

Controlled growth of Ni particles on carbon nanotubes for fabrication of carbon nanotubes

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Abstract

The concentrations of HCHO and $C_4H_4O_6KNa \cdot 4H_2O$ were changed to control the Ni content of the Ni/CNT when the carbon nanotubes boiled in dilute nitric acid solution were immersed in Ni electroless plating bath without activating and sensitizing. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) analysis confirmed that the maximum content of Ni in the Ni/CNT was about 4.69 at.% and the maximum size of the Ni particles deposited on carbon nanotubes about 65 nm. Furthermore, the carbon nanotubes produced with the Ni/CNT were of high quality.

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1. Introduction

In 1976, the group of Endo first synthesized carbon “filaments” through the pyrolysis of mixtures of benzene and hydrogen at 1100 °C [1]. After this, Iijima fabricated carbon nanotubes (CNTs) by arc-discharge in 1991 [2]. In recent years, carbon nanotubes have attracted tremendous attention from scientists in the fields of materials, chemistry and physics because of their unique structure, properties and potential applications [3,4]. Because large-scale synthesis is fundamental for their application, a variety of synthesis methods have been developed. One of these is the catalytic decomposition of hydrocarbon gases with the aid of highly dispersed transition metal elements such as Fe-, Co-, and Ni-supported by many kinds of substrate [5–7], to yield large quantities. However, the removal of some substrates such as SiO_2 , Al_2O_3 may be quite difficult before they can be used. Cylindrically layered and hollow tubular nano-structures with their high

thermal and chemical stability make it possible for carbon nanotubes to function as supports for preparing nano-sized metal and metal oxide particle catalysts [8,9]. And there is no need to remove the substrates. Rh/P [9], Pt- WO_3 [10] and Pt [11] catalysts supported on carbon nanotubes have been studied and show exceptional properties. The deposition of nickel on carbon nanotubes has also been reported [12–14]. In this paper, carbon nanotubes boiled with dilute nitric acid solution were directly immersed in an electroless plating bath, without activating and sensitizing, for the deposition of nickel particles. We controlled the Ni contents and Ni particle size through changing the concentrations of HCHO and $C_4H_4O_6KNa \cdot 4H_2O$ (Rochelle salt crystal). And the Ni particles supported by the carbon nanotubes were used to prepare new carbon nanotubes.

2. Experimental

The carbon nanotubes used as the support were fabricated by pyrolysis of xylene at 1100 °C in a quartz tube furnace and boiled in dilute nitric acid solution for 6 h. The mixed

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solution was filtered with a ceramic filter and washed with distilled water until neutral, and then dried. This support (0.50 g) was dispersed into 10 ml ethanol (99.7%) and the suspension stirred in the Ni bath of composition $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 10 g/l; $\text{C}_4\text{H}_4\text{O}_6\text{KNa} \cdot 4\text{H}_2\text{O}$, 0–50 g/l; NaOH, 5 g/l; HCHO (38 wt.%), 5–20 ml/l. After 15 min the mixture was filtered through a ceramic filter, washed several times with distilled water and dried in air at 80 °C. Thus, nano-sized particles supported on CNTs were obtained. The concentrations of HCHO and $\text{C}_4\text{H}_4\text{O}_6\text{KNa} \cdot 4\text{H}_2\text{O}$ in the Ni bath were varied to study their effects on the rate of nickel deposition.

A known amount (0.05 g) of catalyst precursor was spread in a ceramic boat, and then placed in the reaction region of a horizontal CVD quartz tube furnace, which was heated to 580 °C under nitrogen. The nitrogen was then substituted by hydrogen at a flow rate of 200 ml/min for 30 min, and subsequently the catalyst was reduced. After this the reaction region was heated to 700 °C in hydrogen and ethyne introduced with a flow rate of 100 ml/min. The catalytic decomposition reaction proceeded for 30 min. The products were then cooled to room temperature under nitrogen and the boat with the reaction products was taken out. The black powder produced was dispersed onto a supporting membrane for transmission electron microscopy. For comparison, unsupported Ni nano-particles (average diameter 40 nm and purity 99 wt.%), unsupported Co nano-particles (average diameter 50 nm and purity 99.5 wt.%), and SiO_2 -supported Ni catalyst (Ni particle 25 nm and Ni on the SiO_2 about 20 wt.%) were also used for the synthesis of carbon nanotubes using the same procedure.

For the removal of the amorphous carbon and metallic catalyst in the product, the raw soot produced was first suspended in 0.21 of 4 M diluted nitric acid and refluxed at 117 °C for 2 h. Then the solution was filtered and rinsed with pure water up to neutral and dried. Finally pure carbon nanotubes were obtained.

Transmission electron microscopy (TEM) was used to observe the microstructures and morphology of the carbon nanotubes and the Ni particles and EDX used to determine the elemental compositions of the Ni particles on the carbon nanotubes.

3. Results and discussion

Fig. 1 shows micrographs of the original carbon nanotubes and the nickel-deposited carbon tubes. From Fig. 1a, it can be seen that the original carbon nanotubes are bare multi-wall carbon nanotubes with diameters ranging from 94 nm to 106 nm. The inset of Fig. 1a is the high magnification micrograph of the original carbon nanotubes, which shows that they are hollow and tubular structures. However, after the carbon nanotubes were introduced into the Ni bath and reacted with the Ni solution for 15 min, a number of nano-particles homogeneously deposited on the surface of the carbon nanotubes were observed with a size distribution centered at around 40–65 nm diameter (Fig. 1b), and the distance between two particles was 200 and 300 nm.

The EDX analysis of the original carbon nanotubes showed only C in the original nanotubes. After they had been in the Ni bath for 15 min, Ni, C and O peaks, along with small amounts of K and Na were observed (Ni, 4.69 at.%; C, 74.86 at.%; O, 17.15 at.%; Na, 1.67 at.%; K, 1.64 at.%). The results of the EDX analysis indicated that the maximum relative content of Ni in the CNT-supported Ni catalyst region was about 4.69 at.%. Combining these results with electron microscopy analysis, it is reasonable to conclude that Ni catalyst particles had been successfully obtained on the carbon nanotube substrate.

The results of changing the concentrations of HCHO and $\text{C}_4\text{H}_4\text{O}_6\text{KNa} \cdot 4\text{H}_2\text{O}$ in the Ni bath are shown in Fig. 2a and b, respectively. Fig. 2a shows that the rate of Ni deposition increases greatly with increasing HCHO concentration for values less than 10 ml/l. For higher concentrations it increases more slowly. From Fig. 2b, it is seen that the rate of Ni deposition gradually declines with increase of the $\text{C}_4\text{H}_4\text{O}_6\text{KNa} \cdot 4\text{H}_2\text{O}$ concentration between 25 g/l and 45 g/l. Above this value the rate of Ni deposition decreases greatly.

These results show that carbon nanotube-supported Ni was prepared successfully when the carbon nanotube substrates were boiled in dilute nitric acid without sensitizing and activating and directly immersed in the Ni bath. It is possible that acidic oxidation not only broke the nanotubes, but also introduced a large number of functional groups, such as

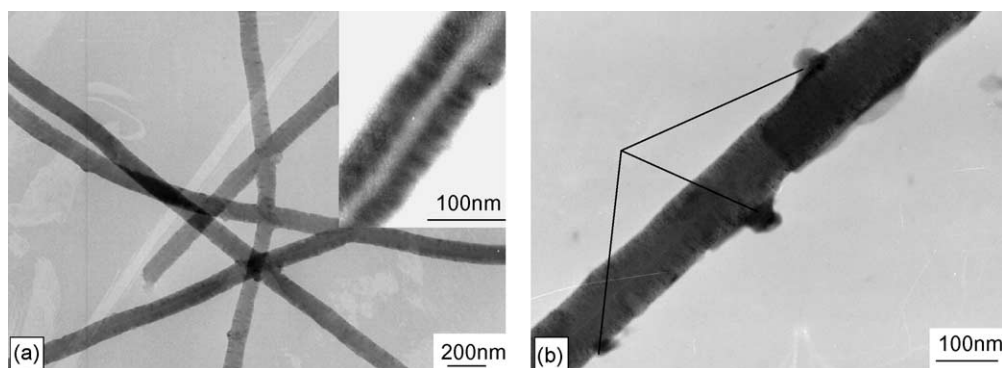


Fig. 1. Micrographs of precursor CNTs and Ni-deposited carbon tubes: (a) original carbon nanotubes; (b) Ni particles deposited on CNTs.

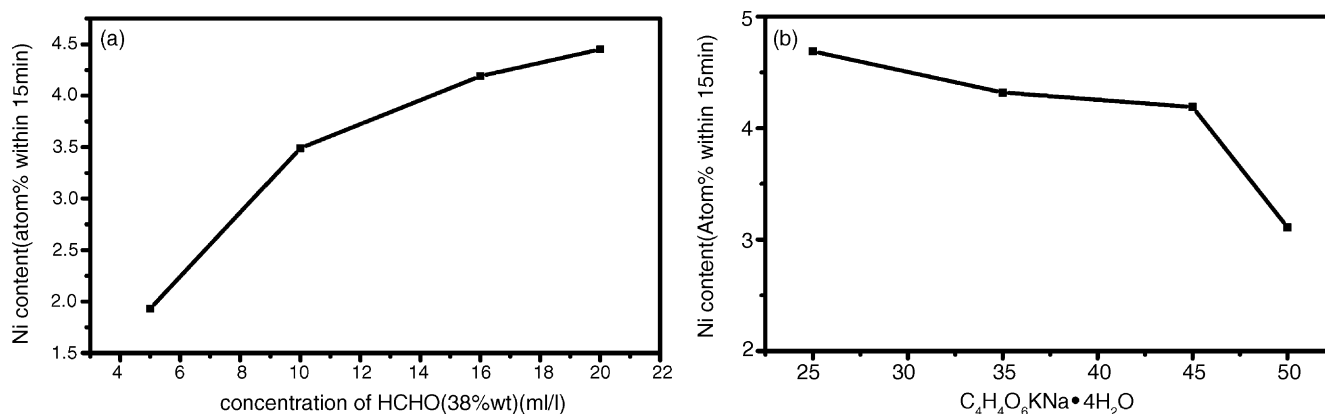


Fig. 2. (a) Influence of HCHO on the rate of Ni deposition on CNTs; (b) influence of $C_4H_4O_6KNa \cdot 4H_2O$ on the rate of Ni deposition on CNTs.

hydroxyl ($-OH$), carboxyl ($-COOH$) and carbonyl ($>C=O$) [13,15]. These functional groups decreased the hydrophobicity of the carbon nanotubes and made the surface more accessible to the aqueous solution of the metal precursors or deposits [16]. During the reactions, Ni^{2+} ions were reduced, conglomerated and formed Ni nano-particles on the carbon nanotubes. TEM and EDX analysis confirmed that no nickel particles were found on the surface of CNTs which had not been boiled in nitric acid when they were dipped into the Ni bath. This suggested that boiling with oxidizing acids was a critical factor for the deposition of the Ni particles. These results are consistent with those obtained by Li et al. [15].

The results show that the optimum range of HCHO concentrations is from 10 ml/l to 20 ml/l. The importance of

$C_4H_4O_6KNa \cdot 4H_2O$ in the Ni bath for Ni deposition on carbon nanotubes was because the rate of Ni deposition increased more rapidly as the concentration of Ni^{2+} increased. If the concentration of Ni^{2+} is too high, nickel deposition would stop because a subsidiary reaction between Ni^{2+} ions takes place. The addition of $C_4H_4O_6KNa \cdot 4H_2O$ could chelate Ni^{2+} and keep the concentration of the free Ni^{2+} low thus preventing the subsidiary reaction of Ni^{2+} ions. When the concentration of $C_4H_4O_6KNa \cdot 4H_2O$ was more than 45 g/l, the rate of Ni deposition decreased greatly. This is because the increasing $C_4H_4O_6KNa \cdot 4H_2O$ concentration chelated more Ni^{2+} so that the concentration of free Ni^{2+} in the solution decreases greatly. Therefore, an appropriate amount of $C_4H_4O_6KNa \cdot 4H_2O$ (25–45 g/l) is beneficial for the reduction of Ni^{2+} and hence Ni deposition.

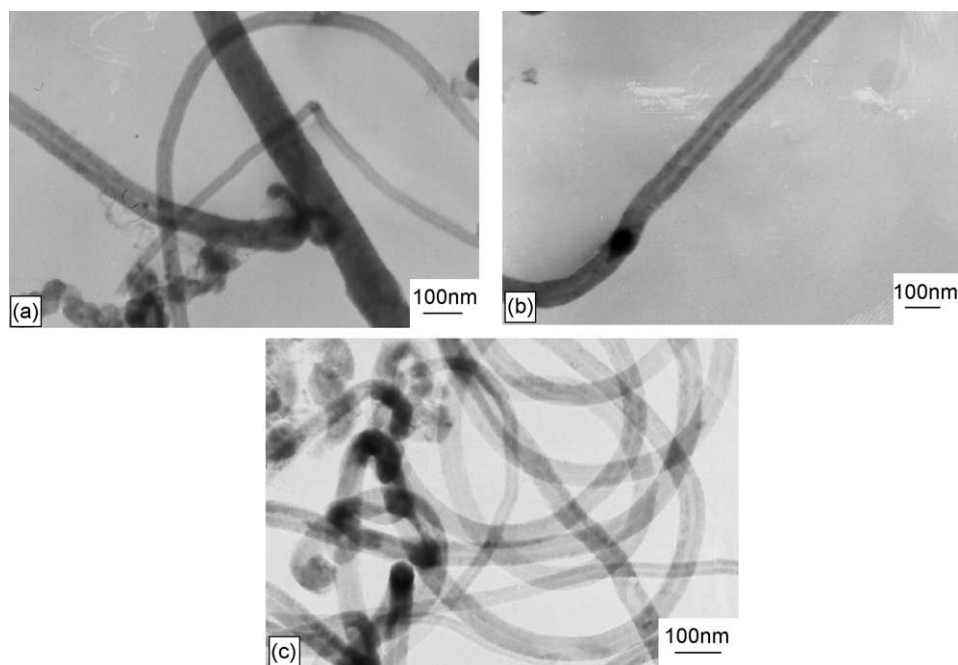


Fig. 3. Transmission electron micrographs of the CNT products produced by carbon nanotube-supported Ni catalyst. (a) Carbon nanotube products on a precursor carbon fiber; (b) carbon nanotube products with encapsulated Ni catalyst particles; (c) curved carbon nanotube products.

Because the carbon nanotube-supported nickel was heat treated in air, the Ni particles were oxidized, and oxygen was introduced to the catalyst. It is not difficult for oxygen to be eliminated in hydrogen at high temperature. The Na and K elements derived from $C_4H_4O_6KNa \cdot 4H_2O$ and NaOH because the functional groups on the surface of the nanotubes promoted the attaching of Na^+ and K^+ ions. Furthermore, the nanometer-sized tubes cannot simply be dipped in and out of the electroless plating solution and a long period of time is needed to spend in filtering and rinsing the solution. Therefore, the removal of the Na^+ and K^+ ions is very difficult and the negligible amount of K and Na elements still remained on the surface of the tubes even if the Ni/CNT catalyst were rinsed many times.

The Ni/CNT catalyst with 4.19 at.% nickel was used to synthesize new carbon nanotubes and the raw products observed by TEM (Fig. 3). The micrographs show that most of the pyrolysis products (about 95 wt.% in total) around the carbon nanotube supports are multi-walled CNTs, either straight or curved, with outer and inner diameters ranging from 30 nm to 70 nm and 10 nm to 20 nm, respectively and length up to several tens of micrometers. The other product is mainly amorphous carbon. Compared with the size distribution of the originally deposited Ni particles, the outer diameters of the carbon nanotubes produced shows a wider distribution at the extremes, which demonstrates that the nickel particles govern nanotube diameter [17]. From Fig. 3a, the new tubes seemed to grow directly from the surface of carbon nanotube substrates. In addition, Fig. 3c shows that some Ni catalyst particles were encapsulated in the middle of CNTs.

The successful preparation of carbon nanotubes indicates that the carbon nanotube-supported Ni nano-particle is indeed an effective catalyst for the pyrolysis of hydrocarbon. The catalyst particles encapsulated in the middle of the CNTs, indicate that the Ni particles had participated in the pyrolysis reaction, including the absorption, diffusion and separation of the active carbon atom in the Ni particles during the reaction at 700 °C.

For comparison, the same amount (50 mg) of unsupported Ni nano-powder and Co nano-powder and SiO_2 -supported Ni catalyst were used for the synthesis of carbon nanotubes using the same procedure. The results show that only carbon nano-fibers were synthesized for unsupported Ni and Co nano-powder. The weight of carbon nano-fibers produced was 0.21 g for Ni nano-powder, 0.23 g for pure Co nano-powder and 0.24 g for SiO_2 -supported Ni catalyst, respectively (Fig. 4). For the carbon nanotube-supported Ni catalyst, the weight of carbon nanotube produced reached 0.57 g. Furthermore, after purification by nitric acid we found that the percentage purity of the products were about 88 wt.% for Ni powder, 85 wt.% for Co powder, 90 wt.% (containing SiO_2) for Ni/ SiO_2 and 95 wt.% for Ni/CNT, respectively. Therefore, carbon nanotube-supported Ni can be used to synthesize CNTs with high yield and high purity, indicating their excellent catalytic activity in the synthesis of CNTs.

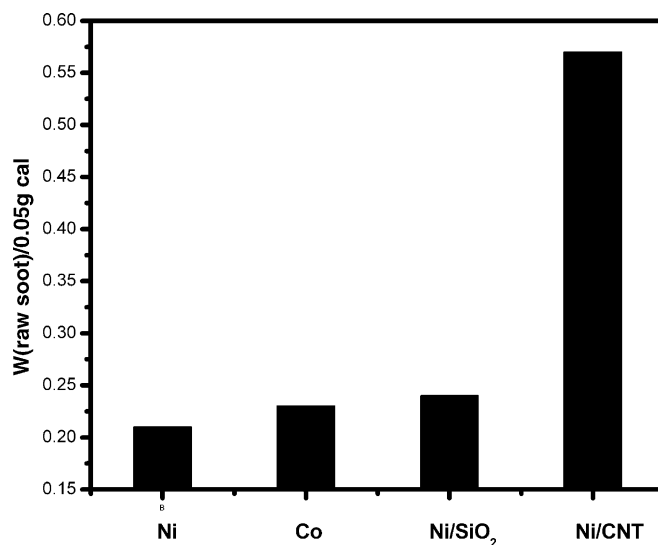


Fig. 4. Weight of carbon nanotube powder for different catalyst with the same amount during the same procedure.

It was reported [12] that maintaining sufficient small Ni particles is necessary for the synthesis of CNTs, and large active phase particles could catalyze carbon fibers during the pyrolysis of hydrocarbon gases. The interaction between CNTs and Ni particles increased the stability of the Ni particles. In addition, the presence of a small amount of K, Na might be beneficial for the stability of the Ni particles [18]. In contrast, pure unsupported Ni, Co nano-particles were less stable due to their growth at high temperature and lack of interaction between the particles and the CNTs, resulting in only nano-fibers being synthesized when they were used as the catalyst precursor [12]. The productivity of SiO_2 -supported Ni was also less than that of CNTs-supported Ni. In summary, CNT-supported Ni was an effective catalyst in the preparation of carbon nanotubes and its future use could be exploited.

4. Conclusions

The relative content of Ni in the Ni/CNT increases with increasing concentration of HCHO and declined with increase of the $C_4H_4O_6KNa \cdot 4H_2O$ concentration. Therefore, we can change the concentrations of HCHO and $C_4H_4O_6KNa \cdot 4H_2O$ to easily control the Ni content and the Ni particle size of Ni/CNT. And when the catalyst Ni/CNT with 4.19 at.% nickel was used to synthesize carbon nanotubes, the carbon nanotubes produced were high quality.

Acknowledgements

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