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Synthesis of carbon nanotubes on graphite substrate through thermal decomposing hydrocarbon

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Abstract: Carbon nanotubes were synthesized by thermal decomposing hydrocarbon gas directly on graphite plate with a layer of nickel (Ni) nanoparticles on its surface in terms of chemical plating technology. Ni nanoparticles were applied as the catalyst for nucleation and growth of carbon nanotubes while hydrocarbon gas was carbon source. The synthesized carbon nanotubes were "multiwall" type and curly in shape with the length of several microns and diameter of dozens nanometers. Method of synthesizing carbon nanotubes is simple, high efficiency, and feasible with low cost for the batch production of carbon nanotubes.

Key words: carbon nanotube; Ni nanoparticles; hydrocarbon; synthesis; catalysis decomposition
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0 Introduction

Since their discovery, carbon nanotubes (CNTs) attracted much attention from scientists in the field of materials, chemistry and physics for their attractive properties.[1-5] CNTs possess many unique properties[6-8], such as high mechanical strength, capillary properties and remarkable surface characteristics and electrical conductivity, suggesting a wide range of potential applications. CNTs were proposed as material for storage of hydrogen, supercapacitors, environmental protection, and environmental protection, etc[3,4,7,9].

Synthesis of CNTs was one of the challenging issues in the new carbon materials field. Several techniques have been developed for CNT growth[1,2,4,6], such as arc discharge, laser vaporization, and catalytic thermal decomposition of hydrocarbons. Catalytic production of CNTs was simpler and more reproducible than other methods[1,4,6]. During these years, decomposition of hydrocarbons became a research focus on growth of CNTs and were obtained by the decomposition of methane, ethylene, benzene, polyethene, etc[1,2,4,6]. There was an abundant supply of hydrocarbons in the world and relatively few means of converting them to more valuable products. Conversion of hydrocarbons attracted more attention all over the world. Synthesis of CNTs on a large scale by the catalytic technique was an attractive and hopefully alternative route. Though there were many factors involved such as temperature, pressure, feedstock gas, reaction time, and flow rate, size of transition metal particles was found to be influential for formation of CNTs[2]. Therefore, it was crucial to select an effective catalyst with the appropriate size of active metal. Several mechanisms was proposed to attempt at explanation of CNT formation and growth by the pyrolysis of hydrocarbons over catalysts[2,4,6].

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Transition metals were excellent catalyst for pyrolysis reactions of hydrocarbon gases. Size of the active transition metal particles can be controlled to some extent by changing preparing conditions. In this work, transition metal nanoparticles as catalyst for CNTs growth was used. The bulk growth of CNTs were obtained by the catalytic decomposition of hydrocarbon gas over Ni nano-particles on graphite plate which were generated by electroless plating process. With this kind of catalyst, some important advantages of preparing nanotubes were obvious. The production efficiency was higher and the reaction temperature was lower compared with other methods [1,4,6]. The diameters of the CNTs were uniform and their purification and separation was easy modulated for reasons that the catalyst was carried on a stable solid mass substrate. The synthesized CNTs were stably fixed on the graphite plate with a high purity, and thus the integration system can be conveniently used in suitable further industrial applications, such as environmental conservation and field of electronic technology, etc.

1 Experimental procedure

A cube thin rectangular graphite plate, with the dimensions of 8 cm × 5 cm × 0.4 cm, was first annealed in air at 600 ℃ for 20 minutes for roughening treatment. Then it was treated by sensitization process. First, it was put in a solution, prepared by mixing 5 g stannous chloride, 500 mL distilled water and 200 mL saturated hydrochloric acid for 1 h under ultrasonication and agitation action. Finally, it was rinsed by distilled water and dried at 85 ℃ for several hours. Then it was treated by activation process: it was put in a solution, prepared by dissolving 100 mg of palladium chloride and 10 mL of saturated hydrochloric acid in 250 mL of distilled water, for 1 h under ultrasonication and agitation action, and then rinsed by distilled water and dried at 85 ℃ for several hours.

The electroless solution contained nickel source, complexant, reductant and buffer additive, as listed in Table 1. After the treatment via roughness-sensitization-activation process, as described in above procedure. The graphite plate was put in 800 mL of electroless solution for two hours under ultrasonication and agitation action, then rinsed by distilled water and dried at 85 ℃ for several hours. Finally, Ni deposited graphite plate was annealed at 920 ℃ under hydrogen gas flux for 3 hours to remove the residual salt compounds.

Table 1 Components of electroless reaction solution and reaction condition

Chemical components	$NiCl_2 \cdot 6H_2O$	$Na_3C_6H_5O_7 \cdot 2H_2O$	$NaH_2PO_2 \cdot 2H_2O$	$PbCl_2$	NH_4Cl	NH_4Cl	Reaction temperature
Concentration /($g \cdot L^{-1}$)	30	100	10	0.08	50	9	90 ℃

The graphite plate deposited with Ni nanoparticles, which acted as the catalyst for decomposition of hydrocarbon gas, was put in the middle of a horizontal furnace, and heated to 680 ℃ under in flowing hydrogen. Then propylene was introduced with a flow rate of 380 mL · min^{-1} and the hydrogen input was reduced to half. The decomposition reaction proceeded for 50 min to complete the creation and growth of CNTs on graphite plate. Then the product, which was the graphite plate carrying CNTs bundles, was cooled to room temperature under flowing nitrogen.

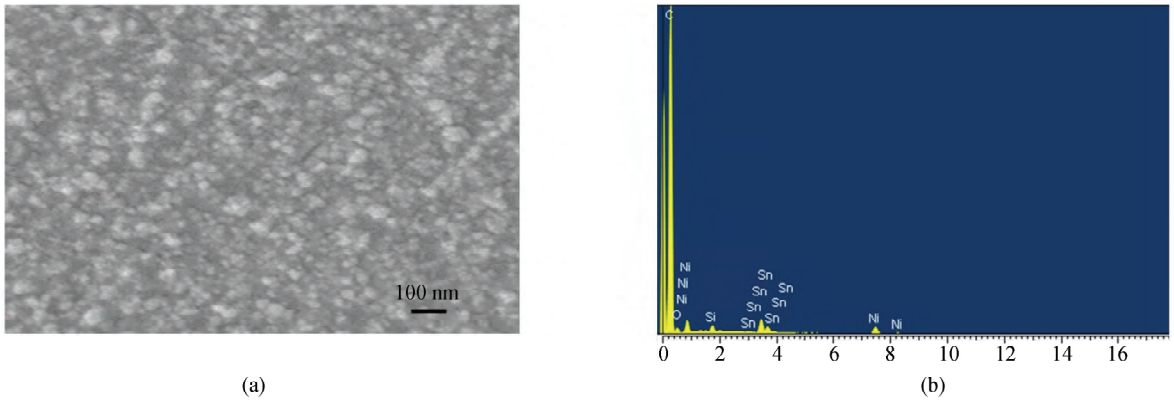
The structure and characteristics were analyzed by transmission electron microscopy (TEM, JEOL-200CX), high resolution transmission electron microscopy (HRTEM, H-9000NAR), field emission scanning electron microscopy (FE-SEM, AMRAY-1910) fitted with an energy dispersive x-ray analytical system for composition analysis (EDX), X-ray diffraction (XRD, Rigaku Dmax γA X-ray diffractometer with Cu-Kα radiation, λ = 0.154 178 nm) fitted with an electron diffraction (ED) system, and RM2000 fiber confocal Raman spectroscope.

2 Results and discussion

2.1 Effect of electroless plating Ni nanoparticles on graphite plate

Graphite plate was first annealed in air for a short time, its surface was oxidized by the air and became rougher. The rough surface increased effective area and afforded the graphitic surface with a higher wettability for forming activated sites. Sensitization and activation of the graphite plate with solution of tin and palladium resulted in the formation of activated sites which could initiate the deposition of Ni nanoparticles, so that

chemical plating generated Ni nanoparticles, which acted as catalyst particles, could be effectively dispersed on it. A SEM image shown in Fig. 1 exhibitd Ni nanoparticles carried on surface of graphite plate after chemical plating. Well dispersed Ni nanoparticles, with the diameters being about 20 nm, on the graphite surface can be observed in the SEM image. The EDX results in Fig. 1(b) showd that the obtained Ni/Graphite sample mainly contained carbon and nickel. A slight content of residual tin and silicon came from pretreatment and electroless processes, and microcontent oxygen might come from air adsorbing.



(a)　　(b)

Fig. 1　SEM image and EPX pattern of Ni nanoparticles carried on the surface of the graphite plate

2.2　State of CNT generated by the decomposition of organic gas

CNTs were prepared by the decomposition of propylene at 600 ℃ to 700 ℃ over nano catalyst coating formed by Ni nanoparticles. 2 g CNTs could be synthesized with action of 150 mg catalyst. The purity of CNTs was approximate to 99.8 percent. ED measurement indicated that the CNTs were multi-walled structure, as presented in Fig. 2 (a). It was found from HRTEM observation that many rope-like structures of with outer diameters ranging from 20 to 30 nm, as shown in HRTEM image of Fig. 2 (b), which was close to the size of the Ni nanoparticles. Some Ni nanoparticles were encapsulated by carbonaceous tubes and some helices, which were also found in the products. HRTEM images confirmed the presence of multi-walled CNTs, which were composed of many cylindrical graphite layers arranging regularly in the inner wall. In addition, it was that some amorphous carbon layers coated the outer periphery of CNTs. Fig. 2 (c) and Fig. 2 (d) respectively showed the characteristic SEM and TEM images of CNTs with crooked and entangled shapes. The length of most CNTs was of the order of micron.

Growth of CNTs during above producing process included the following steps: feed hydrocarbon molecules were adsorbed and decomposed on certain surface-active sites of the catalyst metal particles to form carbon species. Then some of the surface carbon species dissolved into the bulk and diffused through the metal Ni nanoparticles from the front faces, which were the metal-gas interfaces, to the rear faces, which were the metal-CNT interfaces. Finally, carbon species were deposited in the form of CNTs [1,2]. One of the reasons for the curly growth of CNTs might be the roughness of the substrate surface, which could induce an incoherent growth direction. One other possibility was that carbon nanotubes were not crowded enough to have van der Waals effects that made aligned growth of nanotubes possible in the absence of strong electrical field. In addition, some defect structures with pentagons and heptagons might be formed in CNT-walls during the deposition of carbon species. These defect structures could influence the uniform growth and lead to curly shape of CNTs.

2.3　Measurement of crystalline characteristic of the CNTs

XRD was performed on the synthesized CNTs to study their microscopic structure, as shown in Fig. 3. There was a strong and broad peak for turbostratic carbon at 26.48°, giving an interlayer spacing (d002) for the multi-walled CNTs [2,6], slightly larger than that of ideal graphite. In addition, Ni crystallite peaks can be observed at 44.5°, 52.3° and 75.8° due to some Ni crystallite enwrapped by carbon. Fig. 3 also indicated there were a little residual nickel oxide (NiO) component in CNTs, which might be generated by oxidization during annealing process. Fig. 4 showed

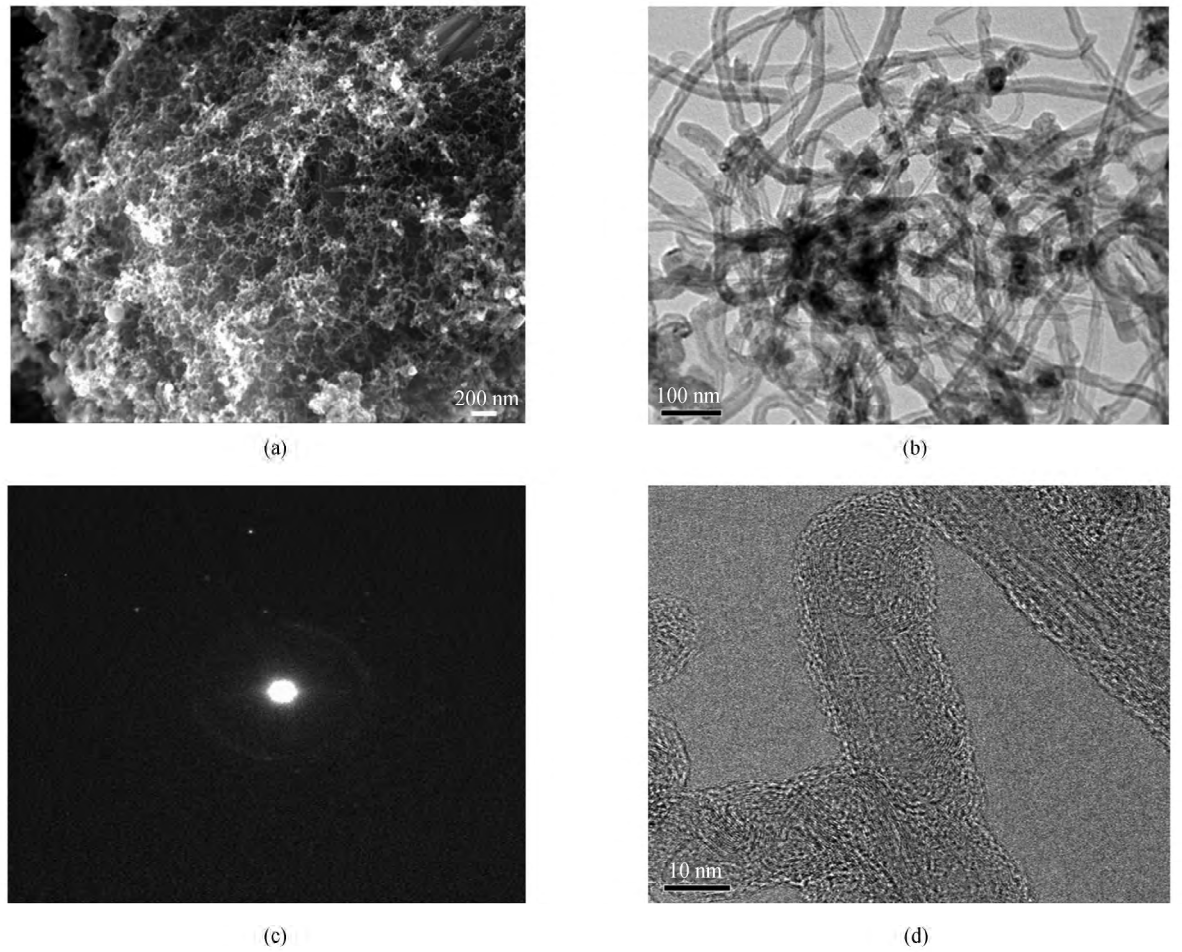


Fig. 2 (a) ED measurement image of synthesized CNTs; (b) HRTEM image of CNTs showing the multi-walled nanotubes composed of well graphitized layers usually covered with amorphous carbon on the outer periphery; (c) SEM image of the CNTs grown on graphite substrate; (d) TEM image of the synthesized CNTs

the Raman shift spectrum of the CNTs, which was measured at room temperature with a frequency range 400 ~ 3 600 cm^{-1}. Two sharp peaks were present at 1 578 (G peak) and 1 352 (D peak) cm^{-1}. They corresponded to the characteristic peak of the graphite structure with a small basal domain size [10-15]. Moreover, there was also a weaker peak around 2 645 cm^{-1} which indicated 2D or D* peak which was not exhibited in this chart. These features, including the wavenumbers and relative integrated intensities, were close to those for multi-walled carbon nanotubes [2, 6, 10-16]. These features also revealed that the grahitization degree of the outer CNT walls was low. This was in agreement with the HRTEM results.

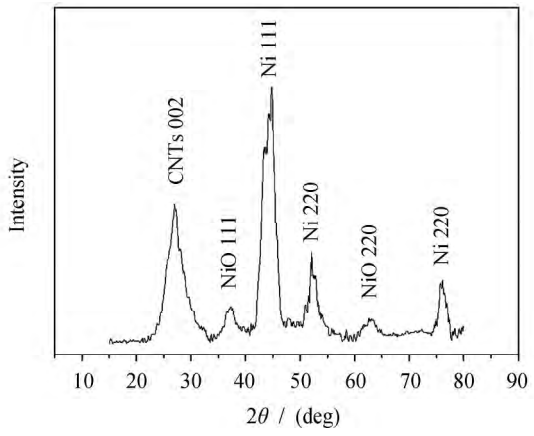


Fig. 3 XRD pattern of the synthesized CNTs

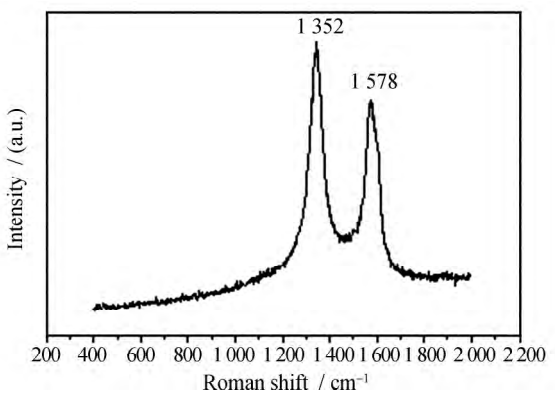


Fig. 4 Raman spectrum of synthesized CNTs

3 Conclusions

Ni nanoparticles supported by graphite plates were used, which are low-priced materials, as a catalyst for the synthesis of multiwalled CNTs, with excellent activity. The graphite substrate showed high thermal and chemical stabilities, and was beneficial to the stability of the catalyst phase and the synthesized CNTs. The nano Ni catalyst was deposited on the graphite surface by chemical plating, sizes and the density of the nucleation centers on the substrate could be well controlled, thus it was beneficial to the synthesis of CNTs during hydrocarbon gas pyrolysis. The reaction temperature of synthesizing CNTs through hydrocarbon gas pyrolysis was relatively lower among the methods of producing CNTs. The synthesized multi-walled CNTs were curly in shape with basically uniform diameters. They had high purity and were easily removed from the substrate, resulting in greatly simplified purification treatment in the latter time, especially avoiding the damage caused by the oxidation treatment. This production of CNTs was high efficiency, large yield and low cost, which was suitable for the batch production process. Moreover, the integration system of CNTs/Graphite plate can be conveniently used in suitable further industrial applications, such as environmental conservation and field of electronic technology, etc.

References:

[1] See C H, Harris A T. A review of carbon nanotube synthesis via fluidized-Bed chemical vapor deposition [J]. Industrial & Engineering Chemistry Research, 2007, 46 (4): 997-1012.

[2] Yadav M D, Dasgupta K, Patwardhan A W, et al. High performance fibers from carbon nanotubes: Synthesis, characterization, and applications in composites-a review [J]. Industrial & Engineering Chemistry Research, 2017, 56 (44): 12407-12437.

[3] Rao R, Pint C L, Islam A E, et al. Carbon nanotubes and related nanomaterials: Critical advances and challenges for synthesis toward mainstream commercial applications [J]. ACS Nano, 2018, 12 (12): 11756-11784.

[4] Maoshuai He M, Zhang S C, Zhang J. Horizontal single-walled carbon nanotube arrays: Controlled synthesis, characterizations, and applications [J]. Chemical Reviews, 2020, 120 (22): 12592-12684.

[5] Zhang S L, Ma Y, Suresh L, et al. Carbon nanotube reinforced strong carbon matrix composites [J]. ACS Nano, 2020, 14 (8): 9282-9319.

[6] Yang F, Wang M, Zhang D Q, et al. Chirality pure carbon nanotubes: Growth, sorting, and characterization [J]. Chemical Reviews, 2020, 120 (5): 2693-2758.

[7] Wu Y Z, Zhao X W, Shang Y Y, et al. Application-driven carbon nanotube functional materials [J]. ACS Nano, 2021, 15, 5, 7946-7974.

[8] Contreras-Torres F F, Salas-Trevino D, Soto-Domínguez A, et al. Carbon nanotubes in tumor-targeted chemotherapeutic formulations: A review of opportunities and challenges [J]. ACS Applied Nano Materials, 2022, 5 (7): 8649-8679.

[9] Kohls A, Ditty M M, Dehghandehnavi F, et al. Vertically aligned carbon nanotubes as a unique material for biomedical applications [J]. ACS Applied Materials & Interfaces, 2022, 14 (5): 6287-6306.

[10] Saini D, Gunture T, Kaushik J, et al. Carbon nanomaterials derived from black carbon soot: A review of materials and applications [J]. ACS Applied Nano Materials, 2021, 4 (12): 12825-12844.

[11] Chen Z, Lan Y H, Hong Y B, et al. Review of 2D graphitic carbon nitride-based membranes: Principles, syntheses, and applications [J]. ACS Applied Nano Materials, 2022, 5 (9): 12343-12365.

[12] Weldekidan H, Mohanty A K, Misra M, et al. Upcycling of plastic wastes and biomass for sustainable graphitic carbon production: A critical review [J]. ACS Environmental Au, 2022, 2 (6): 510-522.

[13] Weight B M, Zheng M, Tretiak S. Signatures of chemical dopants in simulated resonance raman spectroscopy of carboy nanotubes [J]. The Journal of Physical Chemistry Letters, 2023, 14(5): 1182-1191.

[14] Qu M H, Pan M L, Tian K S, et al. Nanocomposites of synthesizing cadmium sulfide/carbon nanotubes through solution reactiong [J]. Journal of Engineering of Heilongjiang University, 2022, 13(2): 42-47.

[15] Zhang X M, Zhang W, Li W. Synthesis and application of carbon-based hollow nanomaterials [J]. Journal of Engineering of Heilongjiang Univesity, 2021, 4 (2): 110-125.

[16] Sudakov I, Goovaerts E, Wenseleers W, et al. Chiality dependence of triplet excitions in (6, 5) and (7, 5) single-wall carbon nanotubes revealed by optically detected magnetic resonance [J]. ACS Nano, 2023, 17(3): 2190-2204.

热解碳氢化合物技术制备生长于石墨基板表面的碳纳米管的研究

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摘 要： 研究开发了有效的合成制备碳纳米管的技术。通过在石墨基板上化学沉积镍纳米粒子。在热解炉中，通以碳氢化合物气体作为碳来源物，以镍纳米粒子作为催化剂基种，在高温作用下，镍催化碳氢化合物热裂解沉积出碳元素，在镍纳米粒子上生长出碳纳米管。制备出植于石墨片基板上的多壁碳纳米管体系，碳纳米管长度一般在数微米以上，直径在20～30 nm。该技术可高效，便利且低成本制备出大批量的承载于石墨片的碳纳米管，便于后续应用于环境及电子领域。

关键词： 碳纳米管；纳米镍；碳氢化合物；合成；催化裂解

Синтез углеродных нанотрубок на графитовой матрице по технологии теплоразложения углеводородов

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Реферат: Углеродные нанотрубки были синтезированы из термически разлагающегося углеводородного газа непосредственно на поверхности графитовой пластины со слоем наночастиц никеля (Ni)，которые были получены с помощью технологии химических покрытий. В тех случаях，когда углеводородные газы являются источником углерода，нанопикель используется в качестве катализатора образования и роста углеродных нанотрубок. Синтетические углеродные нанотрубки представляют собой многостенные типы，закрученные по форме，длиной в несколько микрон и диаметром в несколько десятков нанометров. Этот метод синтеза углеродных нанотрубок прост и эффективен，а также подходит для недорогого массового производства углеродных нанотрубок.

Ключевые слова: углеродные нанотрубки；нано-никель；углеводороды；синтез；каталитическое разложение