

Phase segregation assisted morphology sculpting of nanostructures grown by vapor-solid reactions

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Abstract:

A concept of phase segregation has been proposed in this dissertation. The strategy has been used to assist sculpting of nanostructures, including carbon and silicon, grown by vapor-solid reactions. The inorganic salts MX (M = Na, Mg, Ca; X = F, Cl, Br, I) can act as self templates reagents to support the formation of nanostructures.

First, porous carbon materials with pore sizes from 3 - 200 nm were synthesized by reacting hexafluorobenzene with Na liquid at 623 K. NaF crystals, a byproduct formed in the reaction, acted as nanotemplates to assist the pore formation. By employing hexafluorobenzene to react with Na incorporated within the channels (diameter 200 nm) of anodized aluminum oxide (AAO) membranes at 323 - 623 K, the carbon material can be fabricated into aligned porous nanotube arrays (ca. 250 nm in diameter, ca. 20 nm in wall thickness, ca. 0.06 mm in length, and ca. 3 – 90 nm in pore diameter).

The phase segregation concept was further investigated in the following chapter, C₆F₆ vapor is employed to react with CaC₂ and Mg₃N₂ to grow CaF₂/*a*-C and Mg₂F₂/*a*-C core/shell nanowires (tens of micrometers in length, tens to hundreds of nanometers in wire diameter, and tens of nanometers in core diameter), respectively, in high yields. The growth mechanism is proposed to proceed via a reaction at the interface of the vapor and solid reactant.

Two examples were used to support this idea: graphite and silicon. Porous, fibrous and planar graphite materials were synthesized by reacting CaC_2 with vapors of C_xCl_y (C_xCl_y : CCl_4 , C_2Cl_4 , C_4Cl_6 and C_5Cl_6). The morphology can be adjusted by varying the reaction temperatures. Porous carbon was obtained at low reaction temperatures, 973 - 1023 K. Fibrous carbon and planar carbon were synthesized at medium reaction temperatures, 1073 - 1123 K and at high reaction temperatures, 1123 - 1223 K respectively. Phase segregation of the products CaCl_2 and carbon formed at the vapor-solid reaction interface affects the morphology greatly. Besides, single crystalline silicon showing fertile morphologies is prepared via vapor-solid reaction growth (VSRG) employing SiCl_4 to react with alkaline earth metal silicides M_xSi_y (M_xSi_y : Mg_2Si and CaSi_2) at 1023 - 1223 K. The other ionic salt product MCl_2 crystallizes into a segregated phase and shapes the silicon into various structures depending on the reaction temperature and the Si/MCl_2 molar volume ratio. The morphology includes such as clustered-particle (1023 K, $\text{Si}/\text{MgCl}_2 = 0.29$), porous (1023 K, $\text{Si}/\text{CaCl}_2 = 0.58$), wire-like (1073 K, $\text{Si}/\text{MCl}_2 = 0.29$ or 0.58), coral-like (1123 K, $\text{Si}/\text{MCl}_2 = 0.29$ or 0.58), lamellar or flake-like (1173 K, $\text{Si}/\text{MCl}_2 = 0.29$ or 0.58).

Finally, further evidences are supported the phase segregation idea and the self-templates of different salts effect. These reactions were carried out by using identical experiment apparatus. First, Mg metal was reacted with vapor of C_4Cl_6 at elevated temperatures 1123 - 1223 K. The product exhibits coral-like structure at 1123 K, and uniform core-shell particles were synthesized at 1173 K. The chief tubes structure were prepared at 1223 K. Second, C_6F_6 was reacted with Na at 423 K in Pyrex tube sealed under vacuum. The tubes structure with diameter 80 - 150 nm was synthesized. Third, the products were prepared from CaC_2 and Br_2 . The nanoparticles were observed at 1023 K, and the lamellar plates were formed at 1223 K. Final, the similar result was performed from CaC_2 and I_2 . The nanoparticles were obtained at 1023 K, and the thin lamellar plates were prepared at 1223 K.

相分離輔助之氣固相反應成長與調控奈米結構之形貌


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摘 要

本論文研究提出一個新穎的合成方法，以相分離輔助之氣固相成長反應合成出多樣性的碳、矽奈米材料，其中分別以自生成不同種類的無機鹽類 MX (M = Na, Mg, Ca; X = F, Cl, Br, I) 做為模板，輔助成長並控制奈米材料的形貌。



首先，以六氟苯作為前驅物，與金屬鈉在 623 K 的溫度下反應，合成出具有 3-200 奈米孔徑大小的孔洞性材料，反應的副產物 NaF 做為形成孔洞的模板；進一步升溫使金屬鈉以融熔態流入陽極處裡氧化鋁中，形成一具有反應性的模板與六氟苯反應，於 323-623 K 的反應溫度下，可得到大面積的孔洞性奈米碳管陣列（半徑約 250 奈米，壁厚約 20 奈米，長度約 0.06 厘米，孔洞大小約 3-90 奈米）。

此相分離的概念在接下來的章節中，進一步被證實其可行性，同樣以六氟苯作為前驅物，分別與碳化鈣以及氮化鎂反應生成高產率的氟化鈣-碳、氟化鎂-碳的核-殼奈米線（半徑從數十到一百奈米，長度數十微米，核的半徑為數十奈米）。此反應機制推測是在反應物的氣固相介面進行成長反應。

另兩個例子:石墨與矽，進一步用來支持相分離的理論，以碳化鈣分別與氣態之碳氯化物（四氯化碳、四氯乙烯、六氯-1,3-丁二烯、六氯環戊二烯）反應，合成出孔洞性、纖維狀、片狀的石墨材料。形貌可透過反應溫度進行調控，孔洞性碳材可在較低的反應溫度 973 -1023 K 獲得；纖維狀碳材可以在 1023 -1123 K 得到；片狀碳材在較高的反應溫度 1123-1223 K 獲得，產物氯化鈣與碳產生相分離，發生在氣固反應介面直接影響產物的形貌。此外，以四氯化矽做為前驅物，分別與矽化鎂與矽化鈣進行氣固成長反應，以自生成之無機鹽類氯化鎂和氯化鈣作為模板，可藉由調控不同的反應溫度 1023-1223 K 與產物/鹽類莫耳體積比，生成具多種形貌單晶結構的矽材料。



最後，另四個例子可做為更進一步的證據，用來支持相分離的概念以及不同鹽類做為自身成模板的影響。首先，金屬鎂與氣態前驅物六氯-1,3-丁二烯在 1123-1223 K 的溫度下反應，類似珊瑚結構碳的產物可在 1123 K 的反應溫度下獲得，於 1173 K 的反應溫度可合成均勻的核-殼奈米粒子，在 1223 K 的高溫下反應可製備得到；第二，六氟苯與金屬鈉於低壓下封管在 423 K 下反應，可得到半徑約 80-150 奈米的奈米碳管；最後，利用碳化鈣分別與溴與碘反應，皆可在 1023 K 的反應溫度下獲得碳的奈米粒子，於 1223 K 的溫度下反應製備得到碳的片狀產物。