Nano/microwires of coronene for sensing electron-deficient aromatics

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Abstract

We report the synthesis, characterization, and application of coronene nano/microwires for sensing electron-deficient aromatics. The coronene nano/microwires were prepared by a vapor deposition method. The nano/microwires were approximately 300 nm in diameter and 3-5 μm long. ATR-IR spectroscopy and TG/DTA showed that coronene remains intact and does not undergo polymerization or decomposition during the vapor deposition. Cross-optical polarized microscopy showed a birefringent crystal structure of the coronene microwires. Fluorescent imaging showed that the crystalline coronene nano/microwires can be used as waveguide material. Both the conductivity and fluorescence of the crystalline nano/microwires change selectively in the presence of nitrobenzene vapor, a representative nitroaromatic. This suggests that the coronene nano/microwires may be used for selective detection of explosives since many explosives belong to a group of electron-deficient nitroaromatics.

Introduction

Modern security concerns have led to a high demand for stand-off detection of trace explosive vapors in preventing possible terrorist attacks.[1] Methods available for the analysis of air samples of explosives, such as ion mobility spectrometry and mass spectrometry,[2] are expensive, not easily portable, time-consuming, and often require laborious sample preparation. Methods to detect explosives that rely on the interaction of sensing materials with explosives hold promise for detecting explosives with real-time response, high sensitivity and selectivity, compact size, low power requirements, and low cost.[3] Recent studies have resulted in a variety of materials that change color or fluorescence characters on their interaction with explosives.[4,5] However, there have been few studies on the use of conductivity changes to detect explosives, mainly due to a lack of selectivity.[6,7]

It has been recognized that sensors based on conductivity changes are potentially advantageous in both cost and convenience because they could eliminate the complexity and power consumption inherent to optical instruments. One strategy to enhance selectivity in detecting explosives is to develop appropriate electron-rich materials that can form a strong complex with the explosive material, due to the fact that many explosives belong to a group of electron-deficient nitroaromatics. Examples of electron-rich materials include most polycyclic aromatic hydrocarbons (PAH).[8-10]

To develop conductivity-change based sensors, one-dimensional (1D) nano/microstructures of electron-rich PAHs are expected to achieve higher sensitivity[11] than bulky structures because of their greater surface area. Among the large family of PAHs, coronene (Figure 1) is expected to be a good candidate in the development of a conductivity-based sensor for explosives since coronene is a well-known semiconductive material that may be used for light emitting diodes, photoconductive devices, and solar cells.[12-14] Furthermore, the π−π interaction between coronene molecules is stronger than that of smaller PAHs and the symmetrical structure of coronene can assist the formation and the stability of 1D nano/microstructures.

In this study, we report the synthesis and characterization of 1D coronene nano/microwires and demonstrate our preliminary study on their potential application in detecting electron deficient chemicals, with nitrobenzene as a representative compound. We show that both the fluorescence and conductivity of the coronene nano/microwires can be used for selective detection.

Materials and Methods

Coronene was purchased from Alfa Aesar and used as received. The coronene nano/microwires were fabricated in a furnace according to a vapor deposition method reported previously.[15] An amount of coronene powder was placed in a 50-mL quartz tube. The tube was heated in a vacuum and then left to cool at room temperature. Coronene nano/microwires that had self-assembled on a glass substrate in the tube were collected for analysis.

Fluorescence spectra were obtained with a Hitachi F-7000 fluorescence spectrometer. The excitation wavelength was 325 nm. Attenuated total reflection infrared (ATR-IR) spectra were recorded on a Smith IR microscope. The thermal analysis was obtained with a thermogravimeter/differential thermal analyzer (TG/DTA 6300, SII Nanotechnology Inc). The heating rate was 5° •min[-1] with a nitrogen flow (50 mL•min[-1]). Cross-polarized optical microscopy (CPOM) was performed on a Smith polarized microscope. A Zeiss Supra 50 VP was used to obtain scanning electron microscopy (SEM) images. A JOEL JEM2100 operated at 120 keV was used to obtain transmission electron microscopy (TEM) images. Gas sensing experiments were performed with a microwire resistor device placed in a glass tube 20 cm long and 1.5 cm in diameter. A targeted vapor was transferred to the tube to reach a concentration of 200 ppm. Since several seconds are needed to equilibrate I-V curves and fluorescence spectra upon exposure to the chemical vapor, which may due to the small size of the nano/microwires, the curves and spectra were first collected in N_2 and then collected after the device had been exposed to the chemical vapors for 30 s.

Results and Discussion

Methods to synthesize 1D organic nanomaterials include precipitation from solutions,[16,17] template synthesis,[18] solid phase reaction,[19] and vapor deposition.[20,21] Among these methods, vapor deposition represents an easy approach to develop 1D nanostructures. In our experiments, we developed coronene nano/microwires using a vapor deposition method reported previously[15]. Figure 2 shows SEM images of coronene nano/microwires when the experiment is carried out at 350°C for 30 min. These nanowires have a diameter of approximately 300 nm and are 3-5 μm long. When the heating time increases to 5 h, the diameter increases to approximately 1-2 μm and the length increases to approximately 5-10 μm. When the reac-

tion time is longer than 5 h, no obvious changes in size were observed.

ATR-IR spectroscopy and TG/DTA were performed to compare the molecular structure of the nanowires and the coronene powder. Figures 3 and 4 show no distinguishable difference between ATR-IR or TG/DTA of coronene nano/microwires and powder. This is expected since the $\pi-\pi$ interaction is widely presented in PAH molecules, even in the form of powders. However, one useful conclusion to be drawn from these results is that after the thermal heating process in our experiments, the coronene remains intact and does not undergo polymerization or decomposition.

Figure 5 shows the TEM image of a coronene nanowire. No electron diffraction pattern was observed for the nanowire structure. This may be due to that the self-assembly of coronene molecules can be readily disintegrated under high electron beam voltage, and does not confirm that the nanowire is crystalline or amorphous. The crystallinity of the 1D structures of coronene, however, can be determined from other techniques, such as polarized optical microscopy (CPOM). Figure

6A shows the brightness of CPOM images of a coronene microwire on varying the angle between the long axis of the microwire and the polarization light. Minimum brightness is seen when the long axis is parallel to the polarization light (0°). This position is called the position of extinction for the crystal. The brightness increases when the angle increases from 0° to 45°. The brightness *versus* the angle (Figure 6B) shows four repeat profiles in a complete circle. Minimum brightness occurs at 0°, 90°, 180° and 270°, and maximum brightness occurs at 45°, 135°, 225°, and 315°. Similar results were observed for coronene nanowires. The periodical change in brightness *versus* the angle shows the coronene nano/microwire is a birefringent crystal,[17,22] *i.e.* the crystal has two distinct indices of refraction and it splits one ray of light into two rays.

Figure 7 shows fluorescence spectra (λ_{ex}=325 nm) of coronene nano/microwires and coronene powder. No obvious difference was observed between the fluorescence spectrum of coronene powder and microwires, suggesting they have the same molecular packing. The result is consistent with that

obtained from the FTIR spectra. The fluorescence of the coronene nano/microwires is significantly brighter at the end of the wires. This is due to the light propagation along the length of the nano/microwires, the so-called outcoupling light,[23-25] *i.e.* the light propagation along the nano/microwires[23] as the coronene molecules re-absorb the emitted light. The result shows that the coronene nano/microwires may be used as waveguide material for optoelectronic applications. This optical waveguiding property indicates the high degree of molecular orientation in the nanowire,[26] which is consistent with the results of cross-polarized light experiments.

Figure 8 shows the conductivity and fluorescence changes in a coronene microwire on exposure to a variety of chemicals at the same concentration. The conductivity of the microwire decreases on exposure to any of these chemical vapors, and the most dramatic decrease was when the microwire was exposed to nitrobenzene, a representative nitroaromatic. Since toluene does not have an electron-withdrawing group and dimethylformamide does not have an aromatic ring, these preliminary studies indicated that both an
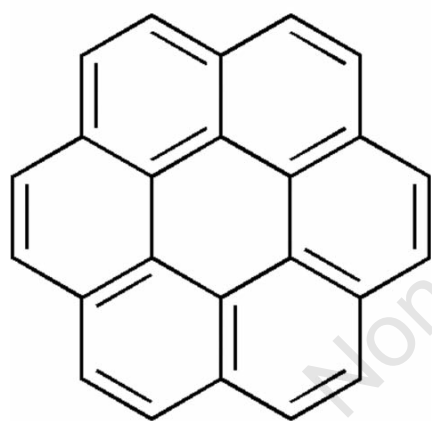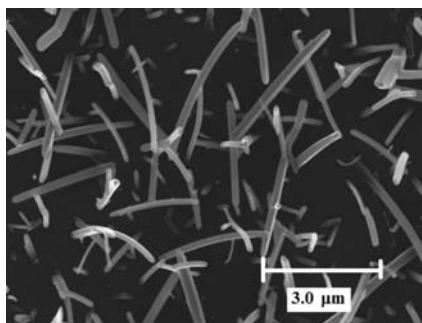

Figure 1. Structure of coronene.

Figure 3. ATR-IR spectra of coronene powder (solid line) and nanowires (dashed line).

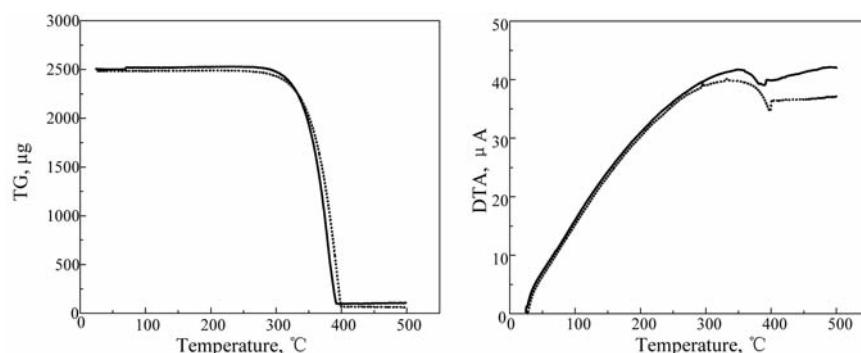**Figure 2. SEM images of coronene nanostructures formed at 350°C for 30 min.**

Figure 4. TG/DTA of coronene powder (soid line) and microwires (dashed line).

aromatic ring and electron-withdrawing groups are required in order to significantly decrease the conductivity of the coronene microwire. The results suggested that nano/microwires of coronene may be used for selective detection of explosives since many explosives belong to a group of electron-deficient nitro-aromatics. In addition to the conductivity change, the fluorescence of the nanowires also showed selective change to nitrobenzene (Figure 8B). The sensing behavior of the coronene nano/microwires will be further studied, and the sensing behavior and sensing mechanism will be reported as soon as these are available. However, it is most likely that the changes in current and fluorescence can be attributed to both surface binding on and diffusion of nitrobenzene in the nanowires.[27-30] Coronene is an electron-rich p-type material, which can form a strong com-
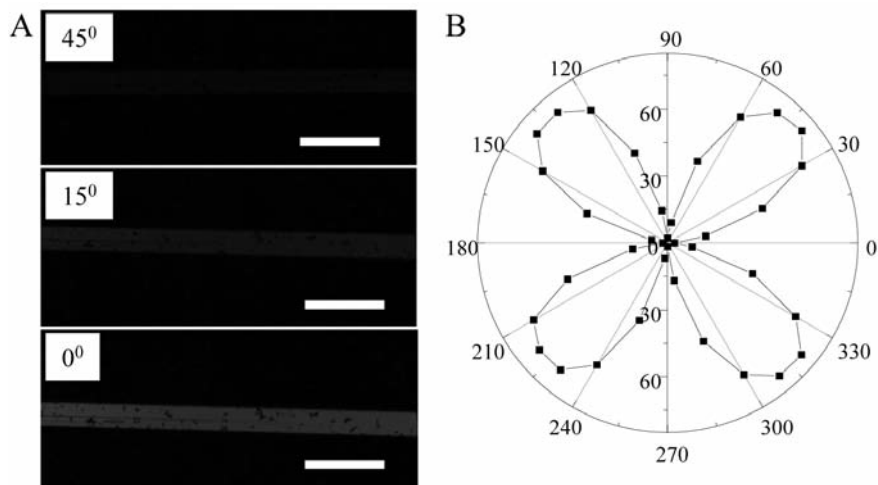

Figure 6. (A) Cross-polarized optical microscopy (CPOM) images of a coronene microwire. Scale bar is 3 μm. (B) Brightness *versus* the angle between the polarization direction of the light and the long (optical) axis of the coronene microwire.
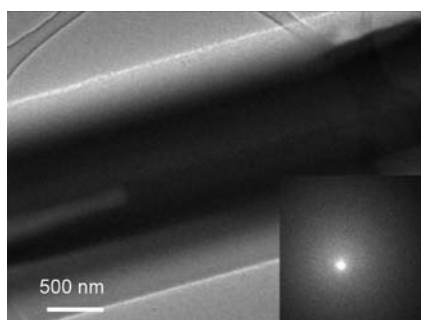

Figure 5. TEM images of a coronene nanowire. The corresponding electron diffraction pattern of a solid nanowire is shown in the insert.
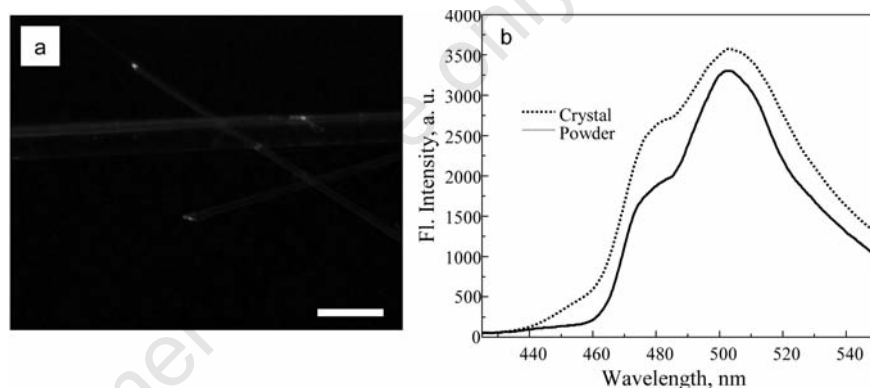

Figure 7. (A) Flourescence microscopy images of coronene microwires, exited with 510-550 nm UV. Scale bar is 5 μm. (B) Emission spectra of coronene powder (dashed line) and microwires (solid line).
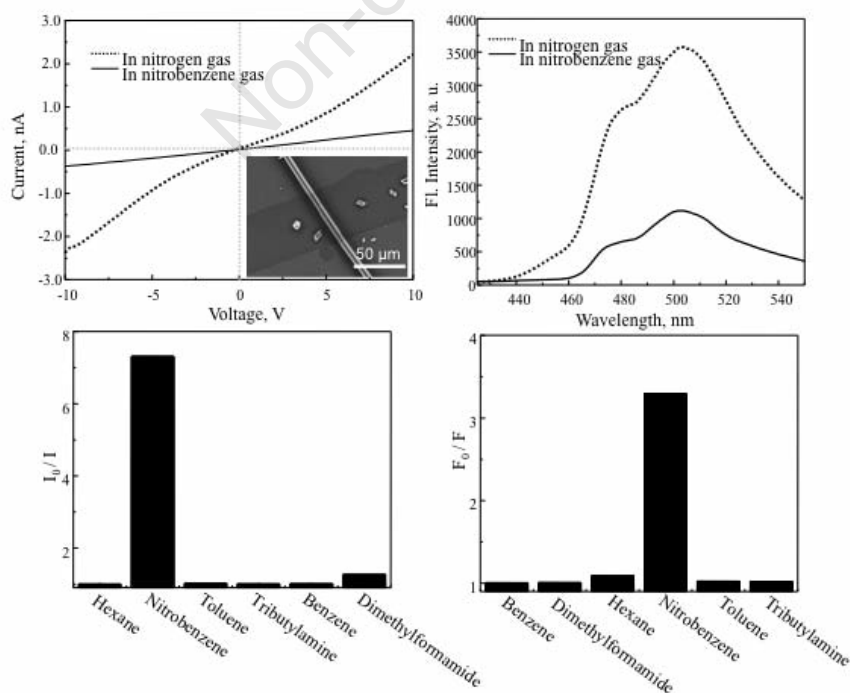

Figure 8. Effect of chemical vapors. (A) Effect on conductivity: a single coronene microwire device with sputtered Al on both ends. (B) Effect on fluorescence of a single coronene microwire (10~20 μm in diameter). I_0/I and F_0/F are the ratios of current and fluorescence, respectively, in the vacuum to those in the presence of chemical vapors at the same concentration (200 ppm).

plex with nitrobenzene due to the fact that nitrobenzene moiety is electron-deficient. This feature means coronene can participate in π-π interactions with nitrobenzene, which decrease the hole transportation and quench the fluorescence of the excitons of the nanowires.

Conclusions

In this study, 1D crystalline coronene nano/microwires were synthesized and characterized. Cross-polarized and fluorescence images show coronene nano/microwires have a crystalline structure and a high degree of molecular orientation. Conductivity and fluorescence of the coronene nano/microwires change selectively in the presence of nitrobenzene, indicating its potential to detect explosive chemicals. The easy synthesis method and its high sensitivity make it competitive in commercial applications.

Since ordered nanostructures can be prepared from a large pool of PAH molecules,[31,32] and heterocyclic PAHs with N, S, or O in the rings, or PAHs with OH, NH_2, or C=O groups, we expect that the semiconductive and optical properties of these nanostructures can be tuned by the selection of different PAH molecules, *i.e.* nanostructures from various PAH materials have different bandgaps or belong to different types, such as n or p type materials. We focused on the characterization of the nano/microwires in this study and the sensing performance of these nano/microwires and other nanostructures to explosives will be investigated and reported in the future. Other potential applications of these nanostructures include nanoelectronics and photoelectronics devices, and solar cells.

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