

有機半導體材料之一維奈米結構的合成與特性研究

摘要

由於一維奈米結構具有迥別於其塊材型態的特殊性質，近年來吸引了許多傑出的研究。除了一般以化學氣相沈積或是化學合成方式來製造一維奈米結構外，近期的研究顯示有機半導體材料能夠利用分子間分散力，以分子自我組裝的方式，在較低溫的環境下形成一維奈米結構。本論文主要探討熟知有機半導體材料製備成一維奈米結構的可能性，並試圖探討各項影響薄膜形貌的可能因子。最終評估本研究所製備而得的一維有機奈米材料的真空場發射電子效益。

在本論文第一部份主要探討多環有機芳香烴-苯暈 (Coronene) 製備成一維奈米結構物的各樣特性。在沒有催化劑的輔助下，直徑 66 奈米的奈米碳纖能以低溫 (~45 °C) 真空蒸鍍技術，輔以分子自我組裝特性，成功的合成在鍍金基板上。此奈米碳纖具有較市售奈米碳管為佳的熱穩定性。在場發射特性量測中，如同奈米碳管般，亦具備場發射電子的能力。在陽極銅棒與基板間距 100 μm 的實驗條件下，其起始電場強度約為 5.4 V/ μm ，場發射增強因子約為 1326 cm^{-1} 。

在本論文第二部份主要探討雜環平面分子酞菁銅 (CuPc) 製備成一維奈米結構物的各樣特性。不同於多環有機芳香烴，平面分子中心包含了銅原子，且在分子環的部分，除了碳與氫原子外，多了氮原子。由於分子團的分子量較大，需要較高的昇華溫度來蒸鍍 CuPc 材料。在本研究中藉由升高基板溫度以降低鍍金基板表面自由能，使得吸附分子能克服界面作用力，而以 π - π 分子間作用力為主，自我組裝成直徑 15-50 奈米，平均長度為 500 奈米的奈米纖維。藉由 X 光繞射分析和拉曼光譜的鑑定，確認此奈米結構為 α 相結構。由高解析度穿透式電子顯微鏡觀察到此奈米纖維是由 CuPc 分子以平行於奈米纖維軸向方向堆疊排列而成。由於此材料為 P 型半導體材料，不利於電子的注入與傳導，所以在場發射電子能力的表現上較弱。在陽極銅棒與基板間距 50 μm 的實驗條件下，其起始電場強度約為 13.6 V/ μm 。

在本論文第三部份主要探討芘四甲酸二酐 (PTCDA) 製備成一維奈米結構物的各樣特性。不同於多環有機芳香烴，分子環的部分，除了碳與氫原子外，多了氧原子。由於分子團的分子量較大，亦需要較高的昇華溫度來蒸鍍PTCDA材料。在本研究中除了藉由升高基板溫度以降低基板表面自由能外，尚利用鈦基板特有柱狀形貌的輔助，使得吸附分子能自我組裝成直徑 84 奈米，長度為 0.1-3 微米的奈米纖維。經由全反射螢光光譜儀的鑑定，觀察到化學氣相沈積法製備的鈦基板上存在大量的氯元素。此為鈦基板反應前驅物 (TiCl_x) 殘留所造成。這些存在於鈦基板上的 TiCl_x 殘留物，扮演為活化位置，助使吸附分子侷限在該區，而形成不連續的島狀形貌。在場發射特性量測中，如同苯暈製備成的奈米碳纖一般，PTCDA 奈米纖維亦具備極佳的場發射電子能力。在陽極銅棒與基板間距 100 μm 的實驗條件下，其起始電場強度約為 8 $\text{V}/\mu\text{m}$ ，場發射增強因子約為 989 cm^{-1} 。當電場為 11 $\text{V}/\mu\text{m}$ 時，可發射達 1.3 mA/cm^2 的場發射電流。



Synthesis and Characterization of One-Dimensional Nanostructures of Organic Semiconductor Materials

Abstract

One-dimensional (1-D) nanomaterials attract a great deal of interest because of their peculiar properties, relative to those of their bulk counterparts, and great potential for application. Many recent studies have indicated that organic compounds can form 1-D nanostructures under low-temperature conditions when intermolecular dispersive forces are exploited in self-assembly processes. The dissertation describes the synthesis of one-dimensional organic nanofibers in an attempt to discover the factors that dominate the film morphology. All of the organic semiconductor materials investigated in this thesis, display π -stacked columnar structures, in which charge can migrate within and emit electrons from the fiber tip when biased in vacuum and in a high electric field.

In the first part of this dissertation, I utilized coronene to form 1D nanostructures. Nanofibers with diameter ca. 66nm have been synthesized from coronene molecules, by low temperature (~ 45 °C) vacuum sublimation without the aid of catalyst. This polycyclic aromatic hydrocarbon-carbon nanofibers (PAH-CNFs) reveal much better thermal stability than commercial carbon nanotubes (CNTs) and 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.

In the second part of this dissertation, I deal with CuPc molecules, a heterocyclic planar molecule to form 1D nanostructure. In this study, substrate temperature that can alter the surface energy plays a crucial role to form the desired nanofiber structure. The average length of these CuPc nanofibers deposited at 100 °C, a temperature much lower than that for synthesis of carbon nanotubes, was ca. 500 nm, with diameters in the range 15–50 nm. XRD analysis of these nanofibers revealed that they possessed a α phase structure. HRTEM images indicated that the CuPc nanofibers formed through layered stacking of CuPc molecules. These 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.

The recently synthesized high-aspect-ratios PTCDA nanofibers are introduced in the last part. 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. Because of the pillared Ti structures and the presence of reactive Ti-Cl sites, the titanium substrate played a crucial role in assisting the PTCDA molecules to form 1D nanostructures. 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 μ m. When the PTCDA nanofibers were biased under vacuum, the emission current remained stable. The turn-on electric field for producing a current density of 10 μ A/cm² was 8 V/ μ m; the maximum emission current density was 1.3 mA/cm², measured at 1100 V ($E = 11$ V/ μ m). 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.

The dissertation is concluded with a chapter, which summarizes the results obtained on organic nanofibers. An overview of the most important conclusions is given and some general remarks relevant to applications in molecular electronic devices are made.

致謝

首先非常感謝黃華宗教授對我研究內容的指導，特別要感謝的是黃老師對我這樣一位在職生所給予的寬容與鼓勵。而黃老師在解惑、授業之餘，對於教化人心以及傳揚救恩的熱忱，也讓我深受激勵。

感謝臺灣大學材料系林金福教授、清華大學材料系周卓輝教授、交通大學材料系郭正次教授、交通大學材料系林宏洲教授於博士口試時所惠賜寶貴意見，讓本論文得以更臻完善。

感謝國家奈米元件實驗室的同仁在實驗及儀器上的協助。感謝黃華宗老師實驗室眾多的同學、學弟、學妹們的幫忙，使得各項實驗得以順利完成。感謝系辦余小姐在博士口試期間於行政事務上的熱心協助。

最後感謝我最親愛的家人對我博士進修的支持與鼓勵，讓我得以完成研究論文，謝謝你們。



