Optoelectronic property and sensing applications of crystalline nano/microwires of decacyclene

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The characterisation and potential sensing applications of nano- and microwires of decacyclene are reported in this study. Attenuated total reflection infrared and differential thermal analyses reveal that the nano/microstructures are composed of aggregated decacyclene molecules that are held by $\pi-\pi$ interactions. Transmission electron microscopy images and the electron diffraction patterns show that, in the nanowires, the decacyclene molecules are oriented with their long axis perpendicular to the wires and the $\pi-\pi$ stacking direction parallel to the wire. Cross-optical polarised microscopy results show a birefringent crystal structure of the decacyclene crystalline wires. Fluorescent imaging shows that the crystalline wires might be used as a waveguide material. Both the conductivity and fluorescence of the nanobelts change selectively in the presence of vapour of nitrobenzene, a representative nitroaromatic, suggesting that the nanowires of decacyclene may be used for selective detection of explosives.

1. Introduction: One-dimensional (1D) organic-based nanomaterials hold potential in fabricating cost-effective electronics and optoelectronics devices [1–4]. Methods to synthesise 1D nanomaterials include precipitation from solutions [1, 5], template synthesis [6, 7], solid-phase reaction [8], vapour deposition [9–11] etc. Among these methods, the vapour deposition demonstrates an advantage in controlling the morphology of the nanomaterials with ease of fabrication and convenient design.

Polycyclic aromatic hydrocarbons (PAH) are one of the major materials for preparing crystalline nanostructures that possess semiconducting and photoluminescence properties [12–14]. The main driving force for self-assembling 1D PAH nanostructures is the $\pi-\pi$ interactions of PAH or PAH derivatives [15–17]. Thin films of decacyclene, a PAH with C3 symmetrical ten-member rings (Fig. 1), have been used to develop light-emitting devices [18, 19], chemical sensing [20], liquid crystals [21, 22] etc. Recently, nanowires of decacyclene have been developed by using a vapour deposition method [23]; however, the properties of these nanowires have not been characterised. In this work, we report the optoelectronic and electronic properties of the nanowires, and their potential sensing applications.

2. Experimental: Decacyclene was purchased from Alfa Aesar and used as received. The decacyclene nanowires were synthesised in a furnace according to an evaporation method reported previously [16]. In general, 5 mg of decacyclene powder was placed in a 50 ml quartz tube. The tube was heated in vacuum for an hour, then the tube was allowed to be naturally cooled to room temperature. Decacyclene nanowires that were self-assembled on a glass microslide were collected for analysis.

UV-vis spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-7000 fluorescence spectrometer. The excitation wavelength is 370 nm. Attenuated total reflection infrared (ATR-IR) spectra were recorded on a Smith IR microscope. Thermal analyses were obtained with thermogravimetry/differential thermal analyser (TG/DTA 6300, SII Nanotechnology Inc.). The heating rate is 5°C/min with a nitrogen flow (50 ml/min). A Zeiss Supra 50 VP was used to obtain scanning electron microscopy (SEM) images. A JOEL JEM2100 operated at 120 keV was used for obtaining transmission electron microscopy (TEM) images. Gas-sensing experiments were performed with a nanowire resistor device placed in a glass tube, which is 20 cm in length and 1.5 cm in diameter. A targeted vapour 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 vapours. Cross-polarised optical microscopy (CPOM) images were collected on a Smith-polarised microscope. The geometric optimisation was performed at density functional theory B3LYP level with a LANL2DZ basis set.

3. Results and discussion: Fig. 2 shows SEM images of decacyclene nano/microwires. When the powder is heated at 400°C for an hour, long decacyclene nano/microwires with smooth surfaces are obtained. These wires have a diameter of 500–2000 nm and a length up to 100 µm (Fig. 2 left). The cross-section of the nanowires is polygonal (Fig. 2 right). Higher temperature and a larger amount of decacyclene power lead to wider and longer decacyclene nano/microwires, and vice versa. However, we did not observe a

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Figure 1 Structure of decacyclene

Figure 2 SEM images of decacyclene nano/microwires fabricated from heating 5 mg of decacyclene powder at 400°C in a 35 ml quartz tube

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correlation between the morphology of the nano/microstructure with the amount of decacyclene in the quartz tube and the heating temperature.

Fig. 3 compares the ATR-IR spectra of nanowires and powder of decacyclene. The peaks at 3057 and 1489 cm⁻¹ in the nanowires are assigned to the C–H stretching and C–C stretching of decacyclene, respectively. The peaks at 1082 and 750 cm⁻¹ in the nanowires are assigned to the C–H in-plane deformation and C–H wagging, respectively, [24]. Compared to the peaks of decacyclene powder, all these peaks red shifted 4–7 cm⁻¹, indicating that the π–π interaction between decacyclene molecules in the nanowires is stronger than that in the powder. The ATR-IR spectra also demonstrate that decacyclene remains intact and does not undergo decomposition or polymerisation after the thermal heating process in our experiments.

Differential thermal analyses (DTA) were conducted to further illustrate the stronger π–π interaction between decacyclene molecules in the nanowires than that in the powder. Decacyclene powder has an endothermic peak at 390°C, which is attributed to phase transition of decacyclene [24]. Fig. 4 shows that the phase transition temperature of decacyclene nanowire increases to 400°C, which is attributed to the stronger π–π interaction between decacyclene molecules in the nanowires. This is consistent with the results obtained from the ATR-IR spectra.

Fig. 5 shows TEM images of the nanowires of decacyclene. The corresponding electron diffraction pattern (Fig. 5 right) indicates crystalline structure of the nanowires and 20.7 Å d-spacing in the perpendicular direction and 3.9 Å d-spacing in the longitudinal nanowire direction, which suggests that the molecules are oriented with their long axis perpendicular to the wire and the π–π stacking direction parallel to the wire, as shown in Fig. 6. The geometry of the decacyclene nanowire has been modelled with the density functional theory and the distance is 20.7 Å between two side-to-side decacyclene molecules, which is the same as it is from the TEM result. The TEM results and calculated results agree with the orthorhombic structures of a decacyclene crystal, which has indices of a = 3.95 Å, c = 20.74 Å [17].

Fig. 7 shows the brightness of CPOM images of a decacyclene nanowire on varying the angle between the direction of a polarisation light and the long axis of the decacyclene nanowire. There are four repeats in a complete circle. The maximum or minimum brightness of the image repeats every 90°. When the long axis is parallel to the polarisation light (0°), the brightness is the minimum. The brightness increases when the angle increases from 0 to 45°. The periodical change of the brightness against the angle shows that the decacyclene nanowires are a birefringent single crystal [25], that is, the crystal has two distinct indices of refraction and it splits one ray of light into two rays. The strong birefringence is associated with the plane-to-plane stacking (H-aggregation) [26] of decacyclene molecules in the nanowires, which is consistent with TEM results and the packing model in Fig. 6.

Fluorescence microscopy images in Fig. 8 show that the fluorescence at the end of these nano/microwires is significantly brighter than that of other sections of the wires, which is so-called the outcoupling light [27]. This phenomenon is generally attributed to the light propagation along the nano/microwires [28], that is, the decacyclene...
molecules along the nano/microwire direction can re-absorb the emitted light. This result shows that the decacyclene nano/microwires may be used as a waveguide material for optoelectronics applications. It is noteworthy that the light intensity of the wires depends on the distance between the nanowires and the microscopy lens. The nanowires that are closer to the lens are brighter than those that are far. Bright spots were also observed long wires along the wires, which might be owing to the crack part of the nanowires.

The nanowire of decacyclene measured in N<sub>2</sub> and O<sub>2</sub> (Fig. 9) shows the conductivity change of a decacyclene nanowire on exposure to a gas phase deposition method. TEM, CPOM, ATR-IR, TG/TDA results showed strong π–π interactions of decacyclene molecules in the crystalline wires. We also demonstrated that the conductivity and fluorescence of the nanostructures of decacyclene change selectively in the presence of nitrobenzene, indicating its potential for detection of explosive chemicals. The sensing performance of these nanostructures to explosives will be investigated and reported in due course. This facile and controllable synthesis method makes it competitive in the fabrication of sensors and potentially other electronic devices.

4. Conclusions: In summary, this work demonstrates that polymeric micro/nanowires of decacyclene can be obtained by means of a gas-phase deposition method. TEM, CPOM, ATR-IR, TG/TDA results showed strong π–π interactions of decacyclene molecules in the crystalline wires. We also demonstrated that the conductivity and fluorescence of the nanostructures of decacyclene change selectively in the presence of nitrobenzene, indicating its potential for detection of explosive chemicals. The sensing performance of these nanostructures to explosives will be investigated and reported in due course. This facile and controllable synthesis method makes it competitive in the fabrication of sensors and potentially other electronic devices.

5 References


Figure 9 I–V of a nanowire of decacyclene measured in N<sub>2</sub> and O<sub>2</sub> and the change in DC current when the gases are switching between N<sub>2</sub> and O<sub>2</sub>.

Figure 10 Effect of five chemical vapours on the conductivity of a single decacyclene nanowire.


