Crystalline Microwires of Rubrene for Chemical Sensing

Hong Wang 1, Xiaohe Xu 1, Ligui Li 1, Patrick J. Carroll 2 and Hai-Feng Ji 1*  

1 Department of Chemistry, Drexel University, Philadelphia, PA 19104  
2 Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104  

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Abstract: Crystalline nano- and microwires of Rubrene are synthesized from a gas phase deposition method and the sensing behavior of microwires is studied. The resistivity of the microwires in N₂ is $8.82 \pm 1.80 \times 10^3 \Omega \cdot \text{cm}$. The current of the microwires increases when the microwires are exposed to O₂, and decreases on exposure to electron deficient aromatic molecules, such as nitrobenzene and benzaldehyde, suggesting the resistivity change of rubrene microwires may have potential applications in selective chemical sensors for O₂ and electron deficient aromatic molecules, particularly nitro-containing explosive chemicals.

Key words: Rubrene, nanowire, microwire, detection of explosives.

Introduction

Organic-based electronic devices hold the promise of low-cost manufacturing and compatibility with flexible substrates. Rubrene is one of the most studied polycyclic aromatic hydrocarbons (PAHs) for making more efficient organic-based devices 1. It has been used for preparing field effect transistor, 2,3 organic light emitting devices 4, electroluminescence devices, 5 and organic photovoltaic devices 6.

Rubrene crystals have also been used to develop chemical sensors, most of which are based on optical properties of the crystals 7. Sensing based on electronic property of crystals holds several advantages, including cost effectiveness and simplicity, over the optical properties of the crystals 8. Recently, the resistivity change of rubrene crystals has been used to determine the pressure applied on a surface 9. However, the electronic properties of rubrene crystals have not been applied to develop chemical and biosensors. Since rubrene crystal is an electron-rich p-type semiconductor 3,10, we expect it can be used to detect electron deficient chemicals because the complexation of electron deficient chemicals with rubrene will affect the electronic properties of rubrene crystals 11.

To develop an efficient and sensitive chemical sensor based on the resistivity change of a rubrene crystal, the size of the crystal should be small, i.e. large surface area, to afford the target molecules to access more rubrene molecules in the crystal. For this reason, a nano- or micro- wire of rubrene could be a better choice than a bulky crystal to fabricate sensors because of larger surface areas of nano-/micro- wires than that of bulky crystals 12,13. A variety of methods have been exploited to synthesize 1D PAH nano-/micro- wires, such as self-assembling in solutions 12,14, template-assisted method 15, Vapor deposition 16, and solid phase
reaction methods. Since rubrene has poor solubility in any solvents, micro- and nanostructures of rubrene were typically prepared by vapor deposition approaches in the gas phase.

In this work, we report the synthesis of rubrene micro-/nano-wires with a modified vapor deposition approach and the sensing behavior of rubrene microwires.

**Experimental section**

Rubrene was purchased from Alfa Aesar and used as received. The bubrene micro-belts were synthesized in a furnace according to an evaporation method reported previously. Zeiss Supra 50 VP was used to obtain scanning electron microscopy (SEM) images. Gas sensing experiments were performed with micro-wire resistor device placed in a glass tube 20 cm in length and 1.5 cm in diameter. 2 ml of the solvent being tested was added to the tube and allowed to evaporate for an hour to reach the saturated vapor pressure. I-V curves were measured before and after the device’s exposure to the saturated vapors. Optical microscopy (OM) and cross-polarized optical microscopy (CPOM) were performed on Smith polarized microscope.

**Results and discussion**

In previous reports, vapor deposition of rubrene was typically carried out in a Ar flow condition and only a small portion (<1%) of the deposited rubrene crystals are 1D nanowires or microwires. We found that the percentage of 1D micro- and nano-wires of rubrene increases significantly (>70%) when the experiments was conducted in a static condition. In this approach, 5 mg of rubrene powder was placed in a 50-mL quartz tube. The tube was vacuumed and heated at 350°C for an hour, then the tube was allowed to be naturally cooled to room temperature.

Rubrene nano- and micro- wires that were self-assembled on a glass substrate in the tube were collected for analysis. The scanning electron microscopy (SEM) images of crystalline microwires of rubrene are shown in Figure 1a. The nano-/micro-wires have a diameter of approximately 500 nm to 10 μm and a length of 10 μm to 50 μm. When the heating time increases or more rubrene powder is used, the diameter and the length of these wires increase, suggesting that the size of the rubrene wires could readily be controlled by heating temperature and the amount of rubrene in the tube.

![Figure 1](image_url)

**Figure 1.** (A) SEM images of rubrene microwires synthesized from vapor deposition of rubrene powder at 350°C (B) Rubrene crystal structure obtained from X-ray diffraction (XRD).
Rubrene wires at micro size were used in this study because an easy control of the microwires for X-ray diffraction analysis and the following studies on the sensing behaviors of these wires, with a sacrifice of sensitivity compared to nanowires, which have higher surface areas. X-ray diffraction shows that the rubrene microwire is crystalline (Figure 1b) and the lattice indices of the rubrene microwires are \( a = 14.3 \text{ Å}, b = 7.2 \text{ Å}, \) and \( c = 26.9 \text{ Å} \). The rubrene microwires grow longer along the b-axis. These lattice indices indicated an orthorhombic structure of the microwires. Cross-polarized optical microscopy (CPOM) images (Figure 2) also show the crystalline property of the microwire. In this experiment, the brightness of the microwire was measured as a function of the angle between the direction of a polarized light and the long axis of the rubrene microwire. The minimum brightness appears at 0°, 90°, 180°, and 270° and the maximum brightness appears at 45°, 135°, 225°, and 315°, indicating the rubrene crystalline microwire has a birefringent character.

![Figure 2. CPOM (left) and brightness of a wire (right) as a function of the angle between the direction of a polarized light and the long axis of the rubrene microwire. The scale bar is 5 μm](image)

Figure 3 shows the scheme of an electronic devices studies in this work. Au electrodes were deposited at each side of the microwire by means of thermal evaporation via a typical photolithography process. The resistivity of the rubrene microwires in \( \text{N}_2 \) is \( 8.82 \pm 1.80 \times 10^3 \text{ Ω\cdotcm} \), which is approximately 10-fold lower than that of bulky rubrene crystals reported previously by Hidekazu. The lower resistivity of rubrene microwires is attributed to the anisotropic charge-carrier mobility of the fabricated rubrene microwires. It is reported that the charge-carrier mobility of the crystals along b-axis is higher than that along a-axis or c-axis and in our rubrene microwires, the wire direction is parallel to b-axis of the crystal.

Figure 4 shows I-V curves of a single rubrene microwire in \( \text{N}_2 \) and \( \text{O}_2 \) and the change in current with time on switching between \( \text{N}_2 \) and \( \text{O}_2 \). The current increases more than 5-fold when the microwire is switched from \( \text{N}_2 \) to \( \text{O}_2 \). The responses when switching between \( \text{N}_2 \) and \( \text{O}_2 \) are quick as shown in Figure 4b.

Since rubrene radical cation was observed in the presence of \( \text{O}_2 \) from electron paramagnetic resonance spectroscopy, we attribute the resistivity decrease of the rubrene microwire to a radical cation-enhanced charge transfer effect.
The sensing behavior of rubrene microwires to chemical vapors was also investigated. Figure 5 shows the change in current of a rubrene microwire upon exposure to a variety of chemical vapors. The resistivity of the rubrene microwire changes significantly when it is exposed to nitrobenzene and benzaldehyde and has a marginal change upon exposure to benzene, ethanol, acetone, hexane, dimethylformamide, triethylamine, aniline, toluene, and nitromethane (only the responses to toluene and nitromethane are shown for clarity). These results suggest that the resistivity of rubrene microwires is only sensitive to electron deficient aromatic molecules, i.e. aromatic molecules with electron-withdrawing groups.

One plausible explanation is that these electron deficient aromatic molecules form complex with the electron rich rubrene, which decrease the charge mobility of the rubrene microwire. The most dramatic decrease and the highest sensitivity are observed when the microwire is exposed to nitrobenzene. The detection limit to nitrobenzene is 0.012 mg/L. Figure 5B shows that the change in the current of the microwire reaches the plateau after 120 seconds. This suggests that the nitrobenzene is adsorbed on the surface of the microwire and adsorption/desorption reaches equilibrium after 120 seconds and the nitrobenzene molecules do not or slowly diffuse into the microwire.
In conclusion, we demonstrated that the resistivity of crystalline microwires of rubrene decreases when exposed to $O_2$ and increases upon exposure to electron deficient aromatic molecules. The most significant increase in resistivity was observed when the rubrene microwire is exposed to nitrobenzene, suggesting the device might be used for detection of explosive materials since most explosive materials contained aromatic rings and electron-withdrawing nitro groups. The detection limit may be further improved by using rubrene wires at nano-scale due to higher surface areas. The responses of rubrene nanowires to chemicals, especially to explosives, is currently under investigation and will be reported in due course.

References