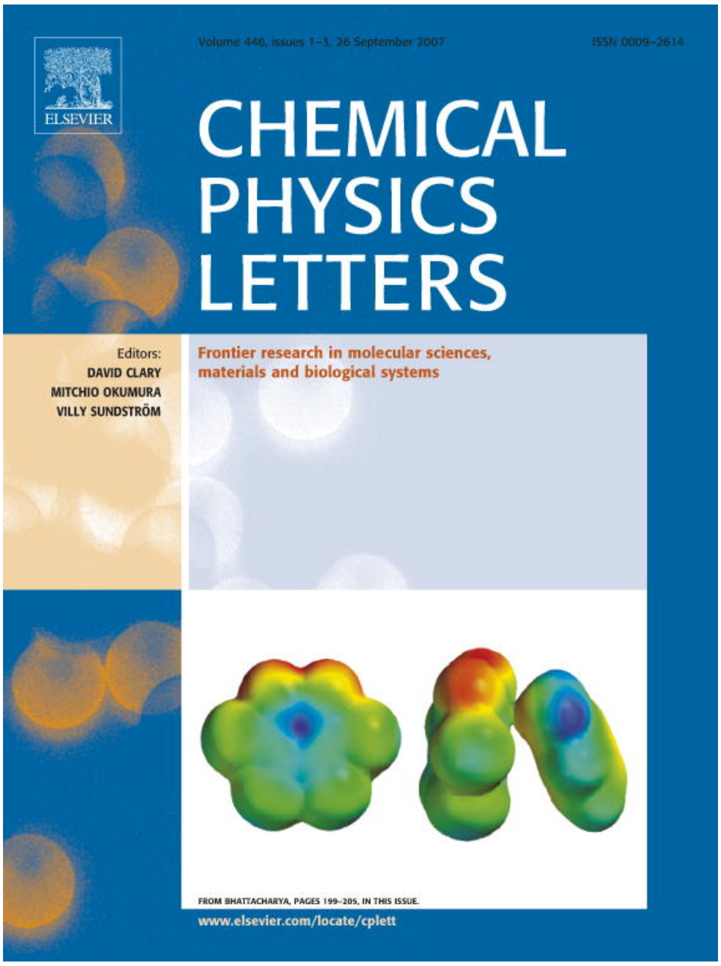

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Investigations of NanoBud formation

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Abstract

The formation of a novel hybrid material, NanoBuds, single-walled carbon nanotubes (CNTs) with covalently attached fullerenes was investigated in a ferrocene–carbon monoxide system. Fullerenes and CNTs were simultaneously formed by carbon monoxide disproportionation on the surface of iron particles in the presence of etching agents such as H_2O and CO_2. On the basis of parametric investigations and *in situ* sampling of the product from different locations in the reactor the mechanisms for NanoBud formation are discussed.

1. Introduction

Fullerenes and carbon nanotubes (CNTs) have attracted great interest from both fundamental and application points of view due to their remarkable physical and chemical properties [1–3]. Fullerenes and CNTs are usually produced in similar conditions and, in fact, were notoriously observed in a carbon arc discharge method [4] intended to produce only fullerenes [5]. In addition to arc discharge, another physical method for carbon vaporization, high-energy laser ablation, has also been shown to generate inhomogeneous mixtures of fullerenes and CNTs. Simultaneous formation of fullerenes and CNTs was also shown to occur in a HiPco reactor [6], where the produced fullerenes were separable in a solvent indicating weak bonding to the CNTs [7]. Transmission electron microscopy (TEM) observations often suggest that the surface of many CNTs is not clean and they are covered with some coating. It has been proposed that this coating can be converted to fullerenes in the intense electron beam of the microscope [8,9]. Also there have been several papers, where the presence of fullerene-like structures (or perhaps even fullerenes) on the surface of CNTs can be distinguished, but are not discussed [10–12].

There have been published very few experimental works attempting to combine fullerenes and CNTs into a single structure. Fullerene and CNT physical merging by means of solid phase mechanochemical reactions was proposed by Li et al. [13]. Theoretically, the combination of a fullerene and a CNT was first shown in a dynamic process of fullerene penetration into a CNT [14]. Recently, we have reported a one-step continuous process for the synthesis CNTs with covalently attached fullerenes [15]. This hybridization of fullerenes and CNTs resulted in the creation of a new material, NanoBuds, with interesting properties [15]. For instance, this structural arrangement of highly curved (chemically reactive) fullerenes and inert, but thermally and electrically conductive, CNTs, was shown to exhibit enhanced cold electron field emission properties [15]. In this paper, on the basis of parametric investigations and *in situ* sampling of the product from different locations in

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the reactor we investigate the conditions and mechanisms for NanoBud formation.

2. Experimental

2.1. Experimental setup

The experimental method used for the continuous synthesis of NanoBuds is based on ferrocene vapor decomposition in a CO atmosphere (Fig. 1a). The catalyst precursor was vaporized by passing ambient temperature CO (with a flow rate of 300 cm^3/min) through a cartridge filled with ferrocene powder [16]. The flow containing ferrocene vapor was then introduced into the high temperature zone of a ceramic tube reactor through a water-cooled probe and mixed with additional CO (100 cm^3/min). The partial vapor pressure of ferrocene in the reactor was, thus, maintained at 0.7 Pa. The reactor set temperature was varied from 800 °C to 1150 °C.

It was experimentally found that small concentrations of H_2O vapor and CO_2 significantly alter the density of fullerenes on the CNTs. Therefore, controlled amounts of H_2O and CO_2 were added together with the carbon source via a mass flow controller in addition to the H_2O and CO_2 produced at the reactor wall. In order to introduce the H_2O vapor, a flow of a carrier gas was passed through a water saturation vessel. The amount of H_2O was varied from 0 to 405 ppm. The concentration of introduced CO_2 was varied from 0 to 12000 ppm. The carrier gas water vapor saturation conditions were monitored on-line by a Gasmet Fourier-transform infrared spectrometer. The product after the reactor was deposited on TEM grids using an electrostatic precipitator. The morphology of the as-obtained product was investigated with a field emission transmission electron microscope (Philips CM200 FEG).

2.2. Experimental results

Fig. 2 shows TEM images of the product at different magnifications when 145 ppm H_2O vapor was introduced in the reactor. Low magnification images suggest that the CNTs are 'dirty', however, increasing the magnification reveals the presence of both spherical and ellipsoidal structures (fullerenes) on the surface of CNTs and catalyst particles (Fig. 2b and c). The diameters of these structures, estimated from TEM images, are in the size ranging from 0.4 to 2 nm [15].

An example of the change in the product morphology with reactor conditions is shown in Fig. 3, wherein the effect of water vapor concentration introduced into the reactor at a temperature of 1000 °C is clearly seen. Experimental conditions without adding additional water resulted in the formation of pure CNTs together with non-active catalyst particles. Nevertheless, the presence of a small number of fullerenes on the surface of the CNTs can always be observed. CNTs decorated by fullerenes start to form in abundance at a water vapor concentration of 45 ppm and higher. Conversely, at high concentrations of H_2O (higher than 245 ppm), the main product consisted of inactive catalyst particles and contained few CNTs

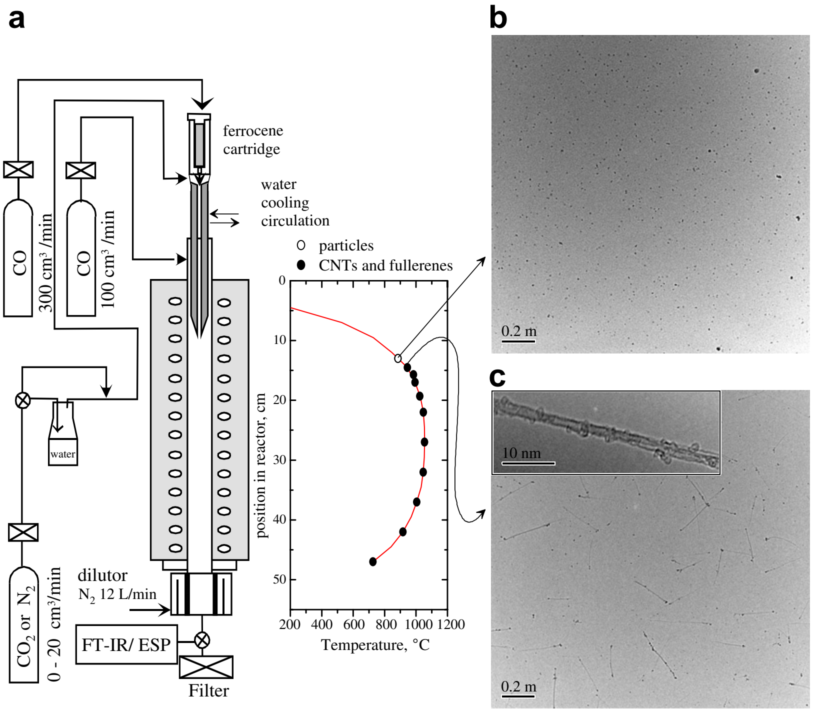

Fig. 1. (a) Schematic presentation of the experimental setup, temperature profile at set temperature of 1000 °C; position and temperature inside the reactor where *in situ* sampling was carried out from. TEM images of products *in situ* collected in the reactor at temperatures of (b) 885 °C and (c) 945 °C.

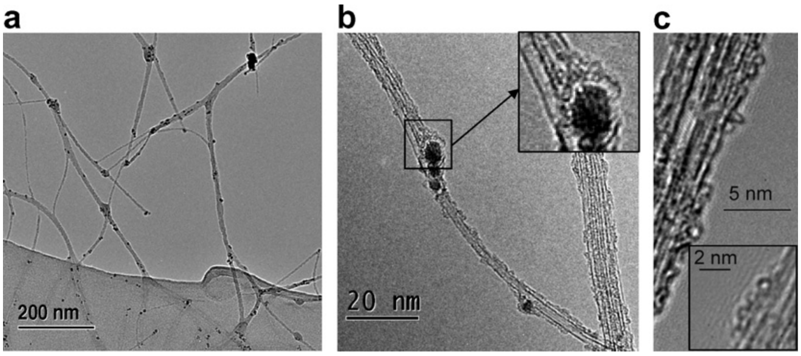

Fig. 2. TEM images of NanoBuds at different magnifications: (a) low magnification TEM image of CNTs seemingly covered by some coating, (b) TEM images at intermediate magnification revealing the presence of spherical structures on CNTs and catalyst particles (inset) and (c) High resolution TEM images showing fullerenes of different shapes and sizes.

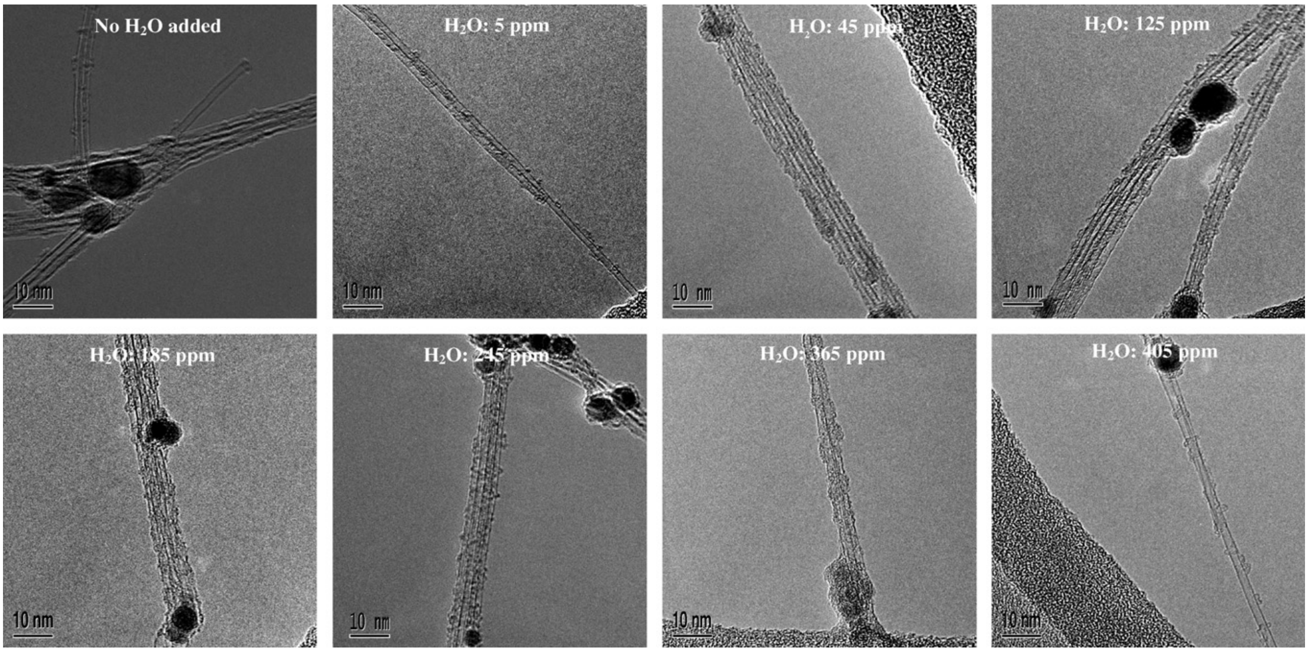

Fig. 3. TEM images of products demonstrating the effect of the concentration of introduced water vapor on the coverage of CNTs by fullerenes.

covered by fullerenes. Similar results were found when the CO_2 concentration was varied in the experimental system. The optimal CO_2 concentration was between 2000 and 6000 ppm.

It was found that, at specific concentrations of H_2O and CO_2, the reactor temperature also plays an important role in the simultaneous synthesis of fullerenes and CNTs. The effect of the reactor temperature on the product was studied with 145 ppm introduced water vapor (Fig. 4). At temperatures of 1100 and 1150 °C (not shown) only non-active catalyst particles were observed. The maximum fullerene coverage was found at 1000 °C and the amount of fullerenes on the surface of CNTs decreased with decreasing temperature down to 800 °C.

Meanwhile, the simultaneous formation of fullerenes and CNTs on the surface of catalyst particles was assumed *a priori*. However, one can propose the mechanism of the fullerene formation either in the gas phase or their catalytic formation and detachment from particles at high temperatures due to their volatility and their further deposition on the surface of CNTs downstream of the reactor. In order to detect the location (and temperature), where fullerenes appear on CNTs, an in situ sampling experiment from the centerline of the reactor was carried out. For this purpose, a stainless steel rod with an attached silica thin film coated nickel TEM grid was rapidly inserted into the reactor and held in a position for 20 s. The product was collected due to the thermophoretic forces between the hot ambient temperature atmosphere in the reactor and the cold sampling rod. The *in situ* sampling experiments were carried out at the set temperature of 1000 °C, corresponding to the maximum reactor temperature of 1058 °C, and in the presence of 125 ppm H_2O introduced in the reactor. The temperatures at the *in situ* sampling locations were measured by thermocouples after collection. Examinations of the *in situ* collected samples at 12 different locations in

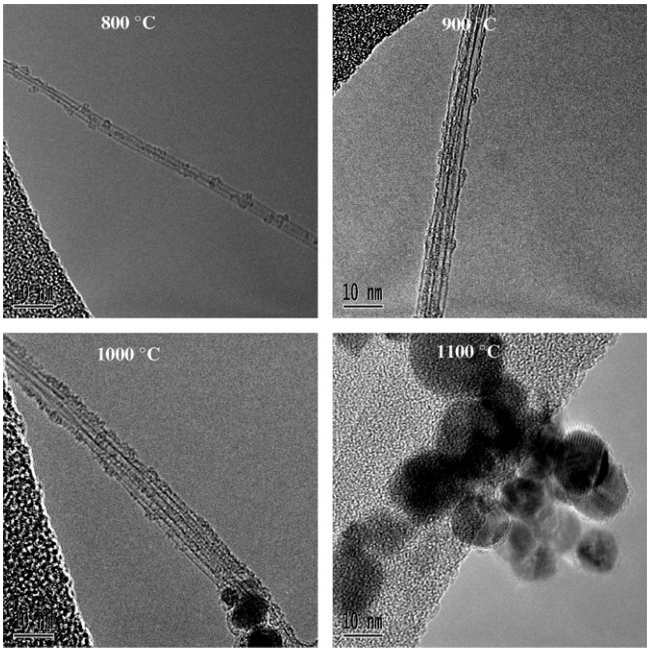

Fig. 4. TEM images of products demonstrating the effect of temperature with 145 ppm introduced water vapor.

the reactor revealed the presence of fullerenes on the surface of CNTs everywhere where CNTs were found. Fig. 1b and c shows the TEM images of the sample collected at the conditions, where the appearance of CNTs was found, i.e. between 885 °C and 945 °C. At 885 °C, only catalyst particles were observed among the sample. At the next sampling location, which was 1.5 cm apart (downstream of the reactor) CNTs were observed. TEM observations revealed the presence of fullerenes on the surface of CNTs at this location and in the samples collected further away (Fig. 1a).

3. Discussion

3.1. Chemical reactions

As has been shown, the fullerene concentration on the surface of CNTs can be altered by changing the concentration of H_2O and CO_2 in the system. It is known from the literature that fullerenes (or even fullerite) can be formed under the effect of acid treatment of single-walled CNTs [17]. Since oxidation may be important for tailoring carbon structures [18] one can expect a similar effect during the CNT growth in our flow reactor when extra water or carbon dioxide are present as oxidizing agents. This can result at certain reactor conditions and H_2O and CO_2 concentrations in the formation of hybrid fullerene/CNT structures, i.e. NanoBuds.

As was shown in our previous Letter [19] there two main reactions occur in the reactor: CO disproportionation,

$$CO_{(g)} + CO_{(g)} \Longleftrightarrow C_{(s)} + CO_{2(g)},$$
$$\Delta H_{900} = -169\ \text{kJ/mol},\quad \Delta G_{900} = 34.7\ \text{kJ/mol}, \tag{1}$$

and CO hydrogenation,

$$H_{2(g)} + CO_{(g)} \Longleftrightarrow C_{(s)} + H_2O_{(g)},$$
$$\Delta H_{900} = -136\ \text{kJ/mol},\quad \Delta G_{900} = 32.5\ \text{kJ/mol}.$$

It is worth noting that reaction (1) is dominant in the system due to the low concentration of hydrogen that is formed only as a product of the ferrocene decomposition reaction. Reactions (1) and (2) are very similar thermodynamically [20]. At low temperatures these reactions are shifted toward the formation of atomic carbon. The thermodynamic equilibrium ($\Delta G = 0$) is observed at a temperature of approximately 700 °C. At high temperatures the inverse reactions prevail. Kinetic investigations of reaction (1) shows appreciable reaction rates in the temperature interval from 470 to 820 °C [20]. At temperatures lower than 325 °C, this reaction is limited kinetically and at temperatures higher than about 900 °C it is prohibited thermodynamically. However, reaction (1) (as well as reaction (2)) can occur even at 900 °C even though $\Delta G_{900} > 0$, since the equilibrium concentration of CO_2 at this temperature is about 2.7%, i.e. higher than the concentration introduced or formed in the reactor. Our previous [16] and current *in situ* sampling experiments at the set temperature of 1000 °C showed that CNTs grow in a temperature window at around 900 °C. At this condition, the inverse reactions (1) and (2) of carbon oxidation (etching) by water or carbon dioxide are favorable. This supports the existence of a mechanism wherein fullerene formation is the result of the oxidation process.

It is worth noting that another important role of CO_2 and H_2O can be the prevention of cementite, Fe_3C, formation, since the formed iron carbide in the presence of CO_2 (or H_2O) would react according to reaction:

$$Fe_3C_{(s)} + CO_2 \Longleftrightarrow 3Fe_{(s)} + 2CO_{(g)},$$
$$\Delta H_{900} = 158\ \text{kJ/mol},\quad \Delta G_{900} = -34.6\ \text{kJ/mol}.$$

This can increase catalyst life time by preventing poisoning of the catalyst particle during CNT growth and also by maintaining reactions (1) and (2) [21–23].

3.2. Mechanism of NanoBud formation

As has been shown by *in situ* sampling experiments, fullerenes were present in all samples, where CNTs were detected. Thus, one can assume that CNTs and fullerenes were formed simultaneously. TEM observations (Fig. 2b) suggest that both fullerenes and CNTs originate from graphitic carbon precipitated on the surface of Fe nanoparticles catalysing CO disproportionation [19,20,24]. This is supported by the results of molecular dynamics simulation [25–27] predicting that various curved carbon nanostructures (fullerenes or fullerene-like structures) can be formed on the surface of catalyst particles. Recently, we discussed the mechanism of CNT formation governed by graphene topology and considered the effect of the presence of pentagons, hexagons, and heptagons [24]. The growth of

CNTs is believed to occur from a dynamic layer of carbon on the catalyst particle surface. The growth of CNTs occurs in a steady-state regime by providing additional carbon from reactions (1) and (2) at the catalyst surface to the edge of the carbon layer. The growth of CNTs can not proceed if the dynamic layer is poisoned by amorphous carbon, since the presence of foreign atoms on the surface of monomolecular carbon layer can destroy its graphitic structure. Therefore, the formation of CNTs occurs in the temperature range where the inverse reactions (1) and (2) are significant either due to the introduction or formation of H_2O vapor and CO_2 upstream the reactor [21].

Before discussing the mechanism of NanoBud formation, let us classify observed NanoBud structures. Fullerenes on the surface of CNTs can possess a complete spherical structure and can be covalently bonded to CNTs via sp^3-hybridized carbon atoms, e.g. by [2 + 2] cycloaddition as shown in Fig. 3b in our previous Letter [11]. For the creation of this type of NanoBud, in addition to hexagons, exactly 12 pentagons should be formed (we do not take into consideration the presence of pentagon–heptagon pairs). The second type, in which all carbon atoms are sp^2-hybridized, can be described as a fully hybrid structure, where a fullerene is a continuous part of a CNT as shown in Fig. 3c–e in [11]. It is important that the continuity of the carbon layer for the incomplete fullerenes demands the generation of less than 12 pentagons. Also, in order to join together an incomplete fullerene and the CNT, a sufficient number of heptagons or octagons should be present in the neck of the hybrid structure to reduce the topological curvature to zero [1]. Thus, the second type of NanoBuds can be envisioned as a short CNT, the formation of which was interrupted at the initial stage of the growth.

However, whatever the structure of the NanoBuds, initially a certain number of pentagons should be generated for fullerene formation. The formation route of those pentagons, promoted by the presence of etching agents, is expected to determine the formation of fullerenes. Fig. 5 schematically depicts our understanding of the formation of pentagons on the surface of a catalyst particle. Carbon atoms at the edge of the dynamic layer (with dangling bonds) can be attacked by etching agents, e.g. H_2O molecules. This results in the release of CO and H_2 and in the closure of the rings consisting of five carbon atoms (pentagon formation). Further, the formed pentagon can be surrounded by hexagons, and new pentagons can be formed due to the suggested schematics. According to the proposed mechanism, the concentration of the etching agents should have some optimal value, since a low concentration of oxidants leads to the formation of pure CNTs (without fullerenes), while high concentrations should suppress the formation of CNTs because of excess positive curvature (by converting too many pentagons from hexagons at the edge of the dynamic layer). This behavior has been experimentally observed.

It is worth noting that budding sp^2-hybridized (type I) fullerenes can turn into fullerenes of type II. It is known that the oxidation rate of CNTs depends on their structural features such as curvature defects (the presence and positions of pentagon and heptagon rings) and their helicity [28]. The neck of the budding fullerene that contains heptagons is more reactive compared to pentagons with such oxidizers as H_2O and CO_2, since a pentagon ring in a graphene sheet possesses a negative charge, while a heptagon has a positive one [29]. Thus, water (and carbon dioxide) molecules having a partially negatively charged oxygen atom tend to react with heptagons rather than pentagons. Consequently, an oxidizer can react with heptagons localized at the narrow neck of a budding fullerene breaking a bond and restructuring the fullerene, which eventually leads to fullerene separation and formation of sp^3-bonded fullerene.

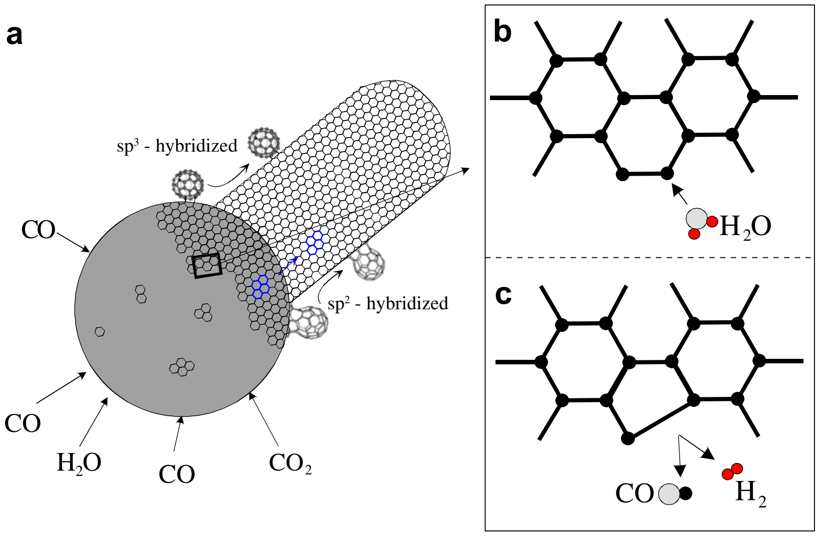

Fig. 5. Schematic presentation of (a) NanoBud growth by continuous transportation of a carbon layer from a particle to a CNT; (b) pentagon formation at the edge of the dynamic layer of a growing CNT and (c) growth mechanism of NanoBuds.

4. Conclusion

We have synthesized NanoBuds, single-walled CNTs covered by covalently bonded fullerenes, in a one-step continuous process by ferrocene vapor decomposition in a carbon monoxide atmosphere. Fullerenes and carbon nanotubes were simultaneously formed by carbon monoxide disproportionation on the surface of iron particles in the presence of etching agents H_2O and CO_2. Varying the introduced H_2O and CO_2 in the reactor revealed that the optimal reagent concentrations were between 45 and 245 ppm for H_2O and between 2000 and 6000 ppm for CO_2. Changing the temperature of the NanoBud synthesis at a introduced H_2O concentration showed its significant effect on the product morphology. *In situ* sampling of the product formed at different locations in the reactor showed that fullerenes were formed together with CNTs in the temperature interval between 885 and 945 °C. A mechanism of the fullerene formation during the CNT growth is proposed.

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