Triphenylene Nano/Microwires for Sensing Nitroaromatics
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ABSTRACT: We report the synthesis, characterization, and application of triphenylene nano/microwires for sensing nitroaromatics. The fluorescence of these wires is dependent on the size of the wires, which can be controlled by heating temperature and time. The cross optical polarized microscopy result shows a birefringent crystal structure of the triphenylene microwires. Fluorescence imaging shows that the crystalline triphenylene nano/microwires may be used as a waveguide material. Both the conductivity and fluorescence of the crystalline nano/microwires change selectively in the presence of vapor of nitrobenzene, a representative nitroaromatic, suggesting that the nano/microwires of triphenylene may be used for selective detection of explosives.

1. INTRODUCTION

Detection of trace explosive vapors is of high demand in preventing possible terrorist attacks. Methods available for the analysis of air samples of explosives, such as ion mobility spectrometry and mass spectrometry, are expensive, not easily portable, time-consuming, and often require laborious sample preparation. Methods for detection of explosives that rely on the interaction of sensing materials with explosives hold promise for detecting explosives with real-time response, high sensitivity and selectivity, miniaturized size, low power requirements, and low cost. Studies in the later methods have resulted in a variety of materials that change color or fluorescence characters on their interaction with explosives. However, little work has been reported based on conductivity changes for detecting explosives, mainly because of a lack of selectivity.

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

To develop conductivity-change-based sensors, 1D nano/microstructures of electron-rich PAHs are expected to achieve higher sensitivity than bulky structures because of their greater surface areas. Of a big family of PAHs, triphenylene (Scheme 1) is expected to be a good candidate for developing a conductivity-based sensor for explosives because triphenylene is a well-known semiconductive material that may be used for light-emitting diodes, photoconductive devices, and solar cell. Furthermore, the $\pi-\pi$ interaction between triphenylene molecules is stronger than that of smaller PAHs, and the symmetrical structure of triphenylene can assist the formation and the stability of 1D nano/microstructures. In this work, we report the synthesis and characterization of 1D nano/microwires of triphenylene 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 nano/microwires of triphenylene can be used for selective detection.

2. EXPERIMENTAL SECTION

Triphenylene was purchased from Alfa Aesar and used as received. The triphenylene nano/microwires were fabricated in a furnace according to a vapor deposition method reported previously. In general, a certain amount of triphenylene powder was placed in a 50 mL quartz tube. The tube was heated in vacuum; then, the tube was allowed to be naturally cooled to room temperature. Triphenylene nano/microwires that were 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). The heating rate was 5 °C min$^{-1}$ with a nitrogen flow (50 mL min$^{-1}$). A Zeiss Supra 50 VP was used to obtain scanning electron microscopy (SEM) images. A JEOL JEM2100 operated at 120 keV was used for obtaining transmission electron microscopy (TEM) images. Gas sensing experiments were performed with a microwire resistor device placed in a glass tube with 20 cm in length and 1.5 cm in diameter. A targeted vapor was transferred to the tube to reach a...
concentration of 200 ppm. I–V curves were measured before and after the device was exposed to the chemical vapors. Cross-polarized optical microscopy (CPOM) was performed on a Smith polarized microscope.

3. RESULTS AND DISCUSSION

3.1. Temperature Effect on the Size of the Nano/Microwires. Methods to synthesize 1D organic nanomaterials include precipitation from solutions,16,17 template synthesis,18 solid-phase reaction,19 vapor deposition,20,21 and so on. Among these methods, vapor deposition represents a facile approach to develop 1D nanostructures. In our experiments, we developed nano/microwires of triphenylene by employing a vapor deposition method reported previously.15 Figure 1 shows SEM images of nano/microwires of triphenylene with three different sizes. When the experiment is carried out at 180 °C for 5 min, triphenylene nanowires on the nanometer scale are obtained. These nanowires have a diameter of approximately 300 nm and a length of 10–20 μm (Figure 1A). When the heating time is increased to 30 min, the diameter increases to ~6 μm and the length increases to ~100 μm (Figure 1B). When the experiment is carried out at 200 °C for 30 min, strip-like microstructures are obtained (Figure 1C). The microstrips have a diameter of 10–20 μm and a length up to 1 cm. These results show that the size of the fabricated triphenylene structures could be readily controlled by heating temperature and time. The size of these structures increases with increasing heating temperature and time.

Further experiments were conducted to illustrate quantitatively the effects of heating temperature and time on the size of fabricated triphenylene nano- and microwires. Formation of 1D structures of triphenylene occurs when the temperature is >160 °C. The diameter and length of triphenylene nanostructures increase significantly when the temperature is increased from 160 to 200 °C, and a marginal change occurs from 200 to 300 °C (Figure 2A,B). When the temperature is >300 °C, however, irregular triphenylene structures occur, which may be due to fast nucleation of triphenylene vapor on the substrate when the vapor is cooled from a higher temperature. The diameter and length of the 1D structures of triphenylene increase as the heating time increases, as shown in Figure 2C,D. The growth rate is faster in the first 30 min and slower after 30 min.

3.2. Crystallinity of the Triphenylene Nano/Microwires. No electron diffraction pattern was observed from the TEM image of a triphenylene nanowire (Figure not shown). This may be due to the fact that the self-assembly of triphenylene molecules can be readily disintegrated under high electron beam voltage and does not lead to a conclusion whether the nanowire is crystalline or amorphous. The crystallinity of the 1D structures of triphenylene, however, can be determined from other techniques, such as polarized optical microscopy (CPOM). Figure 3A shows the brightness of CPOM images of a triphenylene microwire on varying the angle between the long axis of the microwire and the polarization light. When the long axis is parallel to the polarization light (0°), the brightness is the minimum. This position is termed as a position of extinction for the crystal. The brightness increases when the angle increases from 0 to 45°. The brightness versus the angle (Figure 3B) shows four repeat profiles in a complete circle. The minimum brightness occurs at 0, 90, 180, and 270°, and the maximum brightness occurs at 45, 135, 225, and 315°. Similar results were observed for triphenylene nanowires. The periodical change of the brightness versus the angle shows that the triphenylene nano/microwire is a birefringent crystal17,22 that is, the crystal has two distinct indices of refraction, and it splits one ray of light into two rays. The propagation route of a light between polarizer and analyzer inserted by a birefringence crystal is schematically illustrated in Figure 3C. The amplitude of polarized light from polarizer is assumed to be A. During propagation in the crystal, the polarized light is resolved into the ordinary (o) light and extraordinary (e) light in the crystal. The contribution from the polarized light for o-light and e-light can be obtained by dropping projection of the amplitude onto the axis of o-light (amplitude Ao), and e-light (amplitude Ae), respectively. At last, o-light and e-light are further resolved by dropping projection onto the direction of analyzer axis to get the contribution of the o-light and e-light. The relationship between the brightness and the angle could be briefly described using following equation

\[ I = A_o^2 + A_e^2 = 2(A \sin \alpha \cos \alpha)^2 = \frac{1}{2} A^2 \sin^2 2\alpha \]

where I is the light intensity of the composed light passed through analyzer and α is the angle between the analyzer and the long axis of the crystal. Then, when α is 180°/2, the brightness is the minimum. When α is (360°n + 180°)/4, the brightness is the maximum.

3.3. Thermal Analysis and Spectroscopic Properties of Triphenylene Nano/Microwires. ATR-IR spectroscopy and TG/DTA are conducted to compare the molecular structure of

Scheme 1. Structure of Triphenylene

Figure 1. SEM images of triphenylene nano- to microstructures formed under different conditions: (A) 180 °C, 5 min; (B) 180 °C, 30 min; and (C) 200 °C, 30 min.
the nanowires and the powder of triphenylene. Figures 4 and 5 show no distinguishable difference between ATR-IR or TG/DTA of triphenylene nanowires and powder. This is expected because the $\pi-\pi$ interaction between PAH molecules is weak and typically does not result in any obvious changes in IR and TG/DTA of the PAH. However, one useful conclusion drawn from these results is that after the thermal heating process in our experiments the triphenylene remains intact and does not undergo polymerization or decomposition.

Figure 2. Diameter (A) and length (B) of triphenylene 1D structures after heating for 30 min at various temperatures; the diameter (C) and length (D) of triphenylene 1D structures after heated at 180 °C for various time.

Figure 3. (A) Cross-polarized optical microscopy (CPOM) images of microwires obtained at 200 °C for 30 min. (B) Brightness versus the angle between the direction of the polarization light and the long axis of the triphenylene microwire. (C) Scheme demonstrates light propagation between polarizer and analyzer inserted by birefringence crystal.

Figure 4. ATR-IR spectra of triphenylene nanowire obtained at 180 °C for 5 min and triphenylene powder.

Figure 6A shows fluorescence spectra ($\lambda_{ex} = 325$ nm) of triphenylene nano/microwires and triphenylene dissolved in an ethanol solution. The peak of triphenylene in the solution is at 362 nm. The peak shifted to 380, 387, and 394 nm for triphenylene nano/microwires with diameters of 0.2, 6, and 15 μm, respectively. As a comparison, the peak is at 380 nm for the triphenylene powder. The red shift of triphenylene from a solution to the solid states is attributed to $\pi-\pi$ interaction between triphenylene molecules. However, it was not common in organic nano-materials that the peak red-shifted when the diameter of the nano/microwires increased. The size-dependent emission property of triphenylene nano/microwires is likely attributed to the light propagation along the nano/microwires; that is, the triphenylene molecules along the nano/microwire direction can reabsorb the emitted light and result in the red shift of the emission compared with those directly irradiated by a light.
light propagation is proven from the fluorescence microscopy images of triphenylene nano/microwires (Figure 6B). The emission of triphenylene nano/microwires is blue when excited with UV light. Because of the light propagation along the long direction of nano/microwires, the fluorescence of the triphenylene nano/microwires is significantly brighter at the end of the wires, which is so-called the outcoupling light.24–26 The result shows that the triphenylene nano/microwires may be used as a waveguide material for optoelectronics applications.

When a crystalline triphenylene nanowire is annealed at 150 °C for 2 h in the vacuum, we observed a small portion of porous triphenylene nanowire (Figure 7), indicating that at a temperature lower than its sublimation temperature (160–180 °C) the \( \pi-\pi \) interaction between triphenylene molecules can be cracked by the heat. This is a unique example to fabricate organic-based porous nanowires, which offers an obvious advantage over template approaches18,27,28 due to its ease-of-use and the high purity of the porous nanowires. ATR-IR spectroscopy and TG/DTA of the porous nanowires are the same as those of triphenylene powder. The porous nanowires are quite stable, and no spectroscopic and physical change of the nanowires was observed after storing under ambient conditions for months. Because of the large surface area and the stability, the porous nanowires may have applications in capacitor electronic, gas separation, heterogeneous catalysis, ion exchange, and gas storage, which will be fully investigated in the future. However, we are unable to mass-produce the porous structure by choosing an appreciating temperature and annealing time. The condition and the mechanism of the conversion will be further studied and reported in the future.

### 3.4. Potential Application of Crystalline Nano/Microwires in Sensing Nitroaromatics

The porous nano/microwires of triphenylene are not conductive, so we focused on the sensing application of the crystalline triphenylene microwires. Figure 8A–C shows the conductivity change of a triphenylene microwire upon 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 nitroaromatics. Because toluene does not have an electron-withdrawing group and nitromethane and other chemicals do not have an aromatic ring, these preliminary studies indicated that
both an aromatic ring and electron-withdrawing groups are required to decrease significantly the conductivity of the triphe
nylene microwire. The results suggested that nano/microwires of triphe
nylene may be used for selective detection of explosives because many explosives belong to a group of electron-deficient nitroaromatics. In addition to the conductivity change, the fluorescence of the nanowires also showed selective change to nitrobenzene (Figure 8D). The sensing behavior of the triphe
nylene nano/microwires to explosives will be studied, and the sensing mechanism will be reported in due course.

4. CONCLUSIONS

One-dimensional crystalline nano/microwires of triphenylene were synthesized and characterized in this work. The size of the crystalline nano/microwires can readily be controlled by heating temperature and time. The size-dependent red shift of emission is observed from the triphenylene nano/microwires. The conductivity and fluorescence of the nano/microwires of triphenylene change selectively in the presence of nitrobenzene, indicating its potential for detection of explosive chemicals. We focused on the characterization of the nano/microwires in this study, and the sensing performance of these nano/microwires to explosives will be investigated and reported in the future.

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