Chapter 6

Conclusions

In this dissertation, I report that planar organic molecules, which possessed electron-rich central core, can easily form one-dimensional nanostructure by exploiting intermolecular dispersive forces. As compared with other synthesis methods of 1D nanostructure, this process provides a low-temperature way to synthesize organic nanofibers. I have learnt from the series of studies that certain factors would affect the film morphology. In addition, the field emission characteristics of the nanofibers film and of the single nanofiber have been investigated. The primary result obtained in this dissertation are summarized as follows:

(1) Carbon nanofibers with diameter ca. 66nm have been synthesized from coronene by low temperature (~45 ℃) vacuum sublimation onto a gold substrate. Since no catalyst and high temperature process are involved, this process is different from the catalytic decomposition method that normally involves three steps: (i) decomposition of hydrocarbon reactants on catalyst surface; (ii) forming a supersaturated solution of carbon and catalyst; and (iii) precipitation of carbon which extrudes a carbon wall. The main mechanism is ascribed to the function of intermolecular dispersive forces. The needle-like morphology is a result of the competition between intermolecular cohesive force and the interfacial adhesion force. Since the inert gold substrate possesses a lower surface energy, a minor interfacial adhesion force makes the dispersive force dominate. Consequently, coronene molecules self-assemble to form the columnar aggregates.
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(2) CuPc nanofibers with average length ca. 500 nm and diameters in the range 15–50 nm have been synthesized by vacuum sublimating CuPc molecules onto a heated gold substrate (~100 °C). Similar to the synthesis process of coronene nanofibers, no

catalyst is involved. Besides choosing the inert gold film as a reacting substrate, additional heating is necessary to further lower the surface energy of the substrate. As the substrate temperature increase higher, the CuPc nanofibers turn to be longer and had larger diameters at the expense of total fiber density.

(3) I have utilized the π–π interactions between PTCDA molecules and temperature-induced morphology changes to synthesize 1D nanostructures of PTCDA on a heated (ca. 100 °C) titanium substrate through vacuum sublimation. The average diameter of the nanofibers deposited on the Ti-CVD substrate at 100 °C was ca. 84 nm, with lengths ranging from 100 nm to 3 μm. Besides heating the substrate to lower the surface energy and mobilize the adsorbates, the pillar morphology of Ti substrate plays a role as a template to enhance the formation of needle-like morphology of PTCDA. Moreover, the Ti-Cl$_x$ residues also provide preference sites to trap PTCDA adsorbates at certain locations, which results in a discontinuous film.

(4) Among the three systems mentioned above, coronene molecules need the lowest process temperature (~ 45°C) to form the nanofiber structure. I attribute this to two causes: First, coronene molecule has the lowest molecular weight than others; therefore they can sublimate in a much lower temperature. Second, coronene consists of seven peri-fused benzene rings. It is a purely nonpolar aromatic hydrocarbon molecule. When depositing it on an inert substrate, the weak interfacial interaction allows the adsorbates diffuse easily to any energy-prefered site. As for PTCDA and CuPc molecules, the polar side groups or the high electronegative atoms, i.e. oxygen or nitrogen atom on the backbone, result in a stronger interfacial interaction with a substrate. Consequently, they need higher process temperature to activate the adsorbate to diffuse.

(5) The HRTEM images and energy dispersive spectra of Coronene, CuPc and PTCDA nanofibers all show no catalyst exist along the fibers. Despite that HRTEM image indicates that the nanofibers are formed by stacking molecules layer upon layer, the electron diffraction patterns display only amorphous rings, rather than distinct diffractive spots, suggesting an insignificant degree of crystallinity of these organic nanofibers.

(6) This coronene nanofibers exhibit field emission characteristics with the onset electric field 5.4 V/μm and field enhancement factor 1326 cm^{-1} for 100 μm interelectrode distance.   When biasing at 900 V (E = 9 V/μm) for 1800 s, a mean current density of ca. 0.4 mA/cm^2 with a perturbation less than one order of magnitude was observed. The field emission current did not decay during the stability measurements, demonstrating that the coronene nanofibers film is suitable for applications as electron emitting devices.

(7) The CuPc nanofibers exhibit field emission characteristics (with a turn-on field of 13.6 V/μm) and follow Fowler–Nordheim behavior in a manner similar to that of carbon nanotubes.   I observed a smaller current density ca. 3 μA/cm^2, with a perturbation within one order of magnitude as the nanofibers biased at 1000 V (E = 13.3 V/μm) for 1800 s.   The severe undulation may arise from the random orientation of the CuPc nanofibers on the surface.

(8) The turn-on electric field for producing a current density of 10 μA/cm^2 was 8 V/μm; the maximum emission current density was 1.3 mA/cm^2, measured at 1100 V (E = 11 V/μm).   From the slope of the straight line obtained after plotting ln (J/E^2) versus $1/E$, I calculated the field enhancement factor β to be ca. 989 cm^{-1}.   When biased at 1000 V (E = 10 V/μm) for 1600 s, the mean current density of ca. 0.5 mA/cm^2 with a perturbation of less than one order of magnitude was observed.

(9) The energy barrier between the organic nanofibers and the metal substrate will affect the performance of field emission current.   For instance, PTCDA and coronene materials have an electron affinity very close to the work function of metal substrate. Consequently, a higher emission current was observed in both cases. However, as for CuPc material, the interfacial energy barrier limits the electrons to be supplied from the substrate to the nanofiber, hence a poor field emission characteristic.

(10) In addition to minimize the energy difference between organic fibers and metal substrate, the orientation of the fiber growth is also essential to give a better field emission performance.   For instance, PTCDA material has a lower interfacial energy

barrier than coronene material, however, the random orientation of PTCDA naonofibers make the emission diverse hence a relative higher turn on field is needed to emit a equal amount current as compared with the coronene nanofibers.

These results demonstrate an alternative application of organic semiconductor materials as an electron-emitting device and open up an interesting area of study of the anisotropic carrier transfer in 1D organic nanostructure.

Chapter 7

Future Works

This dissertation demonstrates preliminary research results about the field emission characteristic of the organic nanofibers. Further investigation about the carrier conducting behavior inside the nanofiber is still a mystery to be explored. Patterning some metal pads on a wafer in advance, then spin on these nanofibers onto the patterned wafer, and subsequently deposit the contact electrodes on the nanofiber and wire it with the metal pad could do this. By a similar approach as four-probe measurement, one can deduce the contact resistance and the linear resistance of the nanofiber. Meanwhile, the time-of-flight (TOF) measurement is another common method to evaluate the carrier mobility of organic materials. It is also suitable to be utilized to study the anisotropic conducting behavior of the organic one-dimensional nanostructures.

Besides the field emission characteristic, these organic nanofibers also show a different photoluminescence result as compared with their bulk film. Most of them show blue shift spectra, and in certain condition they possess a narrower peak than that of the bulk film. The further research and its possible application open up a space to be explored.

In chapter4 I mentioned that P-type CuPc nanofiber has an inferior field emission performance because of the interfacial barrier, which limit the supply of electrons. Recently a fluorinated CuPc molecule has been reported as a N-type material. I expect this molecule can pile up as a 1D nanostructure, which can perform a better field emission characteristic because a much comparable interfacial barrier.

Finally, organic nanofibers provide one-dimensional channel for carrier transporting. And most of their composition, planar molecules, is chromophor, which can produce

electron-hole pairs as they are illuminated by light. By depositing N-type material on a pillar P-type material or vise verse, the needle-like morphology can increase the heterogeneous interfacial contact area and this can enhance the energy conversional efficiency of an organic photovoltaic cell.

All above topics are the possible future work as an extension of this research. The fascinating properties of the organic materials and their diverse applications provide us an alternative choice beside the well-known inorganic material.