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The effect of catalyst evolution at various temperatures on carbon nanostructures formed by chemical vapor deposition

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Abstract Solid carbon nanofibers (CNFs), hollow CNFs, metal-filled carbon nanotubes (CNTs), and carbon onions were synthesized by chemical vapor deposition (CVD) using a novel Ni/Y catalyst supported on Cu at different reaction temperatures. XRD, TEM, and EDS analyses reveal that the structure of the catalyst changes with increasing reaction temperature. The evolution of Y doped in Ni directly influences the morphologies of the products. At relatively low temperature, Y is doped in Ni and causes CNF formation, and when the temperature is increased to above 650 °C, Y separates from Ni as yttria nanoparticles and carbon onions are synthesized. The catalyst evolution and carbon nanostructure growth mechanism are discussed in detail.

Introduction

Due to their unique properties, such as superior mechanical properties, high electrical conductivity, field emission, metal and semiconductor properties, carbon nanofilaments and carbon onions show promising applications in a range of industrial areas. There are three major methods for these nanostructures to be fabricated: arc discharge, laser vaporization, and chemical vapor deposition (CVD). CVD is the most promising method to commercialize nanostructured graphite growth because of the advantages in its low cost, high yield, and flexibility of control [1, 2]. The as-prepared graphite morphology and microstructure depend on catalyst composition [3], catalyst support [4] and processing conditions, such as gas mixture [5, 6] and reaction temperature [7].

In previous reports [8], we synthesized carbon nanotubes (CNTs) and carbon onions by CVD using a novel Ni/Y/Cu catalyst. However, the nature and evolution of the catalyst, especially of Y element, during the process is still unknown. In this paper, we try to reveal the effect of the catalyst evolution at various reaction temperatures on the morphologies of the carbon products. The results are discussed in light of the current proposed mechanisms for the production of carbon nanofibers (CNFs), CNTs, and carbon onions.

Experimental details

Catalyst preparation

The copper-supported Ni/Y composite catalyst was prepared by means of a homogeneous deposition-precipitation process. In a typical process, the proper amounts of $Ni(NO_3)_2 \cdot 6H_2O$ (7.926 g, 98.0% purity), $Y(NO_3)_3 \cdot 6H_2O$ (1.823 g, 98.0% purity), and 400 mesh electrolytic copper powder (8 g, 99.9% purity) were mixed in 500 mL distilled water. NaOH was dissolved in 300 mL distilled water and added to the previous mixture with constant stirring. The co-precipitate was obtained and then aged at room

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temperature overnight, and the ternary colloid ((Ni(OH)$_2$/Y(OH)$_3$/Cu) was attained. The colloid was washed with distilled water until neutral pH was reached and then dried in a vacuum chamber at 100 °C for several hours. Finally, the dry colloid was ground in an agate mortar and then calcined in a N$_2$ atmosphere at 400 °C for 2 h to form the catalyst precursor supported on Cu particles.

Carbon nanomaterials growth

Carbon nanomaterials were synthesized by the catalytic decomposition of methane over the prepared catalyst. In total, 500 mg of catalyst was put into a quartz boat and placed in a horizontal quartz tube reactor. The quartz tube, mounted in an electrical tube furnace, was heated to the reduction temperature (500 °C) in a N$_2$ atmosphere. Then the hydrogen (100 mL/min, 99.9% purity) was introduced to reduce the catalyst for 2 h. Subsequently, the hydrogen flow was shut off and the quartz tube was heated again to the reaction temperature (500–700 °C) in a N$_2$ atmosphere. A mixture of CH$_4$/N$_2$ (420/60 mL/min, v/v) was introduced into the quartz tube for 60 min. Finally, the system was cooled to room temperature under a nitrogen atmosphere. The percentage yield of the carbon deposit was calculated relative to the mass of elemental nickel used.

Characterization of the products

The catalyst and as-prepared carbon nanostructures were characterized using an X-ray diffractometer (XRD, Rigaku D/max 2500 V/pc), field emission scanning electron microscope (FE-SEM, JEOL JSM-6700), and high-resolution transmission electron microscope (HRTEM, PHILIPS TECNAI G2 F20) equipped with X-ray energy dispersive spectrometer (EDS).

Results

XRD analysis of the products

Figure 1 shows the XRD pattern of the products fabricated by CVD over Ni/Y/Cu catalyst at different growth temperatures. A broad diffraction peak at about 26.2° is assigned to the (002) planes of hexagonal graphite structure. The peaks at 29.1° can be indexed to the (222) planes of yttria. It is obvious that the intensity of these peaks of yttria change with increasing reaction temperature. Below 650 °C, the peaks of the yttria are not apparent. When the temperature increases to 650 °C and above, the peaks of yttria become visible. The nickel peaks shift to lower diffraction angles at 700 °C while the copper peaks have almost no change, indicating that some copper atoms have diffused into the nickel lattice forming a solid solution. The intensity of the C peaks reduces with increasing temperature corresponding to the reduced carbon yield of the samples (Table 1).

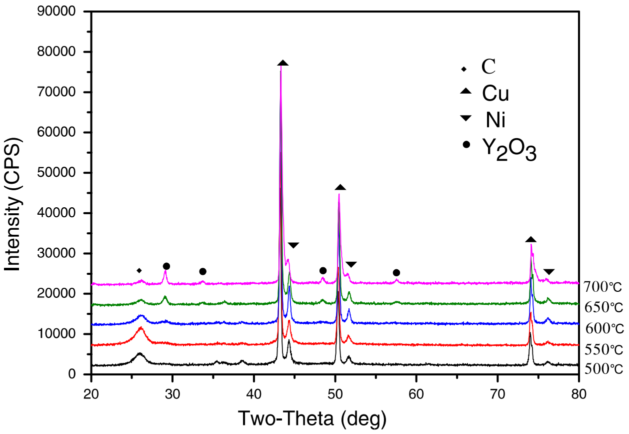


Fig. 1 XRD patterns of as-prepared samples at different reaction temperatures

Table 1 The morphology and yield of the carbon deposited at different reaction temperatures

Sample	Reaction temperature (°C)	Carbon yield (%)	Main product
1	500	519	Solid CNFs
2	550	384	Hollow CNFs and solid CNFs
3	600	319	Hollow CNFs (or CNTs)
4	650	116	Metal-filled CNTs and carbon onions
5	700	58	Solid carbon onions

Microstructure analysis of the products

The SEM and TEM analyses reveal that four types of carbon nanostructures were synthesized as shown in Figs. 2 and 3: solid CNFs, hollow CNFs, metal-filled CNTs, and carbon onions. The reaction conditions and corresponding products are listed in Table 1. At a reaction temperature of 500 °C, only solid CNFs with a diameter of 20–70 nm are formed as shown in Figs. 2a and 3a. It is interesting that some catalyst nanoparticles are attached with two CNFs. The morphology of the CNFs appears to be several tubes inserted in a common ball of catalyst (in Fig. 4a), which is similar to a previous report [9]. For a reaction temperature of 550 °C, CNFs with a small hollow core become the primary product though some solid CNFs still exist. At 600 °C, there are only hollow CNFs formed and the inner diameter of most CNFs becomes larger. The outer diameter of the as-prepared carbon nanofilaments became smaller

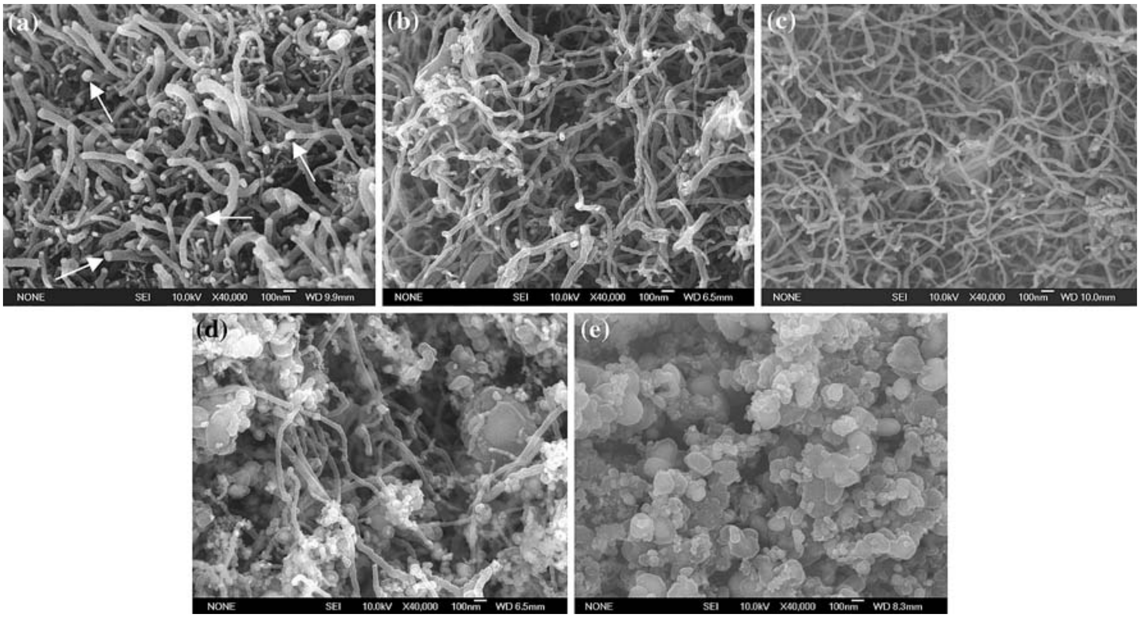


Fig. 2 SEM images of the as-prepared samples reacted at **a** 500 °C, **b** 550 °C, **c** 600°°C, **d** 650 °C, and **e** 700 °C

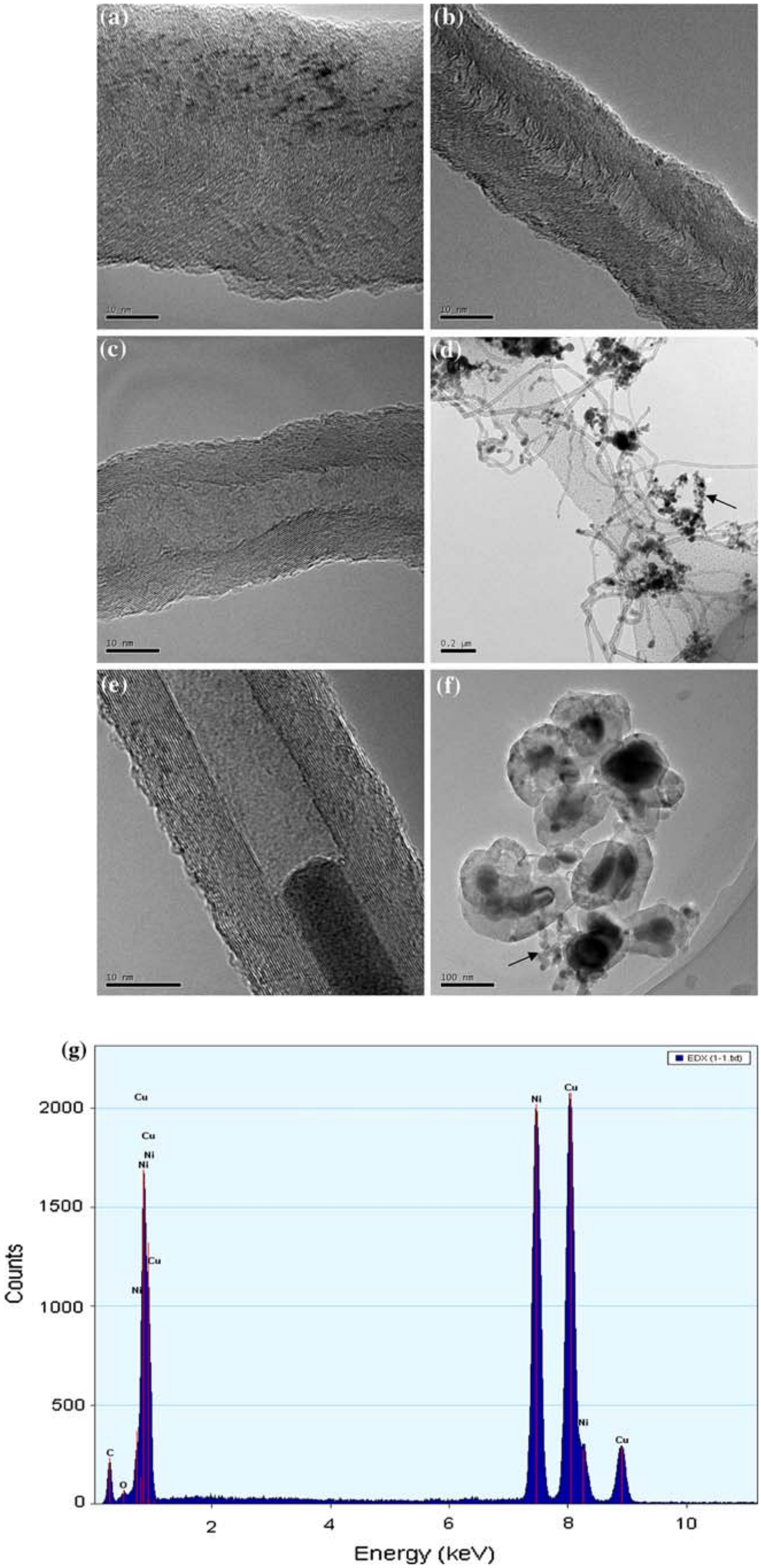
and more uniform with increased temperature as shown in Fig. 2. When the reaction temperature was increased to 650 °C, both metal-filled CNTs and carbon onions existed, similar with our previous report [10]. The outer diameter of the CNTs is in the range of 20–40 nm and carbon onions consist of several concentric layers surrounding either a hollow core or a metal particle. The carbon layer arrangement of the filaments changed from herringbone to cylindrical with the increased reaction temperature (as shown in Fig. 3a–e). At 700 °C, there were almost no filaments formed and only large solid carbon onions with a metal particle encapsulated, as observed in Fig. 3f. The diameter of most catalyst particles encapsulated by carbon shells is in the range of 20–100 nm and there are almost no hollow carbon onions observed by TEM. EDS analysis of the catalyst shows that the highest peaks are related to Cu and Ni (Fig. 3e). Combining the XRD result, it can be inferred that the encapsulated particles consist of Ni and Cu.

Discussion

Evolution of the catalyst

Experience has shown that the reaction temperature has a great influence on the yield and morphology of the carbon products by CVD. The optimal growth temperature of CNTs is usually in the range 600–800 °C and the carbon yield increases with increasing temperature [5, 7]. However, in our results, the carbon yield sharply reduced with increasing growth temperature, indicating that the catalyst composition and evolution, as well as growth temperature, play a key role for carbon nanostructure growth. It is known that phase and morphology of the catalyst during CVD is an important factor to control the microstructure of carbon nanomaterials [11–13]. In this work as shown above, the phase and morphology of the catalyst both changed at different growth temperatures, resulting in various carbon nanostructures. XRD showed that only Ni and Cu phases are detected until the temperature increases to 650 °C. When the temperature was increased to 700 °C, pure Ni peaks disappeared and a new phase, corresponding to a Ni–Cu solid solution alloy, was observed. The morphology of the catalyst particle also changed during the CVD process. At 500 °C, most of the catalyst particles were quasi-spherical or polygonal (Fig. 4a). With increased temperature, the catalyst particles deformed slightly compared with that at 500 °C and became quasi-conical, which caused hollow CNFs growth (Fig. 4b). When the temperature was increased further, the catalyst deformed severely and became encapsulated by carbon shells (Fig. 3d–f), which may be one of the main factors for the rapid reduction of the carbon deposition. When investigated in detail, we can observe some uncovered smaller nanoparticles (Fig. 3d, f). Figure 4c is the HRTEM image of the uncovered nanoparticles. Different crystallographic planes of the particles can be observed. The interplanar spacing $d = 0.303$ nm corresponds to the distance of an yttria plane (2 2 2) while $d = 0.2651$ is consistent with an yttria plane (4 0 0), which imply that these nanoparticles consist of yttria. EDS analysis of the uncovered nanoparticles

Fig. 3 TEM micrographs of the samples synthesized at **a** 500 °C, **b** 550 °C, **c** 600 °C, **d**, **e** 650 °C, **f** 700 °C, and **g** EDS analysis of the catalyst encapsulated in carbon shells at 700 °C



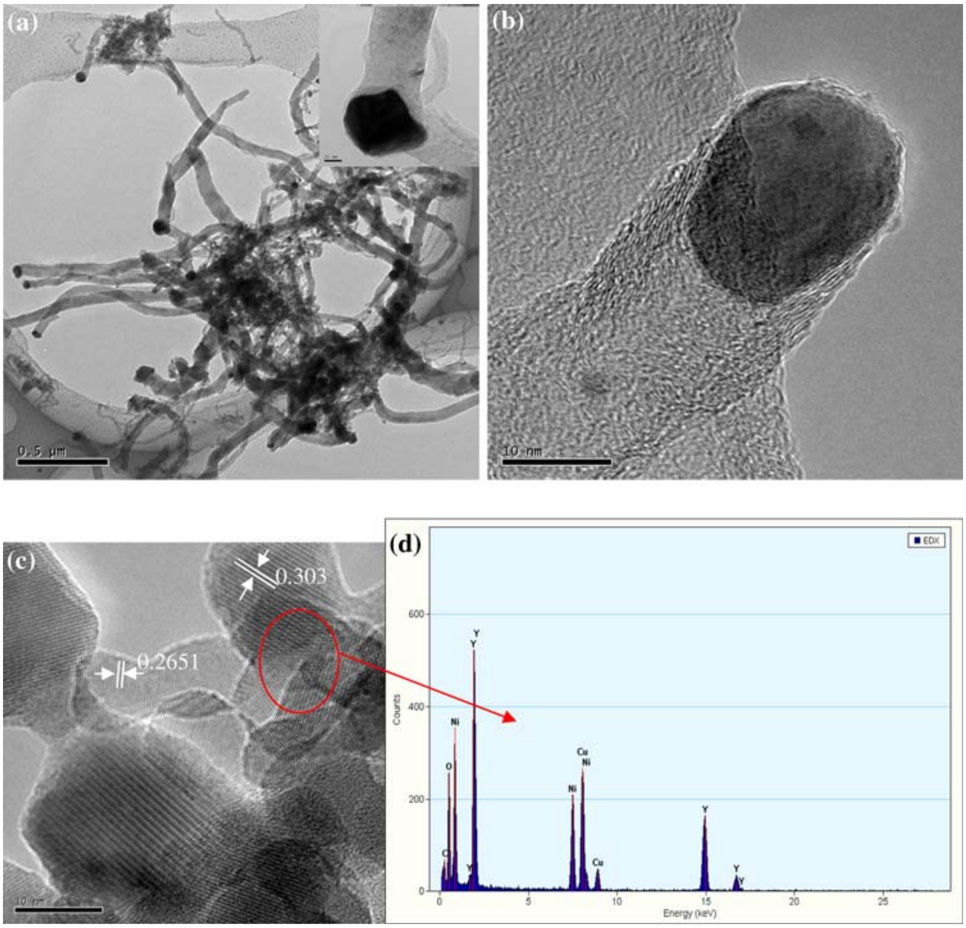


Fig. 4 TEM and EDS analyses of the catalyst after reaction at **a** 500 °C, **b** 600 °C, and **c**, **d** 700 °C

confirmed the high content of Y in these particles (in Fig. 4d). XRD analysis also proved the existence of yttria at relatively high temperature. However, we have not observed these uncovered nanoparticles in samples 1, 2, and 3. In XRD patterns of samples 1, 2, and 3, it is difficult to detect the existence of the phase containing Y. This may be attributed to the fact that yttria is distributed homogeneously in Ni particles and has a small crystal size at lower temperature that cannot be detected by XRD. The nature of the catalyst structure at lower reaction temperature needs further research.

Growth mechanism of the carbon nanoproducts

Generally, the size, shape, and surface nature of the catalyst may have a great influence on the behavior of carbon atoms, and ultimately on the growth morphology of carbon nanomaterials. In our case, the catalysts adopted in all experiments are the same. So the structural evolution of the catalyst with temperature plays a key role in the synthesis of different carbon products.

As described above, yttria may separate from the catalyst with increasing temperature, which consequently influences the growth of carbon nanostructures. The conglomeration and movement of Y through the catalyst requires that the catalyst should be active enough or in a quasi-liquid state. It is accepted that the main reason for "fluidization" at lower temperature is the size effect of the metal at nanometer level and an over-saturation of the metal particles with carbon [14]. When the reaction temperature increases, carbon diffusion through the surface of the catalyst increases, which further reduces the melting point of the catalyst particles and thus reduce the obstacle to deformation for the catalyst. In Ref. [9], we observed that the catalyst was Ni doped with yttria before reaction but after reaction the catalyst becomes pure Ni and yttria separates from the catalyst, indicating that the carbon diffusion may be the main reason for the fluidization and separation of the catalyst particles. For the CNFs synthesis, metal particles are usually assumed to be solid state during the synthesis process [15]. Thus, we speculate that the catalyst remains solid during reaction until the temperature is increased to 650 °C. At 650 °C, both carbon onions and metal-filled CNTs formed. At the initial growth of the metal-filled CNTs, carbon onions were formed at first [9]. Thus, the separation of yttria from Ni may directly lead to the formation of the carbon onions. From the TEM observations, we found that the yttria nanoparticles exist out of the carbon shells, which implies that yttria nanoparticles formed and separated from catalyst particles before carbon precipitation. The separation of yttria consequently changed the crystal structure and selectivity of the catalyst. When yttria separated from Ni, the whole catalyst would be over-saturated by carbon and carbon onion-like nanoparticles formed. When the temperature continues to increase to 700 °C, the catalyst particles begin to alloy with Cu according to the XRD and EDS analysis mentioned above and become larger. In this case, the carbon ions diffuse faster through the catalyst, thus the catalyst begins to fluidize and yttria begins to agglomerate before the carbon over-saturation, which may cause partial failure of Y to function in resisting the diffusion between Cu and Ni. When carbon atoms in the catalyst become over-saturated, carbon layers precipitate, which prevents the further diffusion between Cu and Ni.

Based on the discussion above, the growth mechanism of carbon nanostructures can be explained as follows and is shown schematically in Fig. 5. At a relatively low reaction temperature (below 650 °C), yttria is homogeneously doped in Ni. From Fig. 2a, we can see that the catalyst is on the tip of the CNF, indicating the tip growth mode is suitable for the CNF growth (Fig. 5a). With the increased reaction temperature, the catalyst nanoparticles will deform and the graphite precipitates from slanting surfaces but not from the base plane, a herringbone CNF with a hollow tube is obtained. For a temperature of 650 °C or higher, carbon onions are formed due to the carbon atoms being released from the whole surface of the catalyst particles (Fig. 5b, c).

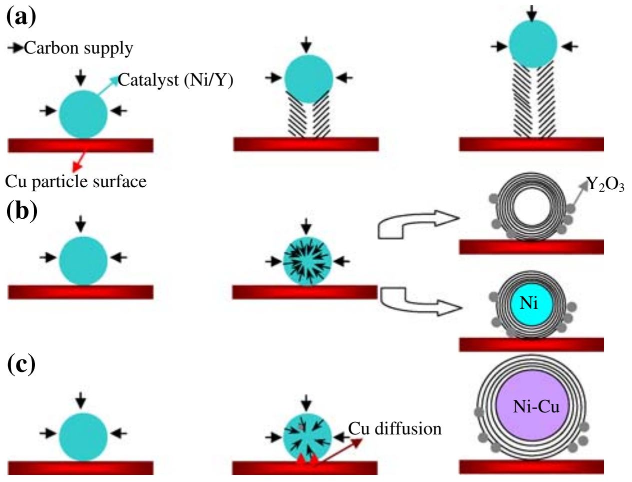


Fig. 5 Schematic description of the growth mechanism of carbon nanostructures obtained at different reaction temperature. **a** At relatively low temperature, the catalyst remains solid state and catalyzes the CNF growth. The inner diameter of the CNF changes with increasing the reaction temperature. **b** At relatively high temperature (at 650 °C), the catalyst becomes quasi-liquid because of the size effect of metal at the nanometer level and an over-saturation of the metal particles with carbon, which may cause the separation of Y from Ni, and carbon onions form. **c** When the temperature is high enough (at 700 °C), some Cu can diffuse into Ni before the carbon layer precipitates and large solid carbon onions form. The catalyst becomes Ni–Cu alloy

Conclusion

Different carbon nanostructures were synthesized by CVD using a novel Ni/Y catalyst at different reaction temperatures. The structural evolution of the catalyst with increased reaction temperature directly influences the morphologies of the products. At relatively low temperature, the main products are CNFs (solid and hollow). The catalyst is solid through the reaction process and the tip growth mode is appropriate for the CNF growth. When the temperature is increased to 650 °C and above, the catalyst is quasi-liquid because of the size effect of metal at the nanometer level and an over-saturation of the metal particles with carbon, which may cause the separation of yttria from Ni, and consequently carbon onions form.

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