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Synthesis, characterization of the pentacene and fabrication of pentacene field-effect transistors*

Tao Chun-Lan (陶春兰)[a], Zhang Xu-Hui(张旭辉)[a], Dong Mao-Jun(董茂军)[a], Liu Yi-Yang(刘一阳)[c], Sun Shuo(孙 硕)[a], Ou Gu-Ping(欧谷平)[a)b)], Zhang Fu-Jia(张福甲)[a)†], and Zhang Hao-Li(张浩力)[c]

[a] *School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China*
[b] *School of Physics, Hunan University of Science and Technology, Xiangtan 411201, China*
[c] *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China*

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A comprehensive understanding of the organic semiconductor material pentacene is meaningful for organic field-effect transistors (OFETs). Thin films of pentacene are the most mobile molecular films known to date. This paper reported that the pentacene sample was successfully synthesized. The purity of pentacene is up to 95%. The results of a joint experimental investigation based on a combination of infrared absorption spectra, mass spectra (MS), element analysis, x-ray diffraction (XRD) and atom force microscopy (AFM). The authors fabricated OFET with the synthesized pentacene. Its field effect mobility is about 1.23 $cm^2/(V\cdot s)$ and on–off ratio is above 10^6.

Keywords: pentacene, OFETs, MS, XRD, AFM
PACC: 6855, 7865T, 7280L, 0785

1. Introduction

During the last few years, the development of organic field-effect transistors (OFETs) has attracted much interest.[1−12] The production of OFETs has been studied because organic molecules offer the opportunity of deposition over large surface areas and are compatible with flexible plastic substrates. A number of organic compounds have been proposed for use in light-emitting diodes, field-effect transistors and photovoltaic cells.[13,14] The pentacene, which is commercially available but expensive, has shown good field effect mobility on vacuum-deposition.[7] Its carrier mobility is higher than any other organic semiconductors, generally reaching $2cm^2/(V\cdot s)$. The mobility of single crystal pentacene could increase to $58cm^2/(V\cdot s)$ at 225K and $35cm^2/(V\cdot s)$[15] at room temperature. This property can compete with amorphous hydrogenated silicon (a-Si: H), making pentacene the ideal material for fabricating organic semiconductor devices. Pentacene have been widely used in OFET,[16−20] organic light-emitting diodes[21,22]and organic solar cells[23,24]as the active layers.

The authors have successfully synthesized the pentacene, and characterized it by infrared absorption spectra (IRAS), mass spectra (MS), element analysis, x-ray diffraction (XRD) and atom force microscopy (AFM). The pentacene is insoluble and cannot be characterized with NMR-spectroscopy. The pentacene OFETs have been fabricated and its field effect mobility is about $1.23cm^2/(V\cdot s)$ and on-off ratio above 10^6.

2. Experiment

2.1. Synthesize pentacene

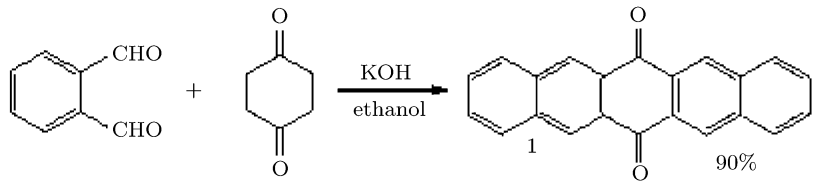
The most widespread method to prepare pentacene was first described by Bruckner and Tomasz[25] in 1961.

Firstly, pentacenequinone (1) is prepared by condensation of 0-phthalaldehyde and 1, 4-cyclohexanedione (scheme1). This is a high yielding reaction and the starting materials are cheap and readily available.

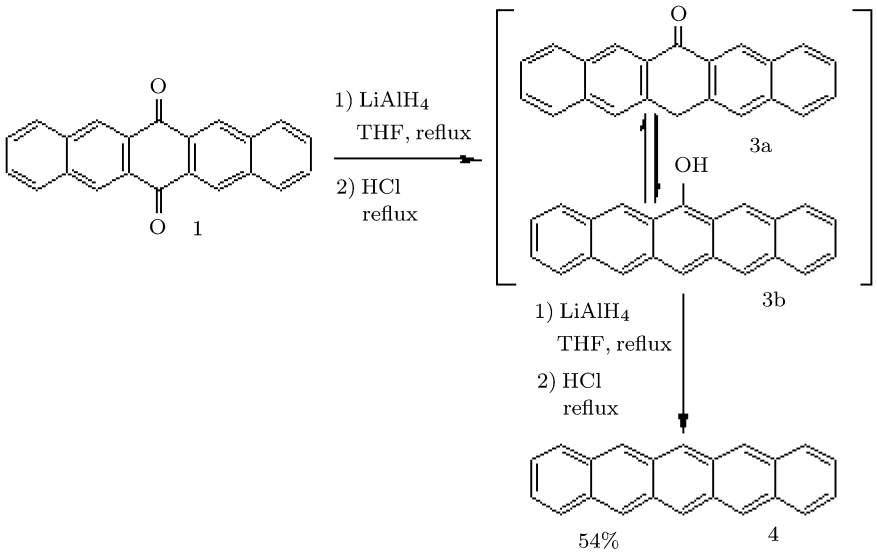
Secondly, the pentacenequinone can be reduced to pentacene (4) with Al-amalgam. Because of the

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†E-mail: prof_zhangfj@sina.com

health and environmental risks involved in the use of mercury, we have been looking for an alternative reduction process of quinine 1, proceeding in a reproducible and clean way (scheme 2).



Scheme 1



Scheme 2

2.2. Fabricate the pentacene organic field effect transistors

The schematic diagram of OFET was shown in Fig.1.

Firstly, a heavily doped silicon (111) wafer was used as a convenient substrate and gate electrode. Thermally grown silicon dioxide was used as the gate dielectric, about 300nm. Source and drain contact were deposited on the dielectric layer by evaporating gold through a shadow mask.

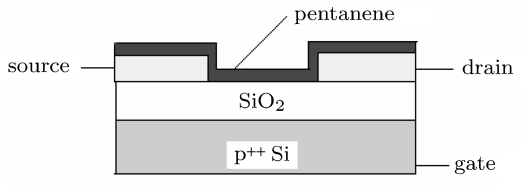


Fig.1. Schematic diagram of organic field-effect transistor.

Secondly, pentacene active layer was deposited by thermally evaporation at a nominal rate of 1–5nm/s and its thickness was 50nm. Typical system base pressure was 1.2×10^{-4}Pa. So the OFETs were fabricated.

3. The results and discussion

3.1. The infrared absorption spectra of the pentacene

The IRAS (4000–400cm^{-1}) of the pentacene shown in Fig.2 were determined with KBr discs on a Therrno Mattson FTIR spectrometer. The peaks at 906 and 732cm^{-1} are attributed to the bending vibration of C–H bond in aromatic ring. Skeleton stretching vibration of C=C bond in aromatic ring appears at 1623, 1580, 1496, 1444cm^{-1}. The peak at 3041cm^{-1} is assigned to the stretching vibration of =CH bond in aromatic ring. The vibration at 3437cm^{-1} is assigned to the stretching vibration of lattice water.

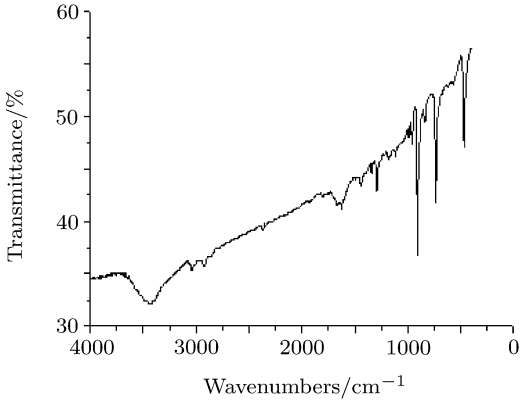


Fig.2. The infrared absorption spectra of the pentacene.

3.2. The mass spectra of the pentacene

The MS of the pentacene was shown in Fig.3. The EI-MS was obtained on a VG ZAB-HS spectrometer at 70eV. The peak at m/z=277.9 corresponded to the molecular weight of pentacene (m/z=278).

3.3. Element analysis of the pentacene

The element analysis of the pentacene was measured on an Elemental Vario EL analyser. The results suggest that the purity of pentacene is up to 95%. $C_{22}H_{14}$ requires C, 94.96%; H, 5.04%. Found: C, 90.5%; H, 4.78%.

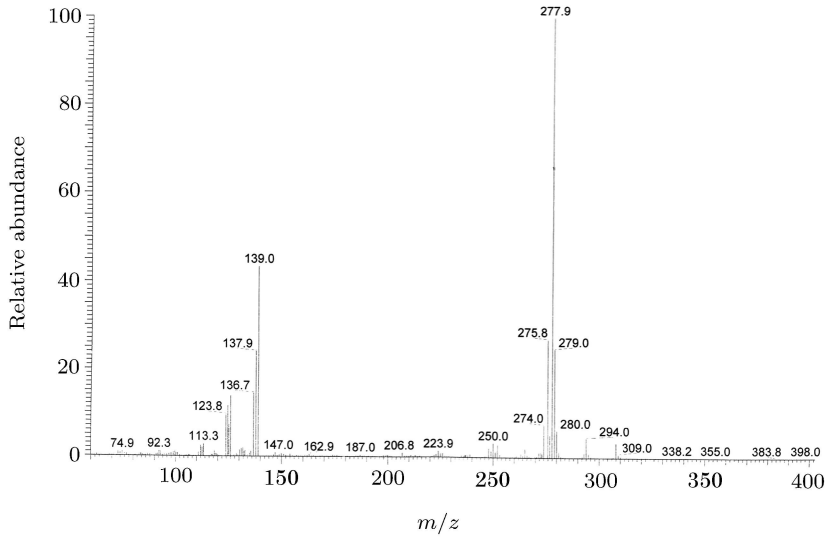


Fig.3. The mass spectra of the pentacene.

3.4. X-ray diffraction pattern of the pentacene thin films

XRD pattern of the sublimed pentacene thin films was shown in Fig.4. Strong peaks corresponding (00n) lines (n=1 to 4) appeared which indicated the long axis of pentacene aligned perpendicularly to the substrate surface. From these peaks, according to Bragg equation: $n\lambda = 2\mathrm{d}\sin\theta$, it was obtained that the spacing of c-axis was 1.55nm. Similar diffractograms had been reported by Minakata *et al*,[26] who reported that d_{001} =1.53nm. It was close to thin film phase.[25] The peak half width of the sublimed pentacene thin films was 0.017 degree. XRD indicated that the crystals were oriented regularly to form conduction plane on the substrate plane. The degree of 2θ=28.82° was the diffraction peaks of Si(111) face.

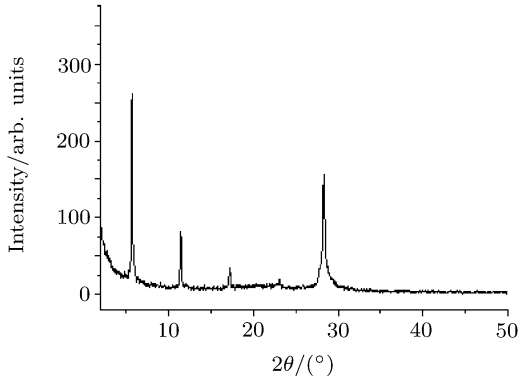


Fig.4. X-ray diffraction pattern of the pentacene thin films fabricated on Si (111) substrate.

3.5. The AFM micrograph of the pentacene thin films

The surface morphology of the pentacene films was examined with atom force microscopy (AFM) was shown in Fig.5 AFM micrographs from a film deposited at substrate temperature (T_{sub}) equal to 45° show that the films are polycrystalline with an average grain diameter of approximately 0.2–0.4μm. This result was expected, considering that the substrate was the amorphous SiO_2 insulating layer of OFET.

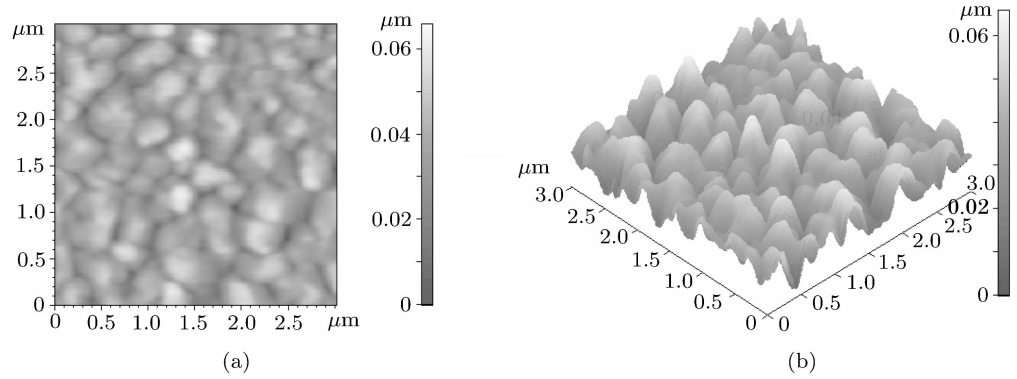


Fig.5. The AFM micrograph of the pentacene thin films on SiO_2 substrate, (b) is the three-dimension image of (a).

3.6. The $I-V$ curves of the pentacene OFET

The electrical characterization of the devices was done in Ar atmosphere inside the glove box. The Keithley 2400 SMU was used to study the OFET characteristics.

Pentacene OFETs are adequately modelled by standard field-effect transistors equations,[27] as shown previously for other OFETs.[28,29] The pentacene used in the present devices behaved as a p-type semiconductor. A typical plot of drain current, I_D, vs drain voltage, V_D at various gate voltages, V_G, is shown in Fig.6 and I_D, vs gate voltage, V_G at a constant drain voltage of 40V (saturation regime), is shown in Fig.7. The pentacene layer in this devices was deposited at 45°. It consists of the thin film phase of pentacene and corresponds to the XRD pattern of Fig.4. When the gate electrode is biased negatively with respect to the source electrode (grounded), pentacene OFETs operate in the accumulation mode and the accumulated charges are holes. At low V_D, I_D increases linearly with V_D (linear regime) and is approximately given by the equation:

$$I_D = \frac{WC_i}{L}\mu\left(V_G - V_T - \frac{V_D}{2}\right)V_D.$$

Where L is the channel length, W is the channel width, C_i is the capacitance per unit area of the insulating layer (500nm thermally grown SiO_2 with C_i=6.9×10^{-9}F/cm^2), V_T is the threshold voltage, and μ is the field-effect mobility.

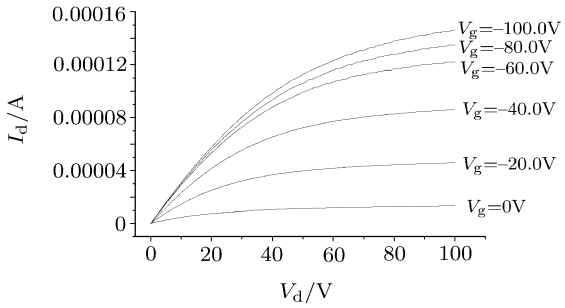


Fig.6. The $I_d - V_d$ curves of the pentacene OFET.

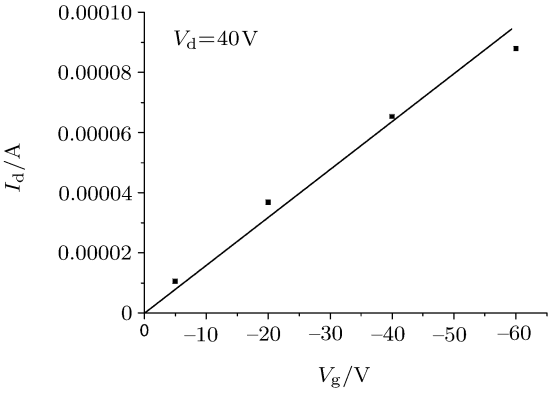


Fig.7. Plot of drain current vs gate voltage at a constant drain voltage of 40V (saturation regime) from the same device as in Fig.6.

For V_D greater than V_G, I_D tends to saturate (saturation regime) due to the pinch off of the accumulation layer, and is modelled by the equation

$$I_D = \frac{WC_i}{2L}\mu(V_G - V_T)^2.$$

In the saturation regime, using the values W = 8mm, L=1mm, C_i=6.9×10^{-9}F/cm^2, we have obtained a value of mobility of 1.23cm^2/(V·s) and a threshold voltage of 0V. The on/off ratio was above 10^6.

4. Conclusion

We had synthesized the organic semiconductor material pentacene, and investigated its characteristics by IRAS, MS, element analysis, XRD and AFM. The purity of pentacene is up to 95%. The OFETs with the pentacene as the active layer had been fabricated and its field effect mobility was about 1.23cm^2/(V·s) and on-off ratio above 10^6.

Acknowledgments

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