for obtaining microcrystals of ET₂I₃ (ET stands for bis(ethylenedithio)tetrathiafulvalene) by recrystallization or by treating the ET microcrystals with iodine vapors.^[9] However, these methods are limited to particular materials and, for a general applicability, the use of electrocrystallization techniques is required.^[10] Fabrication of microcrystals of the charge-transfer salt (TTF)Br_x grown electrochemically was previously achieved on a graphite surface catalyzed by platinum nanoparticles.^[11] Here we have employed two new methodologies to grow (TTF)Br_x microcrystals electrochemically. The first method combines both bottom-up and top-down approaches, involving the growth of microcrystals from their precursor molecules on electron-beam-patterned gold microelectrodes. Interestingly, this method gives rise to the production of a large amount of conducting microcrystals. The second strategy allows for the fabrication of microcrystals on an insulating SiO₂ surface. Thin layers of SiO₂ are good insulators for electron transport but allow an ion current to pass through them. This makes it possible to grow crystals electrochemically on an electrically insulating substrate. Such a process could be attractive for the preparation of electronic devices where SiO₂ substrates are typically employed.

The setup used in our first approach is illustrated in Figure 1. The prefabricated microelectrodes (4 nm of Ti,

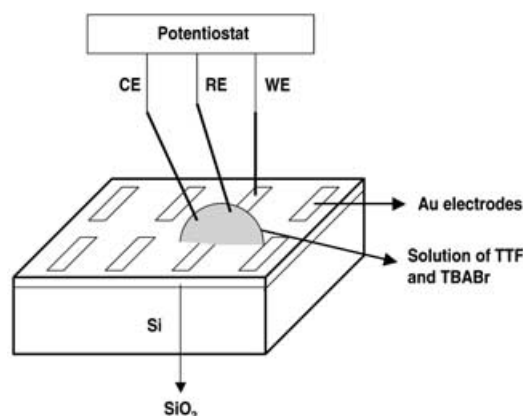


Figure 1. Schematic drawing of the experimental setup. The abbreviations WE, RE, and CE stand for working electrode, reference electrode, and counter electrode, respectively.

acting as a sticking layer, covered by 26 nm of Au) were fabricated by electron-beam lithography on a silicon wafer with a 200-nm-thick thermally grown oxide layer and with a double layer of poly(methyl methacrylate) as resist. Five microliters of a 0.1 M solution of tetrabutylammonium bromide (TBABr) and 5 mM of TTF in dimethylacetamide were placed on the prefabricated electrodes. The electrochemical experiments were performed by coupling a potentiostat to a Microscope Probe Station. A gold needle in contact with one of the prefabricated gold electrodes was used as a working electrode and two platinum wires were used as counter

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and pseudo-reference electrodes. The application of a series of 20 voltage pulses of 0.4–0.6 V vs. Pt with a duration of 0.2 s resulted in the electrochemical growth of microcrystals on the working electrode. The samples were then rinsed with ethanol and carefully dried under a flow of nitrogen. Under these experimental conditions, the product of the oxidation is known to be the nonstoichiometric salt $(\text{TTF})\text{Br}_x$, where x is close to 0.76.^[3]

Figure 2 shows scanning electron microscope (SEM) images of the $(\text{TTF})\text{Br}_x$ crystals grown on the prefabricated gold electrodes. Long, thin crystals with smooth surfaces

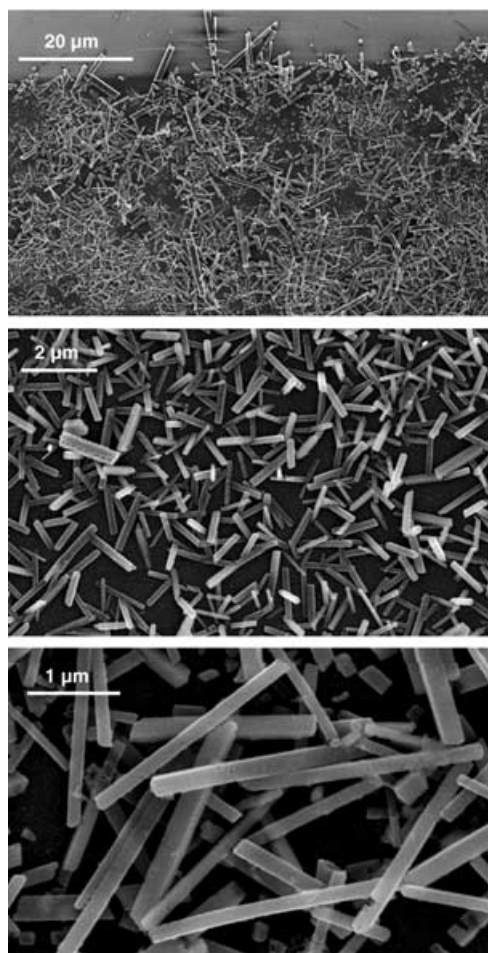


Figure 2. SEM images of $(\text{TTF})\text{Br}_x$ microcrystals grown electrochemically and on prefabricated gold electrodes, shown (top to bottom) with increasing magnification.

and well-defined faces are obtained. On average, the crystals prepared are 1–2 μm long and about 200 nm wide. $(\text{TTF})\text{Br}_x$ crystallizes by forming π -stacks of TTF/TTF^+ along the c axis of the crystal arranged parallel to rows of Br^- .^[3] The mixed-valence character of this salt, together with the electron delocalization along the stacking direction, leads to conducting crystals along the c axis. Thus, during the electrocrystallization the $(\text{TTF})\text{Br}_x$ crystals grow preferentially along c , resulting in long, narrow crystals.

The second variant of the electrochemical experiment was carried out by using a silicon wafer with only an 8-nm-

thick SiO_2 layer. Gold nanoparticles were deposited from solution onto the SiO_2 surface prior to the electrochemical experiment. The growth of the $(\text{TTF})\text{Br}_x$ microcrystals was carried out as described previously but using the Si substrate as the working electrode. Pulses of 4 V (versus Pt) of 0.2 s duration were applied. Although in this case the working electrode is not in contact with the electrolyte solution, due to an ionic leakage current through the SiO_2 dielectric, $(\text{TTF})\text{Br}_x$ microcrystals grew on the SiO_2 surface predominantly from the deposited gold particles, which act as nucleation points (Figure 3).

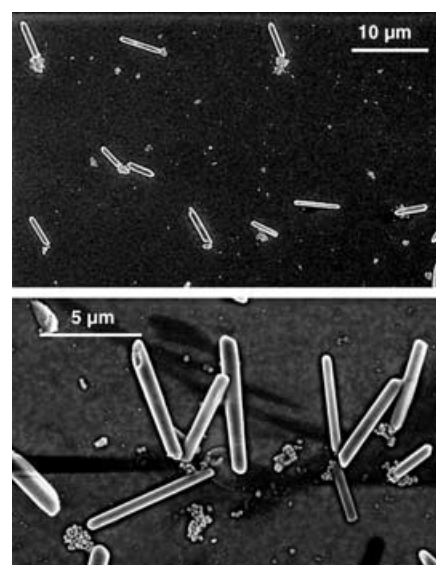


Figure 3. SEM images of $(\text{TTF})\text{Br}_x$ microcrystals grown electrochemically on a silica substrate, with gold nanoparticles acting as nucleation points.

The electrical properties of a single microcrystal were measured on the prefabricated electrodes. Figure 4 shows the current–voltage characteristics of one $(\text{TTF})\text{Br}_x$ crystal placed between gold source and drain electrodes 5 μm apart. An SEM image of the measured crystal is shown in the inset of this figure. The crystal exhibits a resistance of 20 M Ω . A plot of the source–drain current at a source–drain voltage of 0.5 V while sweeping the gate voltage applied to the Si substrate is also shown in the inset of Figure 3. No clear gate-effect is observed, which would be expected for a metallic material.

In conclusion, we have reported the electrochemical synthesis of large quantities of microcrystals of the conducting charge transfer salt $(\text{TTF})\text{Br}_x$ on gold microelectrodes and on a silica substrate using gold nanoparticles as crystalline nucleation points. This technique could be extendable to the preparation of a vast number of charge-transfer salts and, therefore, organic microcrystals with a large variety of electrical properties or even combining different physical properties could be accessible. The controlled fabrication of microcrystals with specific electrical properties represents a step forward in the chemical synthesis of electronic components.

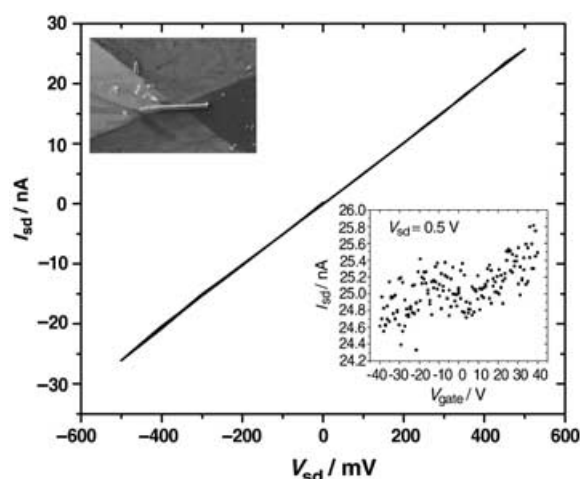


Figure 4. Source-drain current (I_{sd}) versus source-drain voltage (V_{sd}) for a $(TTF)Br_x$ crystal placed between two prefabricated gold electrodes 5 μm apart. Insets: SEM image of the measured device and plot of the I_{sd} dependence versus the gate voltage at $V_{sd}=0.5$ V.

Experimental Section

Tetrathiafulvalene (TTF; >98%), dimethylacetamide (99%), and tetrabutylammonium bromide (TBABr; 99%) were purchased from Aldrich and were employed without further purification. A solution of gold nanoparticles of diameter 250 nm was purchased from Ted Pella Inc. The electrochemical experiments were carried out with a $\mu\text{Autolab III}$ potentiostat coupled to a Karl Süss Microscope Probe Station.

The electrode fabrication was carried out with an electron-beam pattern generator (EBPG5 HR 100 kV FEG) using a double poly(methyl methacrylate) resist. Four nanometers of Ti and 26 nm of Au were evaporated at liquid-nitrogen temperature to ensure a smooth surface; lift off was done in warm acetone. The samples were then rinsed with isopropanol and dried under nitrogen.

The samples were inspected with a scanning electron microscope (Philips XL30SFEG).

Keywords:

charge transfer • conducting materials •
electrochemical methods • molecular electronics •
nanowires

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