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EFFECTS OF SYNTHESIS CONDITIONS ON THE SYNTHESIS OF CARBON NANOFIBERS BY ETHANOL CATALYTIC COMBUSTION

WPLYW WARUNKÓW SYNTEZY NA SYNTEZĘ NANOWŁÓKIEN WĘGLOWYCH METODĄ KATALITYCZNEGO SPALANIA ETANOLU

In this paper, the effects of position of substrates in flames, preparation time, stability of flames and catalyst precursors on the synthesis of carbon nanofibers (CNFs) by ethanol catalytic combustion (ECC) were investigated. For investigating the effects of these influence factors on the synthesis of CNFs, several sets of controlled experiments were performed, such as preparation experiments with different position of substrates in flames, different preparation time, stable and unstable flames, and different catalyst precursors. In our experiments, the catalyst precursors were iron nitrate, cobalt nitrate, nickel nitrate, and iron chloride, cobalt chloride, nickel chloride. The as-synthesized products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Our results indicate that the optimal position of substrates in flames is more than 1cm and less than 2.5cm, the optimal preparation time is more than 5min and less than 30min for massive yield, stable flames would be tent to synthesize CNFs with mainly single-type morphology and could improve the graphitization of CNFs, and the catalyst precursors obviously have effects on the synthesis of CNFs.

Keywords: carbon nanofibers; ethanol catalytic combustion; influence factors

W niniejszej pracy zbadany został wpływ położenia substratów w płomieniach, czasu przygotowania, stabilności płomieni i prekursorów katalizatora na syntezę nanowłókien węglowych (CNFs) metodą katalitycznego spalania etanolu (ECC). W celu zbadania wpływu tych czynników na syntezę nanowłókien węglowych przeprowadzono kilka zestawów kontrolowanych eksperymentów, przy różnej pozycji podłoża w płomieniach, różnym czasie przygotowania, płomieniach stabilnych i niestabilnych i przy użyciu różnych prekursorów katalizatora. W naszych eksperymentach jako prekursory katalizatora stosowano azotany: żelaza, kobaltu i niklu oraz chlorki żelaza, kobaltu i niklu. Tak otrzymane produkty syntezy scharakteryzowano za pomocą skaningowej mikroskopii elektronowej (SEM), transmisyjnej mikroskopii elektronowej (TEM) i spektroskopii Raman'a. Nasze wyniki wskazują, że optymalna pozycja podłoża w płomieniach to więcej niż 1 cm i mniej niż 2,5 cm, a optymalny czas przygotowania to więcej niż 5 min i mniej niż 30 min dla dużej wydajności. Stabilność płomieni będzie sprzyjać syntezie nanowłókien o morfologii jednego typu i może poprawić ich grafityzację, a rodzaj prekursora katalizatora ma wpływ na syntezę nanowłókien.

1. Introduction

Combustion method is a simple method for synthesizing carbon nanotubes (CNTs) [1] and CNFs, which employs flames of carbon-contained reactant to synthesize CNTs and CNFs. It has been proved that combustion method is an effective method for synthesizing CNTs and CNFs [2]. Up to now, various nanostructures have been produced by combustion method, such as single-walled CNTs [3, 4], multi-walled CNTs [5-7], bamboo-like CNTs [8], and Y-junction CNFs [9], etc. However, different carbon products, such as CNTs,

nanocoils, non-coiled CNFs, Y-shaped CNFs, etc., are symbiotic in deposits synthesized by flames. It is difficult to obtain single-type products, such as non-coiled CNFs, or nanocoils, because there are many factors that could influence on carbon products prepared by combustion method. It has been reported that flame temperature [6, 7], catalyst [4, 5], carbon source [2, 5] and additive [2] have some influence on carbon products prepared by flames.

In our previous work, we have synthesized CNFs by using ethanol catalytic combustion (ECC) [8, 9]. But

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we didn't study that how many factors could affect the synthesis of CNFs and how they could affect the synthesis of CNFs by employing ECC. In this paper, we have systemically studied that the effects of several influence factors on synthesis of CNFs by employing ECC.

These influence factors are described in detail as follows:

The first influence factor is the position of substrates in flame. The bottom position of the flames is defined as the reference position and the upward direction is defined as y axis, then height h represents the position of substrate in flames. In our experiments, the flames of ethanol are diffusive. The height of stable flames is about 8cm, but the part of flames over 5cm is very unstable. We have measured the temperature of flames at different height by thermocouple within 5cm of height. We found that the temperature of flames varied from position to position. So, different position of substrates for sampling corresponds to different synthesis temperature. The second influence factor is preparation time. It is the time that substrates for sampling stay in flames.

The third influence factor is stability of flames. The fuels that provide both carbon source and synthesis energy by combustion is commonly either gas phase, such as methane, carbon monoxide, acetylene, etc. or liquid phase, such as ethanol, methanol, acetone, etc. There are special burners for synthesizing CNTs and CNFs by employing gas phase fuel and the flames commonly are premixed [6, 10]. So, the flames are relatively stable due to a closed environment. However, there are no special setups for synthesizing CNTs and CNFs by employing liquid phase fuel. The flames are diffusion flames and in air atmosphere. So the flames are unstable and can be away from substrates during synthesis due to air perturbation. Therefore the stability of flames must be considered when liquid phase fuels are employed to synthesize CNTs and CNFs. In ECC, the flames can be easily affected by external atmosphere perturbation and sway continually in air, even can sway away from substrate. So the preparation experiments should be carried out in a relatively closed room. Further more; the stability of flames can be improved by external shield in our experiments. The shield is cylindrical cover with a diameter of 10cm by winding of thin copper plates. The flames without shield are unstable and the flames with shield are relatively stable.

The forth influence factor is catalyst precursors. In our experiments, iron nitrate, cobalt nitrate, nickel nitrate, iron chloride, cobalt chloride and nickel chloride were employed as catalyst precursors. The products that were synthesized by different catalyst precursors have differences in morphology.

2. Experimental procedure

CNFs were synthesized by ECC. The process of ECC has been described in references [8, 9]. Here, we make a simple description yet. In ECC, copper plates were employed as substrates, iron salt, cobalt salt and nickel salt as catalyst precursors, ethanol as both carbon source and fuel to provide energy for CNF growth. Copper plates were ultrasonically washed in acetone for several minutes. Catalyst precursors were dissolved in absolute ethanol to form precursor solutions. Then some drops of catalyst precursor solution were dripped to cleaned surface of copper plates. After dried naturally, the coated copper plate was inserted into ethanol flames for about 10min. At last, wool-like deposits were found on the surface of copper plate.

For investigating the effects of position of substrates in flames, preparation time, stability of flames and catalyst precursors on the synthesis of CNFs, several sets of controlled experiments are performed. We made samples at different position in flames, at different preparation time, with stable and unstable flames, with different catalyst precursors by ECC.

For analysis, the as-synthesized products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy.

3. Results and discussion

3.1. Effects of the position of substrates in flames on the synthesis of CNFs

Synthesis temperature is a key parameter for growth of CNFs. Generally, too lower temperature is unsuitable for synthesizing CNFs. In ECC, ethanol flames provide energy for the growth of CNFs, and the temperature at the position of substrates in flames is that of synthesizing CNFs. On the other hand, ethanol vapor in flames acts as carbon source because combustion of ethanol is insufficient. It is well known that temperature of flames is related to the degree of combustion of fuels. The lower temperature of flames means that the combustion of fuel is more insufficient. For investigating the effects of position of substrates in flames on synthesis of CNFs, we have synthesized CNFs for sampling at different height in flames. We find that the yield of deposits is affected by the height of substrate in flames. When the height is less than 1cm, no visible deposits are found on substrates. When the height is more than 1cm and less than 2.5cm, plenty of deposits grow on substrates. When the height is more than 2.5cm, fewer deposits, even no visible deposits, grow on substrates.

To understand these experimental results, we have measured the temperature of ethanol flames and plotted the curve of Temperature-Height (that is, T-h curve). Fig. 1 shows the T-h curve. The horizontal axis represents height of substrates in flames, and the vertical axis represents temperature of flames at height h . This curve is primarily in agreement with the result of Pan et al. [7]. From T-h curve, we know that the temperature of flames is less than 500°C when h is less than 1cm, and the temperature is about 550°C when h is more than 1cm and less than 2.5cm, and the temperature is more than 600°C when h is more than 2.5cm.

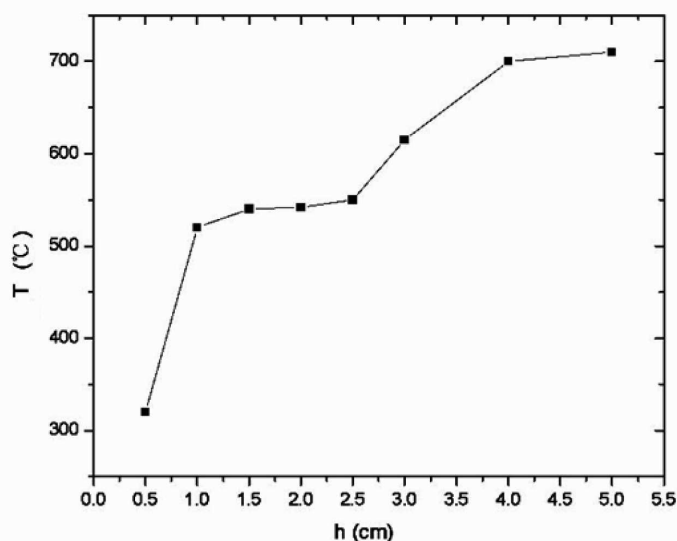


Fig. 1. T-h curve of ethanol flames

So the results could be easily understood. When $h < 1\text{cm}$, the temperature of flames is too low to grow CNFs although carbon source is sufficient. When $1\text{cm} < h < 2.5\text{cm}$, the temperature of flames is suitable for the growth of CNFs and the carbon source is also sufficient, so mass deposits grow on substrates. When $h > 2.5\text{cm}$, the temperature of flames is very suitable for the growth of CNFs, but the carbon source is insufficient because of sufficient combustion of ethanol, so fewer deposits grow on substrates. So, according to these results, we conclude that the optimal position of substrates in flames is $1\text{cm} < h < 2.5\text{cm}$.

3.2. Effects of preparation time on the synthesis of CNFs

To investigate the effects of preparation time on the synthesis of CNFs, we have prepared several samples for 1min, 5min, 10min, 30min, and 1h. The copper substrates for sampling were normally located at the position of 2cm in height. Like other methods, the preparation time also has an influence on the yield of deposit in ECC.

When the preparation time is less than 1min, no visible deposits are observed on substrates. This result can be considered as follows. In our experiments, we employ iron salt, cobalt salt or nickel salt as catalyst precursors. When catalyst precursor-coated substrates are inserted into ethanol flames, these catalyst precursors have decomposition into catalyst particles. Fig. 2a is a SEM image of surface of copper substrate when it stays in ethanol flames for 1min (The catalyst precursor is iron nitrate). This image clearly shows catalyst particles with several tens of nanometers in diameter.

After the formation of catalyst particles, CNFs start to grow. In TEM observation, we can find that catalyst particles with several tens of nanometer locate at the tip of CNFs (see Fig. 2b). So, at the initial stage of synthesis, no deposits grow on substrates.

When preparation time reaches 2min, visible black deposits grow on copper substrates with small yield. With increasing preparation time, the yield of deposits is obviously increased. When the preparation time reaches 30min, mass products are deposited on substrates.

If the preparation time is prolonged continuously, the deposits partly become burning in flames due to excessive products on substrates. Therefore, this phenomenon results in decreasing yield of deposits. This is a great difference with other methods, such as arc discharge, chemical vapor deposition [11, 12]. In that synthesis system, the growth of CNFs/CNTs is protected under inert carrier gas [13-16]. So the yield of products can increase by prolonging preparation time if possible. But in ECC, the growth of CNFs is conducted directly in air, so the deposits could burn if they are massive on the substrate. This limits that the yield of deposits could not increase by excessively prolonging the preparation time.

So, according to these results, we conclude that the optimal preparation time is 5-30min. Generally, in our experiments, substrates stay in flames for about 10min.

3.3. Effects of stability of flames on the synthesis of CNFs

Fig. 3a and b show low magnification SEM images of deposits prepared on copper substrates by using unstable and stable ethanol flames. From these images, we find that the deposits consist of incompact thin films (see Fig. 3a) when the flames have a relatively lower stability without shield, while the deposits are compact and even thin films (see Fig. 3b) when the flames have a relatively higher stability with shield.

The difference of morphology of deposit films is strongly relative to the stability of ethanol flames. During our experiments, we noted that the ethanol flames swayed in air even could be away from substrate when

the flames were unstable. So the products deposited on substrates formed incompact thin films due to partly burning of deposits during synthesis duration. When the flames were stable with shield, the ethanol flames had a slight sway and the substrates always located at the

center of ethanol flames during synthesis duration. So the deposits formed a thinly even film. These results indicated that the relatively stable flames could provide a relative stable synthesis environment and tend to produce a thinly even deposit film.

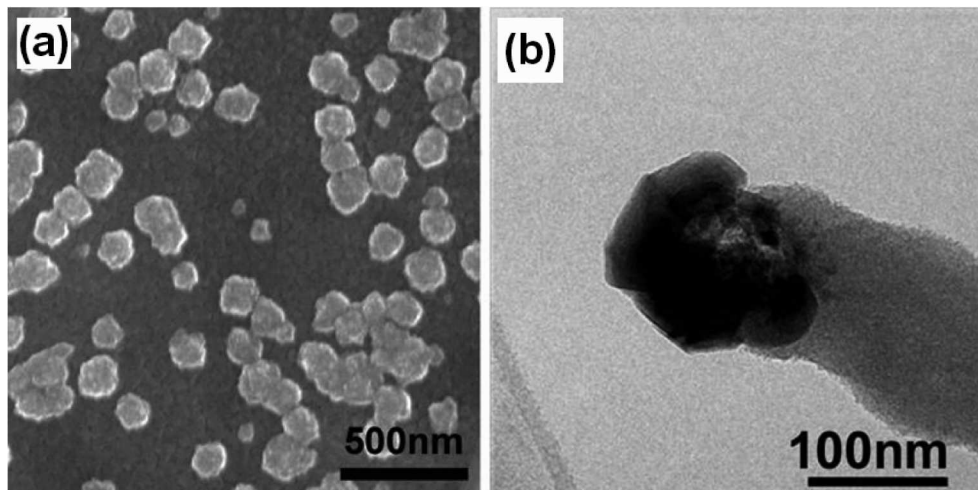


Fig. 2. Catalyst particles (a) on substrates, (b) located at the tip of CNFs

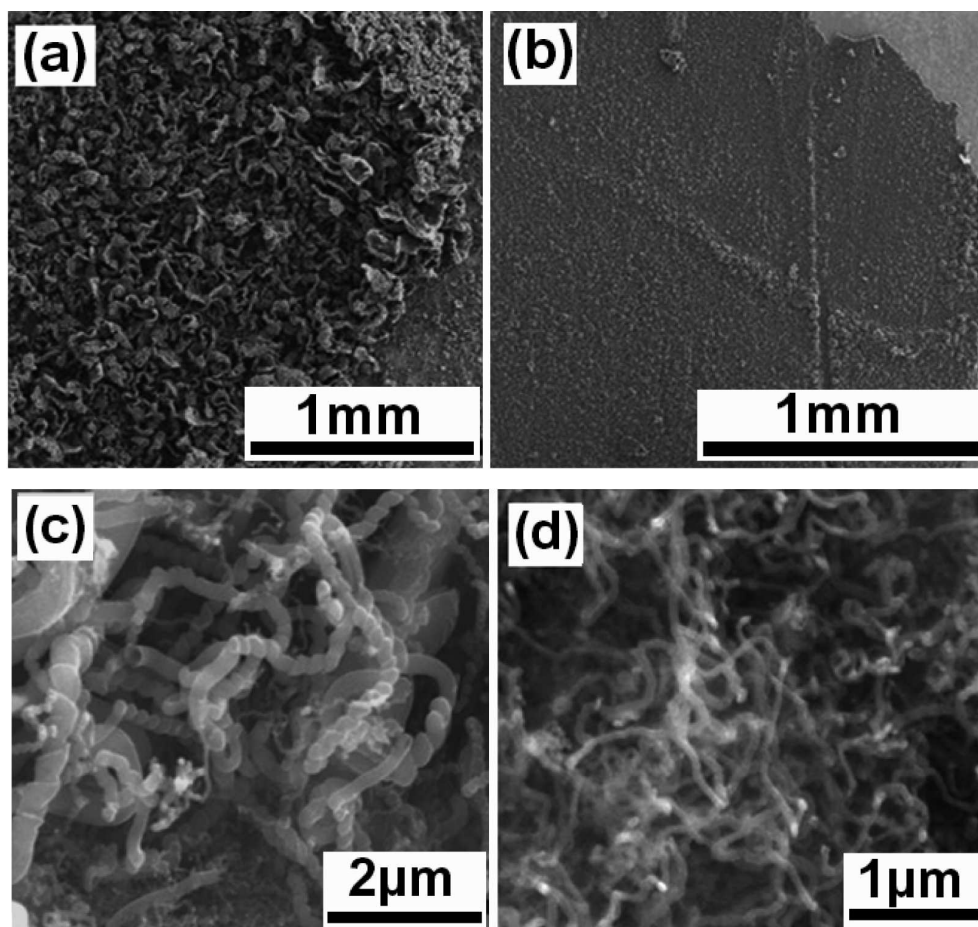


Fig. 3. Low magnification SEM images of deposits with (a) unstable, (b) stable flames. High magnification SEM images of deposits with (c) unstable, (d) stable flames

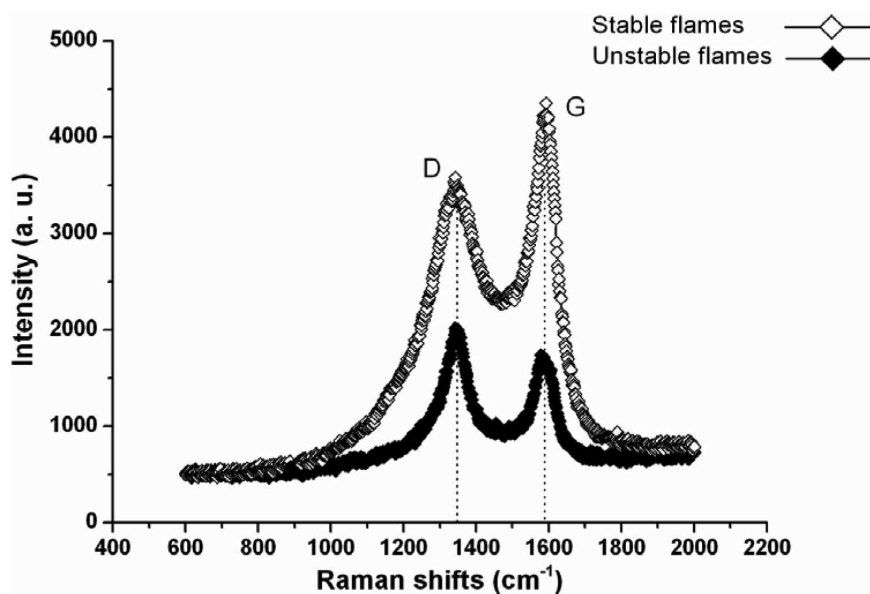


Fig. 4. Raman spectra of deposits with stable and unstable ethanol flames

Fig. 3c and d show high magnification SEM images of deposits prepared by unstable and stable ethanol flames. From Fig. 3c, we know that the carbon film consists of different carbon nanostructure, such as helical CNFs, non-helical CNFs, and the diameters of these carbon nanostructures have relatively wide distribution ranging from several tens of nanometers to about 500nm when the flames are unstable without shield. From Fig. 3d, we find that the carbon film mainly consisted of non-helical CNFs, and the diameters of these CNFs are almost less than 100nm and have a relatively narrow distribution when the flames are stable with shield. These results indicate that there are abundant carbon nanostructures in deposits when unstable flames are employed and there are mainly non-helical CNFs in deposits when stable flames are employed. Fig. 4 shows Raman spectra of deposits prepared by unstable and stable ethanol flames. The wavelength of excitation laser is 514.5nm. These spectra show clear G peaks and D peaks. The G peak is graphite mode which is produced from high degree of symmetry and order of carbon materials and the D peak is disorder-induced phonon mode [17, 18]. The intensity ratio of D peak and G peak I_D/I_G has been employed to characterize the graphitization degree of carbon materials [19-21]. The smaller the value of I_D/I_G , the higher the graphitization degree of carbon materials. According to our experiment, we know that the value of I_D/I_G is about 1.143 when the flames are unstable, and the value of I_D/I_G is about 0.820 when the flames are stable. It is obvious that the value of I_D/I_G is smaller when the flame is stable. So, these Raman spectra indicate that the graphitization degree of CNFs can be improved by employing stable flames.

3.4. Effects of catalyst precursors on the synthesis of CNFs

To investigate the effects of catalyst precursors on the synthesis of CNFs, we have synthesized CNFs with different catalyst precursors. The copper substrates for sampling are normally located at the position of 2cm in height. The preparation time is about 10min.

Fig. 5a-d shows SEM and TEM images of CNFs by employing iron nitrate, cobalt nitrate and nickel nitrate as catalyst precursors. From these images, we find that the morphology of CNFs is affected by catalyst precursors. CNFs are relatively thin with diameter less than 100 nm and a good uniformity when the catalyst precursor is iron nitrate (Fig. 5a). When the catalyst precursor is cobalt nitrate, there are lots of defects to discriminate a complete CNFs (Fig. 5b). And the CNFs have a relatively large diameter commonly more than 100 nm with various types, such as helical structure, Y-shape structure when the catalyst precursor is nickel nitrate (Figs. 5c and d).

Fig. 5e-h shows SEM and TEM images of CNFs by employing iron chloride, cobalt chloride and nickel chloride as catalyst precursors. These images show that the morphology of these CNFs is obviously different. When the catalyst precursor is iron chloride, CNFs are relatively thin and their diameter is less than 100nm with a good uniformity (Fig. 5e). When the catalyst precursor is cobalt chloride, CNFs have a relatively wide distribution in diameter (Fig. 5f), and non-fiber-like deposits also exist (Fig. 5g). When catalyst precursor is nickel chloride, CNFs are relatively thick and their diameter is more than 100nm, and various types of CNFs are co-exist in deposits, such as helical structure and non-helical structure (Fig. 5h).

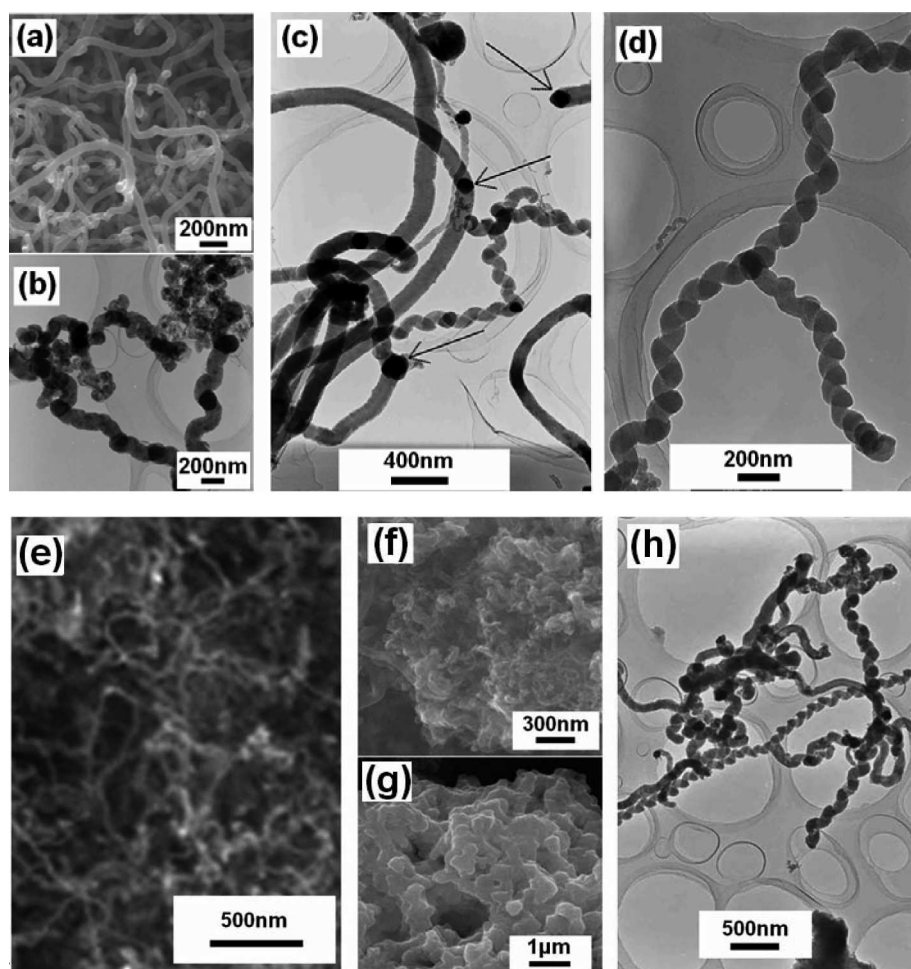


Fig. 5. SEM and TEM images of as-synthesized CNFs by employing (a) iron nitrate, (b) cobalt nitrate, (c) and (d) nickel nitrate, (e) iron chloride, (f) and (g) cobalt chloride, (h) nickel chloride as catalyst precursors

For carefully observing Fig. 5, we find that the morphologies are similar when catalyst precursors are iron nitrate and iron chloride, or cobalt nitrate and cobalt chloride, or nickel nitrate and nickel chloride. This result is easy to understand. In ECC, catalyst precursors, metal salts, have decomposition into metal oxide. Metal salts that contain the same metal ion are decomposed to form the same metal oxide, in another words, iron nitrate and iron chloride, or cobalt nitrate and cobalt chloride, or nickel nitrate and nickel chloride are decomposed to form iron oxide, or cobalt oxide, or nickel oxide, respectively. These different catalyst precursors but contain the same metal ion actually corresponds to the same catalysts. So, the CNFs have similar morphology when iron salt, or cobalt salt, or nickel salt is employed as catalyst precursors. Whereas, that different catalyst precursors that contained different metal ion corresponds to different catalysts, such as iron nitrate, cobalt nitrate, and nickel nitrate corresponding to iron oxide, cobalt oxide and nickel oxide, respectively. Therefore, the CNFs

have different morphology when different nitrate salt or chloride salt is employed as catalyst precursors.

Our experimental results indicate that when iron salt is employed as catalyst precursors, the deposits mainly consist of non-helical CNFs with uniformity in diameters; when cobalt salt is employed as catalyst precursors, besides CNFs, non-fiber-like deposits exist abundantly; when nickel salt is employed as catalyst precursors, besides non-helical CNFs, helical CNFs mostly exist in deposits.

In ECC, we note that helical CNFs are found at some cases. First, as discussed above, when iron chloride is employed as catalyst precursor, unstable ethanol flames tend to produce helical CNFs. Second, whether ethanol flame is stable or unstable, nickel salt is employed as catalyst precursor. We believe that it should be not occasional to find helical in deposits when nickel salt is employed as catalyst precursors. It should be related to catalyst performance of nickel [22, 23].

4. Conclusions

The optimal position of substrates in flames is more than 1cm and less than 2.5cm for massive yield, the optimal preparation time is more than 5min and less than 30min for massive yield, stable flames would be tent to synthesize CNFs with mainly single-type morphology and could improve the graphitization of CNFs, and the catalyst precursors have obvious effects on CNFs. For iron salt as catalyst precursors, the deposits mainly consist of non-helical CNFs with uniformity in diameters; for cobalt salt as catalyst precursors, besides CNFs, non-fiber-like deposits exist abundantly; for nickel salt as catalyst precursors, besides non-helical CNFs, helical CNFs mostly exist in deposits.

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