



# High yield synthesis of helical carbon nanotubes catalyzed by porous precursor with terrace morphology



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## ABSTRACT

Superfine and uniformly dispersed catalyst precursor was obtained through a novel precipitation/sol-gel/reduction technique, which had multi-scale multi-layered porous structures with large surface areas. Helical carbon nanotubes (HCNTs) with good purity were then synthesized through chemical vapor deposition (CVD) by acetylene decomposition over the as-obtained precursor. The yield of the HCNTs was nearly three times of the highest value ever reported. The high yield and good quality of the HCNTs was attributed to the peculiar structures of the precursor that could decompose into catalyst with large surface area and high activity. Furthermore, the structures and catalytic efficiencies of the catalyst precursors prepared through other two different approaches were also investigated to reveal the relationship between the structures of the precursor and their capability differences in catalyzing the HCNTs growth.

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## 1. Introduction

Discovered in 1994 [1], helical carbon nanotubes (HCNTs) have attracted continuous and wide attention [2–5] due to their unique three dimensional helical structures [6], special physical [7,8] and/or chemical [9] properties and a number of potential applications [10–12]. Extensive research has been done on the synthesis and mass-production of HCNTs. However, an efficient synthesis of high purity HCNTs still remains as a challenge [13–15].

In general, the morphology and the quality of helical carbon species depend on the selection of catalyst, carbon source, reaction temperature, gas-flow rate, feedstock pressure, etc. [16]. Certain preparation methods, such as arc discharge and laser vaporization, which are usually used in the synthesis of CNTs, are not suitable for the preparation of HCNTs. Because the high temperature to vaporize solid graphite and the high mobility of carbon atoms lead to the formation of only straight CNTs [15]. Liu et al. have reported that the delivery patterns of carbon source gases and substrates species play important roles in controlling the morphology HCNTs [17]. Tang et al. performed systematic experiments to investigate the specific effect of catalytic particle size (CPS) on the selective growth of HCNTs. It showed that the CPS is of great importance in the selectivity to HCNTs and morphology of the carbon

products [18]. Other factors that may influence the morphologies (straight or helical) of carbon nano-materials include catalyst morphology [19,5] and certain external stresses, such as chiral, soft templates and applied magnetic fields [20–22].

HCNTs are usually synthesized through catalytic chemical vapor decomposition (CVD) of carbon source substances such as acetylene, pyridine and toluene over the catalysts of transition metals and their alloys at the reaction temperature over 700 °C [2,23,4]. Tang et al. reported that catalyst played an important role on the selectivity growth of HCNTs, such as on the morphology, yield, mobility of carbon atoms, and the purity of carbon products [18]. Compared to the direct usage of catalyst for the synthesis of HCNTs, catalyst precursors are more preferable due to their higher reactivity for CVD process originated from fresh interfaces through gas induction on catalyst precursors [24,10]. Meanwhile, both the species and synthesis methods of catalyst precursor could influence the yield of the final product. Transitional metal Ni and Fe are two kinds of catalyst frequently used for the synthesis of HCNTs synthesis. The Ni-based catalyst precursors are more efficient in the synthesis of HCNTs.

The synthesis method of catalyst precursor has significant influence on the yield of HCNTs. Usually, the yield of HCNTs is defined as  $\text{yield} = \frac{m_{\text{total}} - m_{\text{catalyst}}}{m_{\text{catalyst}}}$ . The ratio of g-HCNTs/g-catalyst is used as the unit for yield, which means the production of HCNTs (gram) per gram catalyst. Tang et al. obtained the crystalline HCNTs in the pyrolysis of acetylene at 450 °C over Fe nanoparticles generated by means of a sol-gel/reduction

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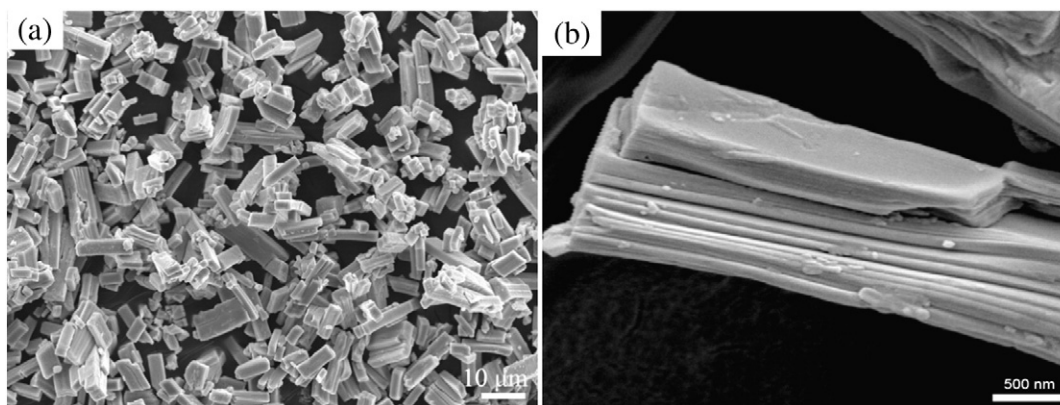


Fig. 1. a and b FESEM images of tartrate nickel with different magnifications.

technique, with a yield of about 10.80 g-HCNTs/g-catalyst [25]. Qi et al. prepared Fe nanoparticles adopting a combined co-precipitation/reduction method for synthesizing high purity HCNTs by acetylene decomposition at 450 °C and obtained a yield of about 74.74 g-HCNTs/g-catalyst in a run of 6 h [16]. Wen et al. prepared HCNTs using Ni nanoparticles as the catalyst generated by means of a combined sol-gel/reduction method and reported that the yield was up to 93.33 g-HCNTs/g-catalyst [4].

In this study, a Ni-based catalyst precursor with small size and uniform dispersion was prepared by a novel precipitation/sol-gel/reduction technique. The as-prepared precursor was then applied to the CVD process and HCNTs with regular morphology and high yield were obtained. The comparison among catalyst precursors through different methods was carried out and the mechanism for the high yield of HCNTs was examined.

## 2. Experimental

### 2.1. Synthesis of catalyst precursor

50 mL  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solution (0.1 M) was slowly dropped into 50 mL  $\text{C}_4\text{H}_4\text{O}_6\text{KNa}$  aqueous solution (0.1 M) with continuous stirring for 20 min. After the filtration and drying for 12 h, the precipitate and citric acid were mixed (stirring for 6 h) in 100 mL absolute ethanol for the generation of sol. The xerogel obtained after removal of ethanol was then heated in air at 350 °C for 5 h to prepare the catalyst precursor.

### 2.2. Synthesis of HCNTs

The as-prepared catalyst precursors in the form of powder (0.01 g to generate 0.00786 g of Ni after reduction) were dispersed on a quartz boat. They were well distributed inside a quartz tube (6 cm in diameter

and 120 cm in length, equipped with temperature sensor and gas-flow controls) located in a tubular furnace. After the catalyst precursor reducing under  $\text{H}_2$  at 350 °C for 1 h, acetylene was introduced into the reaction system at 475 °C for additional 1 h at an atmospheric pressure. The final product was collected after cooling down to room temperature.

### 2.3. Materials characterization

The as-obtained catalyst precursor and HCNTs were examined on a Philips X'Pert Pro X-30 X-ray powder diffractometer at RT for the crystal-line structural characterization using  $\text{Cu K}\alpha$  radiation. Raman spectroscopic investigations were performed on a Renishaw Invia instrument with 514 nm laser excitation. Thermo gravimetric analysis (TGA) was performed with TG 209 F1 in air with a heating rate of 10 °C/min from RT to 800 °C. The morphologies of the samples were examined over field-emission scanning electron microscope (FESEM, JSM-7500 F), transmission electron microscope (TEM, JEM-4000EX) and high-resolution TEM (HRTEM, JEM-4000EX).

## 3. Results and discussion

### 3.1. Characterization of catalyst precursor

A green powder with multi-layered brick-like morphology was obtained after the filtration of the precipitate. As shown in Fig. 1, the as-prepared precipitate was evenly dispersed with similar size. Fig. 1(b) displays the multi-layered structure of one brick. The uniform structure of the precipitate could offer similar reactivity in the sol-gel process and obtain better dispersion of the catalyst precursor.

Sol-gel method is usually used for the preparation of nanomaterials by which uniformity at molecular level can be obtained within a short time. In this study, a porous catalyst precursor with complicated terrace morphology was obtained. Fig. 2a shows the as-prepared catalyst

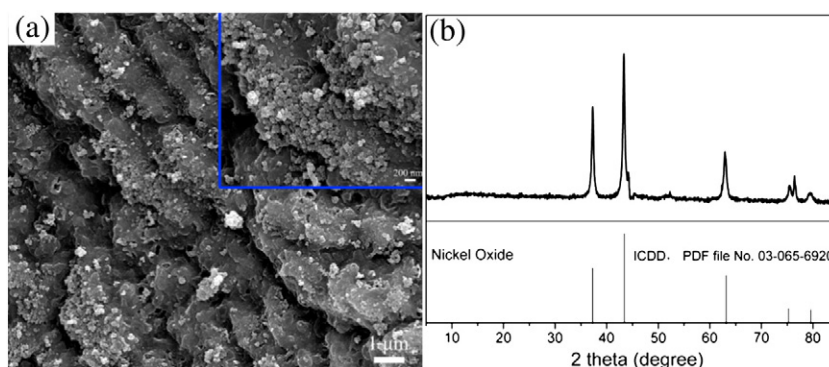


Fig. 2. a FESEM images and b XRD pattern of catalyst precursor (NiO), the inset of a is the partial enlarged view.

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