奈米碳材料的合成及電化學電容器之應用

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摘要

奈米碳管具有優異且獨特的化學與物理特性，應用於各種領域深具有淺力，例如場發射顯示器、儲氫材料、能量儲存、奈米電子元件及複合材料等。奈米碳管主要的合成法包括：雷射蒸發法、電弧法以及化學氣相沈積法，作為觸媒之用的過渡金屬（鐵、鈷、鎳）對於採用化學氣相沈積法尤其重要。

本研究論文採用偏壓輔助微波電漿化學沈積系統合成多種結晶性奈米碳材料於碳布以及不鏽鋼片上，包括垂直以及交錯成長的奈米碳管、接合奈米碳薄片的奈米碳管以及二維和三維結構的奈米碳薄片，這多樣的奈米碳結構可以經由通入不同的氣氛系統而達到，包含了甲烷/氫氣以及甲烷/二氧化碳系統; 甲烷/氫氣(1:4)的系統可用作在含有鐵觸媒的基板上成長純奈米碳管的前驅物氣體來源。當中，交錯成長的奈米碳管是在沒有施加外部偏壓的情況下可以得到，而垂直成長的奈米碳管則是藉由施加相對於在系統上電極的-150 伏特偏壓而得到，除此之外，有趣的是,接合奈米碳薄片的碳管也可以藉由相同的系統得到，只是鍍有鐵觸媒的基材在氮氣的氣氛下需先經過 400℃退火 5 小時，類似的接合結構也可以在不鏽鋼基材上藉由甲烷/二氧化碳(3:2) 的系統得到，同樣地考慮施加偏壓，這樣的接合結構只有在施加-150 伏特偏壓 的情形下才能達到，相較之下，在不施加偏壓以及-100 伏特的情形下會得到奈米碳薄片以及球狀奈米碳薄片的結構;在相同的甲烷/二氧化碳系統之下，我們利用沒有觸媒的沈積方式，藉由碳原子間碰撞的原理，可以在碳布上得到二維的碳薄片結構，在不用觸媒的考慮下，我們也嘗試著將二維的結構轉為三維的堆疊，利用醋酸在 90℃下進酸化 6 個小時，便可以在原本的二維結構上繼續碳的沈積以轉變為具有花簇狀碳薄片的第二層堆疊。這

些碳結構則是藉由掃描式、穿透式電子顯微鏡、拉曼光譜儀以及 X 光繞射儀進行量測。

論文的第二部份則事先藉由不同濃度的醋酸(2M 及 14M)在 90°C 以及不同的時間條件下對垂直成長的奈米碳管進行酸化以探究官能基的數量極限，我們發現官能基的數量極限在 2M 以及 14M 的條件下分別可以在 12 小時以及 6 小時候得到。應用在超高電容器上，有著奈米碳薄片接合的碳管，其電容量則會有效的提昇，可以達到將近 194 F/g，幾乎是純碳管電極的兩倍;在不用觸媒沈積的碳薄片方面，三維碳薄片結構的電極顯示出較二維碳薄片結構近四倍大的電容量，這主要是因為孔洞的尺寸分佈趨近於 3 nm，這樣的結果是有利於電荷的儲存;在本論文研究中，所有的含碳結構的電極其循環效率在經過 2000 次的循環之後都還可以超過 90%，我們認為含有奈米碳薄片的碳結構也許在能量儲存系統的應用上可以提供一個另外的選擇，尤其是在電化學電容器上。

Synthesis of Carbon Nanomaterials and Applications on Electrochemical Capacitor

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Abstract

Carbon nanotubes (CNTs) have unique properties that make them suitable for use in various applications, such as field emission displays, energy storage, chemical sensors, nano-electronic devices, and composite materials. The available methods for synthesizing CNTs include arc-discharging, laser vaporization, and chemical vapor deposition using transition metals (e.g., Fe, Co, Ni) as catalysts.

In the studies reported in this Thesis, we used a bias-assisted microwave plasma-enhanced chemical vapor deposition (MPCVD) system to synthesize various crystalline carbon nanomaterials, including aligned and interlaced CNTs, CNTs decorated with carbon nanowalls (CNWs), and two- and three-dimensional CNWs on carbon cloth (CC) and stainless-steel (SS) substrates. The nature of the resulting carbon structures varied depending on the choice of the gaseous system (CH_4/H_2, CH_4/CO_2). The CH_4/H_2 system at a ratio of 1:4 served as a precursor for the synthesis of pure CNTs on both the CC and SS substrates, with Fe as the catalyst. Interlaced CNTs formed in the absence of an applied external bias; aligned CNTs formed when applying an external bias of at least –150 V with respect to the upper electrode in the MPCVD system. Interestingly, CNTs decorated with CNWs on their surfaces were synthesized on the Fe-coated CC subjected to annealing under a N_2 atmosphere at 400 °C for 5 h; an analogous structure was formed on the SS substrate when introducing the mixture of CH_4 and CO_2 at a specific flow ratio of 3:2. CNTs decorated with CNWs were obtained when applying a negative bias of –150 V, whereas CNW sheets and spherical CNWs resulted at biases of 0 and –100 V, respectively. In the same CH_4/CO_2 system, but without any added catalyst, normal 2D CNWs were formed on the CC substrate through the collision of carbon atoms. Using catalyst-free conditions, we turned these 2D structures into 3D

constructions by stacking flower-like aggregates of CNWs onto the 2D sheets, which had been functionalized under the influence of HNO_3 at ca. 90 °C for 6 h. The structures were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and X-ray diffraction (XRD).

The second part of this Thesis describes the quantitative limitations of the number of functional groups that could be formed on aligned CNTs after oxidizing them with various concentrations of HNO_3 at 90 °C for various periods of time. Using 2 and 14 M HNO_3, the maximum number of functional groups was obtained after 12 and 6 h, respectively, as measured in terms of quantity of Pt particles. Subsequently, the different kinds of carbon materials described in this Thesis were functionalized with 14 M HNO_3 over 6 h to test their applicability for use as supercapacitors. The capacitance was increased dramatically to ca. 194 F/g after attaching the CNWs to the CNTs, almost doubling the value of the electrode formed from pure CNTs (ca. 100 F/g). The 3D construction of CNWs exhibited an enormous increase in capacitance to ca. 200 F/g—over four times larger than that of the 2D sheets of the pure CNWs—because of their optimal pore size distribution (ca. 3 nm). For all of the electrodes tested in this study, the supercapacitor efficiency remained greater than 90% after 2000 cycles. The unique structures of the CNT-CNF and 3D CNW electrodes may provide another route for the application of carbon-based materials to energy storage systems, especially electrochemical capacitors.

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