Effect of citric acid to carbon nanotube growth

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Abstract. Carbon nanotube (CNT) was synthesized by catalytic chemical vapor deposition using LaNiO$_3$ as the catalyst precursor, where LaNiO$_3$ was prepared by citric acid complexometry. The results show that the catalyst precursors prepared with different citric acid dosages could all grow CNT, but the CNT yield and patterns obtained with these catalyst precursors were different. Different citric acid dosages could result in different (111) crystal face contents of Ni particle in the catalysts (the products obtained from catalyst precursors reduced by the H$_2$) and thus affected the CNT yield and patterns, which is the result of the complexation between the carboxyl (came from citric acid) and metal ions in lower temperature ($80^\circ$C) during the catalyst precursor preparation.

1. Introduction
Carbon nanotube (CNT) has come to be one of the most actively studied materials for their novel nanometer-hollow-carbon-tube structure and extraordinary physical properties since it was rediscovered by Iijima in 1991 [1, 2]. Based on its excellent properties, CNT could use in many field. Many methods were found to prepare CNT, amongst which the catalytic chemical vapor deposition (CCVD) appeared as the most promising technique for scaling up the CNT preparation at a relatively low cost [3]. An efficient catalyst with perovskite structure made by citric acid complexometry (for example, LaNiO$_3$) was developed to prepare CNT with this method [4]. The adding of the citric acid during the catalyst preparation was order to obtain the effective size catalyst particles (for example, Ni metal particles) to grow CNT by the complex reactions between the citric acid and catalyst metal ions [5]. And the citric acid did not exist in the obtained catalyst precursors (for example, LaNiO$_3$). But in our experiments, the experimental data showed that the change of citric acid dosage could greatly affect the CNT yield and patterns. The research results showed that the citric acid dosage affected the CNT yield and patterns via affecting the crystal face contents of the active element (Ni) in the catalysts.

2. Experimental
LaNiO$_3$ catalyst precursors were synthesized by a citric acid complexometry. AR grade Ni$_2$O$_3$ and La$_2$O$_3$ were dissolved in nitric acid at the 1:1 of Ni and La atomic ratio, and then respectively added in AR grade citric acid, the complexing agent, as different atomic ratios of the citric acid and metal ions (total of Ni and La) ($0 : 1$, $1 : 1$, $2 : 1$, $3 : 1$, $4 : 1$, $5 : 1$, $6 : 1$, $7 : 1$ and $8 : 1$). Then, the obtained powders were named as catalyst precursor I, II, III, IV, V, VI, VII, VIII and IX and used as the
catalyst precursors to grow CNT [4]. The CNT was synthesized in a horizontal-chamber reactor with an electron auto control temperature system as the CCVD [4]. Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and Infrared spectrum (IR) were used to characterize the obtained CNT and the produced catalysts.

3. Results and discussion

Table 1 is the relationship between the different LaNiO$_3$ catalyst precursors obtained with different citric acid dosages and the obtained CNT yield. From the Table, we can see that the CNT can also be prepared with the catalyst precursor I obtained without citric acid and its CNT yield is about 5.15 (g CNT / g Catalyst precursor. h). With the adding of the citric acid, the CNT yield obtained using the catalyst precursor greatly increases to 8.47 (g CNT / g Catalyst precursor. h), indicating the adding of citric acid can obtain more effective catalysts by the complex reaction between the citric acid and metal ions. With increasing the citric acid dosage, the CNT yield further increases. And the CNT yield increases up to 13.46 (g CNT / g Catalyst precursor. h) at the 2 : 1 atomic ratio of the citric acid and the metal ions (Ni and La). And then, the CNT yield begins to decrease with the increase of citric acid dosage. The CNT yield is only 4.07 (g CNT / g Catalyst precursor. h) at the 3 : 1 atomic ratio of the citric acid and the metal ions (Ni and La). After that, the CNT yield begins to increase and drives to a relative stabilized value (about 7 g CNT / g Catalyst precursor. h) with further increasing the citric acid dosage. From the above experimental data, we see that citric acid dosage can greatly affect the CNT yield.

Table 1. Correlative data with the catalyst precursors obtained with different citric acid dosage and metal ions (Ni and La).

| Citric acid : Ni and La (Atomic ratio) | Catalyst precursor | Yield of CNT (g CNT / g LaNiO$_3$. h) | Ni particle size / nm |
|---------------------------------------|--------------------|----------------------------------------|----------------------|
|                                       |                    |                                        |                      |
| 0 : 1                                 | I                  | 5.15                                   |                      |
| 1 : 1                                 | II                 | 8.47                                   |                      |
| 2 : 1                                 | III                | 13.46                                  | (111) 27.5           |
|                                       |                    |                                        | (200) 13.7           |
| 3 : 1                                 | IV                 | 4.07                                   | (111) 22.5           |
|                                       |                    |                                        | (200) 68.6           |
| 4 : 1                                 | V                  | 6.70                                   |                      |
| 5 : 1                                 | VI                 | 8.21                                   |                      |
| 6 : 1                                 | VII                | 7.60                                   |                      |
| 7 : 1                                 | VIII               | 6.48                                   |                      |
| 8 : 1                                 | IX                 | 6.81                                   |                      |

Fig. 1 is the XRD patterns of the catalyst precursors III, IV (a) and their reduced products III’ (b), IV’ (c) by H$_2$ at high temperature. From Fig. 1a, we can see that catalyst precursors III and IV have very similar XRD patterns. Analyzing the catalyst precursors crystal structure by the XRD PDF database with the XRD scanning program, we can find that catalyst precursors III and IV both are LaNiO$_3$ (perovskite-type crystal structure, hexagonal system). Observing the curves III and IV in Fig. 1a in detail, we can find that there are some fine differences between the curve III and IV though the two curves are very similar in the trend, that is the intensity of the peaks of LaNiO$_3$ is different. In order to study the difference, we compare the intensity of the main peak ((110) crystal face peak), the secondary main peak ((202) crystal face peak) and the tertiary main peak ((122) crystal face peak) in
From these intensity ratio values, we can find that the value of the \( I_{IV}(202) / I_{IV}(110) \) is greater than that of the \( I_{III}(202) / I_{III}(110) \) and the value of the \( I_{IV}(122) / I_{IV}(110) \) is greater than that of \( I_{III}(122) / I_{III}(110) \). These data show that though the catalyst precursor III and catalyst precursor IV both are LaNiO₃, they have different crystal face contents. These differences may result in the difference of their reduction products (catalysts). Fig.1b and Fig. 1c are the XRD patterns of the reduction products from catalyst precursor’s III (catalyst III’) and IV (catalyst IV’). Researching by the XRD analyzing software, we can find the catalysts III’ and IV’ both are the mixture of La₂O₃ and Ni, where the metal Ni peaks are marked and the others are the La₂O₃ peaks. But if we observe Fig. 1b and c in detail, we can find that the La₂O₃ peaks in Fig. 1b are different from that in Fig. 1c. La₂O₃ peaks in Fig. 1b are the mixture of orthorhombic system and tetragonal system crystal structure La₂O₃ peaks. But in Fig. 1c, there is only one crystal structure that is orthorhombic system. Of course, the multiplicity of La₂O₃ in the obtained catalyst III’ can also have the contribution on dispersing the active element (Ni) and avoiding the agglomeration of the Ni particle, which can also improve the effectivity of the catalyst growing CNT. Moreover, further researching the Ni peaks in Fig. 1b and Fig. 1c, we can find that the intensity ratios of the two Ni peaks are different. The value of \( III’ (111) / III’ (200) \) in Fig. 1b is greater than that of \( IV’ (111) / IV’ (200) \), indicating that the two crystal face contents of Ni element in the two catalysts are different. The (111) crystal face content of Ni element in catalyst III’ is higher than that in catalyst IV’. The content of Ni (111) crystal face has great effect on the CNT growth [6]. The (111) crystal face sizes of Ni element in catalyst III’ and IV’ are calculated by the SCHERRER equation and also listed in Table 1.

**Fig. 1** XRD patterns of the catalyst precursors III, IV (a) and their reduced products III’ (b), IV’ (c) by H₂ at high temperature.

Fig. 2 is the TEM images of the obtained CNT with the catalyst precursor’s I, II, III, IV, V and VI (named as Fig. 2a, b, c, d, e and f). Considering the CNT yields from the catalyst precursors VII, VIII and IX are very similar to that from catalyst precursors V and VI, so we only study the CNT TEM images obtained from the frontal five catalyst precursors. From Fig. 2, we can see that the obtained CNT all have well nanometer-hollow-tube structure, and thus prove LaNiO₃ is a type of excellent catalyst precursor to grow CNT. Researching Fig. 2a to f in detail, we can find that the CNT in Fig. 2a have a wider tube-diameter-distribution than that in Fig. 2b, about from 24 to 70 nm; the CNT in Fig. 2b have a smaller tube-diameter-distribution than that in Fig. 2a, about from 26 to 50 nm, indicating that the adding of citric acid can contribute to obtain uniform CNT by affecting the Ni particle. The CNT in Fig. 2c have the smallest tube-diameter-distribution in all the obtained CNT, about from 30 to 40 nm; the CNT in Fig. 2d have a wider tube-diameter-distribution than that of Fig. 2c, about from 28 to 50 nm; the CNT in Fig. 2e and f both have a wider tube-diameter-distribution than that in Fig. 2d, about from 12 to 50 nm and from 26 to 50 nm, respectively. But the tube walls of the obtained CNT change to thinner and smoother with increasing the citric acid dosage. So, we can see that the
modification of citric acid dosage during the catalyst precursor preparation can affect not only the CNT yields but also the CNT patterns.

Comparing Fig. 2c and d, we can find that the inner diameters of the CNT in Fig. 2c range from 25 to 30 nm and that in Fig. 2d from 20 to 30 nm, which is just right the (111) crystal face sizes of the Ni particles listed in Table 1. Based on the research results that the Ni (111) crystal face is the key factor to the CNT growth, we can deduce that the modification of citric acid dosage affect the CNT yield and patterns by affecting the Ni (111) crystal face content in the catalyst particles by the complexation reactions between the citric acid and metal ions (Ni and La).

**Fig. 2** TEM images of the obtained CNT with the catalyst precursors I (a), II (b), III (c), IV (d), V (e) and VI (f).

Fig. 3 is the IR graphs of the complex intermediate III (a, dried in vacuum at 100 °C for 48 hours), IV (b, dried in vacuum at 100 °C for 48 hours) and complex intermediate III’ (c, dried in vacuum at 200 °C for 48 hours). There are both clear adsorption peak and adsorption bands at 1380 cm⁻¹ and from 1410 to 1630 cm⁻¹ in Fig. 3a and b, which are the characteristic adsorption peaks of the complex samples between the carboxyl and metal ions. And there are both broad adsorption peaks above 3000 cm⁻¹ in Fig. 3a and b, which are the characteristic adsorption peaks of carboxyl. Comparing Fig. 3a to b, we can find that there is nice difference between Fig. 3a and b, that is the different ratio of peaks intensity between 1620 and 1380 cm⁻¹ (i.e. 11620 cm⁻¹ / 1 1380 cm⁻¹) in Fig. 3a and b. 11620 cm⁻¹ / 1 1380 cm⁻¹ in Fig. 3a is greatly smaller than that in Fig. 3b, indicating that complex intermediate III in Fig. 3a is different from complex intermediate IV in Fig. 3b, maybe by different complexation mode or maybe by different complexation degree. But we can sure that the two complex intermediates are different only by modifying the dosage of citric acid. However, there is no peak in Fig. 3c, indicating that there is no organic radical groups in the complex intermediate III’ obtained with being dried in vacuum at 200 °C for 48 hours, which also proves that the citric acid does not exist in the obtained catalyst precursors.

The adding of the citric acid during the catalyst preparation is order to obtain the effective size catalyst particles (Ni metal particles in our experiments) to grow CNT by the complex reactions

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between the citric acid and catalyst metal ions [6]. After that, the citric acid was decomposed and removed as gases during the high-heat-treatment in the latter. The citric acid does not exist in the obtained catalyst precursors and the catalysts (products reduced by H₂). The modification of the citric acid dosage during the catalyst precursor preparation can modify the crystal face content of the obtained catalyst precursors, and then modify the crystal face content of the obtained catalysts (Ni), and thus affect the CNT growth. Considering the research results in Table 1, we have the result that the modification of the citric acid dosage affect the CNT growth by affecting the (111) crystal face content of the obtained catalysts (Ni).

![IR graphs of the complex intermediate III (a), IV (b) and complex intermediate III’ (c).](image)

**Fig. 3** IR graphs of the complex intermediate III (a), IV (b) and complex intermediate III’ (c).

4. **Conclusions**

All the catalyst precursors obtained with different citric acid dosages could prepare CNT, but the catalyst precursor with a 2 : 1 atomic ratio of citric acid and metal ion (La and Ni) had the highest yield, about 13.46 (g CNT / g Catalyst precursor. h). Different citric acid dosage during the catalyst precursor preparation result in different Ni (111) crystal face content in the obtained catalyst (Ni), and thus resulted in different CNT yield and patterns.

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