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Full Paper

Growth of a Carbon Micro- and Nanocoils Mixture using NiSO₄ as the Catalyst Precursor**

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A mixture of carbon micro- and nanocoils (CMCs/CNCs) is synthesized by catalytic pyrolysis of acetylene at 650 °C using NiSO₄ as the catalyst precursor. The morphology of the grown product is analyzed by scanning electron microscopy (SEM). Experimental results indicate that, in general, the CMCs are in double-helical form, while most of the grown CNCs are in twisted single-helical form. The coil diameters of CMCs and CNCs are approximately 4 to 10 μm and 300 to 400 nm, respectively. Raman spectra indicate that the real active catalyst precursor for growing CMCs/CNCs is NiSO₄, while NiO is not an effective catalyst precursor for synthesizing CMCs or CNCs.

Keywords: Carbon microcoils, Carbon nanocoils, Catalyst precursor, Growth mechanism, NiSO₄

1. Introduction

In 1990, Motojima et al. reported the growth of helical carbon fibers.^[1] Since then, there has been growing interest in the synthesis and potential applications of these helical carbon fibers or tubes due to their unique three-dimensional (3-D) morphology and interesting growth mechanisms.^[2,3] On the micrometer level, these 3-D materials have potential for use as field emitters,^[4,5] nano/micro springs or actuators,^[6,7] infrared detectors,^[8] etc. Macroscopically speaking, they can be used as wave absorbers,^[9–11] vibration-absorptive materials, elastic composites, etc. With regard to the study of the electromagnetic wave absorption, much work has been reported. In the work of Tang et al.,^[10] the maximum reflection loss of the twin CNCs reached –36.09 dB. Motojima et al. tested the electromagnetic wave absorption properties in the gigahertz region (12–110 GHz) of CMCs, and a value of the reflection loss greater than –20 dB (above 99% absorption) in 30–35, 50–55, 75–80, and 95–100 GHz can be obtained.^[9] Although both CNCs and CMCs have excellent wave absorption properties, a mixture of the two is needed to achieve wideband absorption.

Both CMCs and CNCs have been successfully synthesized by many groups. Transition metals have always been applied

as the catalyst to synthesize CMCs/CNCs. Fe-In-Sn or Fe-Sn as the catalysts have been used by our group to prepare high yields of CNCs on ITO, Si, or SiO₂, and the diameters of the CNCs are in the range of several tens to several hundreds of nanometers.^[12–14] Wang et al. prepared Cu nanoparticles with a narrow size distribution to grow the CNCs with a diameter of less than 200 nm.^[15] Nickel is also one of the typical catalysts for growing the helical carbon fibers (CFs). Motojima and co-workers were the first to use a Ni catalyst to synthesize CMCs.^[16–18] According to their research, CMCs were mainly prepared by metal-activated pyrolysis of acetylene containing a small amount of sulfur or phosphorus impurity. Similarly, Chen et al. have prepared CMCs by catalytic pyrolysis of acetylene containing a small amount of thiophene using Ni foam as both catalyst and substrate.^[19] Jian et al. used Ni nanoparticles to synthesize three kinds of carbon coils, with the coil diameter ranging from 150 nm to 3 μm, by adjusting the gas flow rate of N₂,^[20] however, the synthesis of the mixture of CMCs and CNCs in a growth process has not been realized. Furthermore, during the CMCs or CNCs growth using the methods mentioned above, a small amount of toxic S- or P-containing gas compound is needed, and a considerable amount of these substances is required for the large-scale CMC or CNC synthesis. In this work, we have successfully synthesized the mixture of CMC and CNC using only NiSO₄ as the catalyst precursor without feeding the toxic gases (S or P) and H₂ addition. The mechanism of the growth of the CMC/CNC mixture has also been discussed.

2. Results and Discussion

Figure 1 shows the SEM images of carbon deposits synthesized at temperatures a) 550 °C, b) 650 °C, and c) 750 °C using NiSO₄·6H₂O, which has been initially calcined

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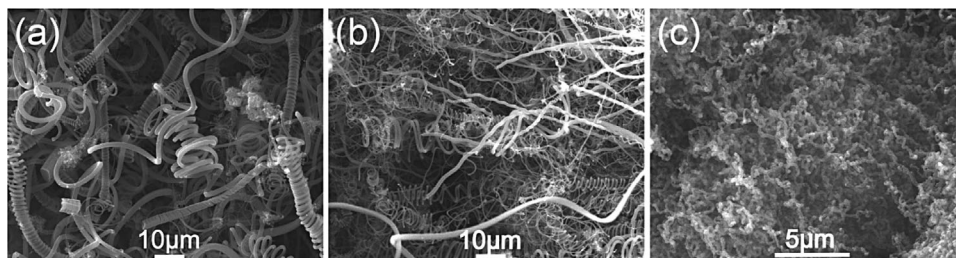


Fig. 1. SEM images of the carbon deposits synthesized at the reaction temperatures of a) 550 °C, b) 650 °C, and c) 750 °C.

at 650 °C, as the catalyst precursor. At a lower growth temperature of 550 °C, a high yield of CMCs with coil diameters of 4 to 10 μm, and a small amount of carbon fibers are obtained (Fig. 1a). At 650 °C, besides the CMCs, many carbon nanofibers (CNFs) are grown by the grain catalysts (Fig. 1b). In fact, these small CNFs are not straight but spiral, as corroborated by the enlarged transmission electron microscopy (TEM) image in Figure 2b. This demonstrates that a mixture of CMCs and CNCs can be obtained at 650 °C. It is interesting to note that, when the reaction temperature reaches 750 °C, no CMCs or CNCs, but some irregular short CNFs, are grown from the catalysts. It is considered that the catalytic activity, the shape, or the composition of the catalyst may change with the increase in

temperature, which leads to the growth of different carbon deposits at different temperatures.

Figure 2a and b show the low magnification SEM images of two typical areas for the carbon deposits grown at 650 °C. The carbon micro/nano deposits grown comprise different structural forms such as, fibrous, coiled, non-fibrous, and non-coiled, however more than 90% of carbon products on the surface are helical CMCs and CNCs, with a 1:1 ratio in quantity. Careful observation of Figure 1b and 2a shows that most of the grown CMCs are double-helical forms, which is similar to findings reported by Motojima and co-workers.^[18,21] The inset in Figure 2b shows a typical enlarged TEM image of the grown CNCs, most of which are twisted single-helical forms and are approximately 300 and 400 nm

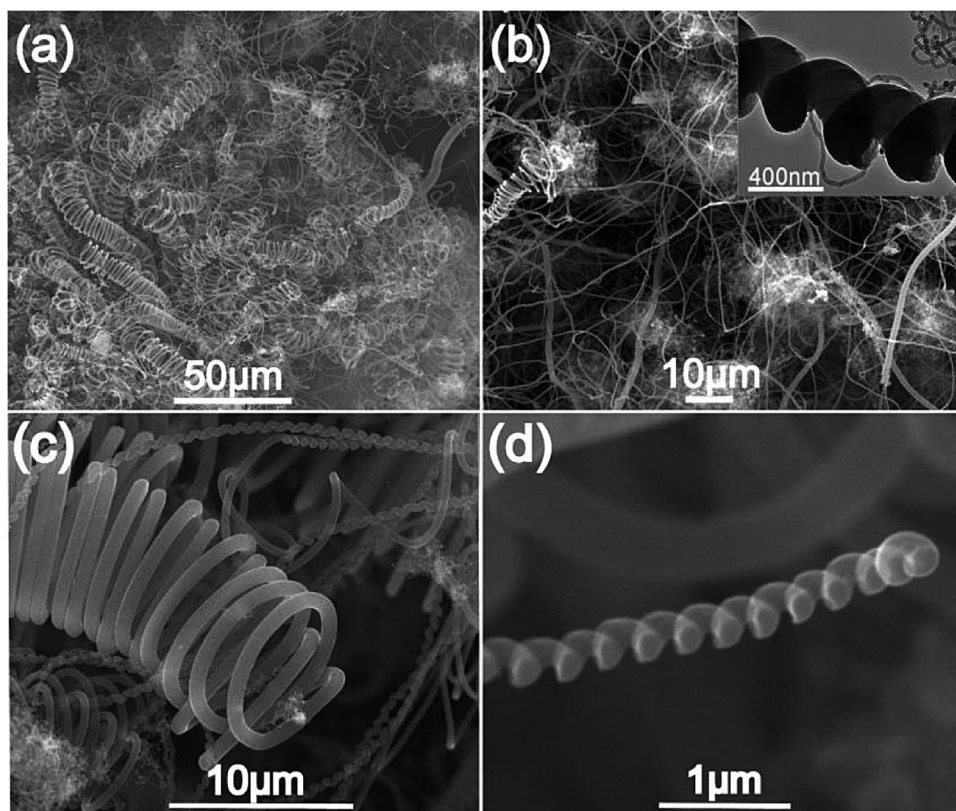


Fig. 2. SEM images of the mixture of a) CMCs, and b) CNCs grown at 650 °C. Inset in b) is an enlarged TEM image of the grown CNC. Typical SEM images for the tips of c) single CMC, and d) CNC.

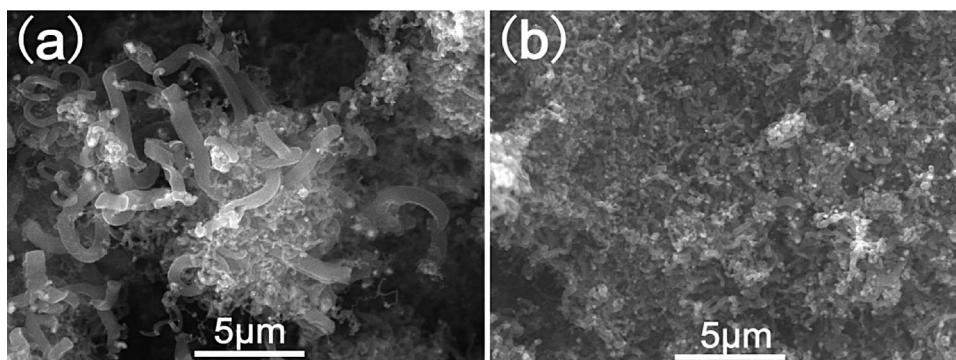


Fig. 3. SEM images of the carbon deposits synthesized at 650 °C by the catalysts calcined in air at a) 750 °C, and b) 850 °C.

in fiber diameter and coil diameter, respectively. Figure 2c and d show the SEM images of the tips of as-grown CMCs and CNCs using NiSO_4 as the catalyst precursor. On the tip of the CMCs, a grain of Ni catalyst is observed, from which two fibers grow and intertwine to form a double-helical CMC (DH-CMC). This observation is similar to that reported by Motojima et al. who have proposed a three-dimensional growth model of DH-CMCs which is based on the anisotropy for the carbon deposition among three crystal faces of the catalyst.^[22] The presence of catalyst particles are not observed at the CNC tips, as shown in Figure 2d, indicating a possible bottom growth mechanism for the CNCs. The carbon structures in CMCs/CNCs are inspected by Raman spectral analysis with an excitation laser wavelength of 632.8 nm. Two main peaks appear in the Raman spectra, one is around 1317 cm^{-1} , known as D-band, and the other is around 1596 cm^{-1} , known as G-band. The carbon product has an average ID/IG of 0.9, indicating a low degree of crystallinity in the structures of CMCs/CNCs. The mechanism for the formation of the CMC/CNC mixture needs further study.

In the beginning, it was speculated that the catalytic activity of the catalyst would be decreased with the increase in temperature, which should be further confirmed. Keeping the reaction temperature of 650 °C unchanged, the calcination temperature was raised from 750 to 850 °C. Figure 3 shows the SEM images of carbon deposits synthesized at 650 °C by the catalysts calcined in air at a) 750 °C and b) 850 °C. It is found that no CMCs or CNCs are grown, but only some irregular and short carbon fibers are formed, totally different from the carbon deposits prepared by the catalyst calcined at 650 °C. Therefore, this result is the confirmation of dependence of catalytic activity or catalyst composition on calcination temperature. The chemical composition of calcined catalyst at different temperatures was demonstrated with Raman spectra analysis, as shown in Figure 4. Table 1 shows the corresponding frequency shifts observed for the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ after calcination at different temperatures. At the bottom of Figure 4 is the Raman spectrum of

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ before calcination, which is similar to that reported by Krishnamurti, where the wave number shifts up to the value centered at 206 and 244 cm^{-1} .^[23] With the increase in temperature, the removal of crystalline water occurs for $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, however this loss occurs in two steps.^[24] It is observed that, when the calcination temperature rises to 550 °C, the material has changed from the original $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ to pure NiSO_4 . With a further increase in calcination temperature (from 550 to 650 °C), the decomposition of NiSO_4 does not occur because only NiSO_4 is detected in the Raman spectra. Raman peaks for NiSO_4 were still observed, even when the calcination temperature reached 750 °C, however the peaks at 452.9 and 497.4 cm^{-1} at temperature 650 °C broaden with blue shift to 460.3 and 503.7 cm^{-1} , respectively (as indicated by the arrows). This indicates that the decomposition of NiSO_4 takes place at 750 °C. At higher temperatures, up to 850 °C, only a single broad peak for NiO is observed, indicating that NiSO_4 has been completely decomposed at this temperature. The above preliminary results demonstrate that the real active catalyst precursor for the CMC/CNC growth is NiSO_4 , whereas NiO cannot serve as an effective catalyst

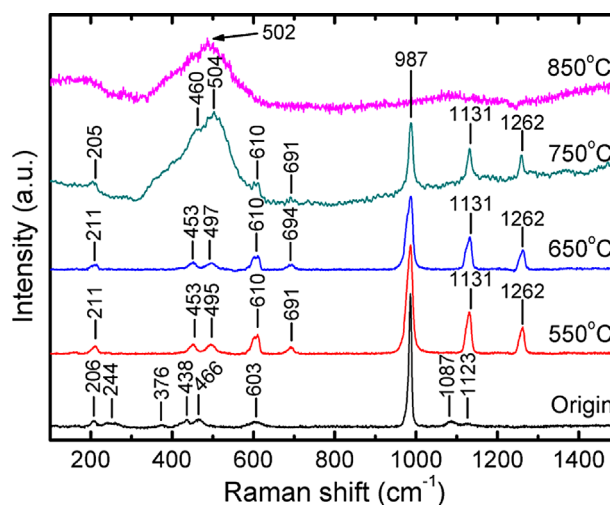


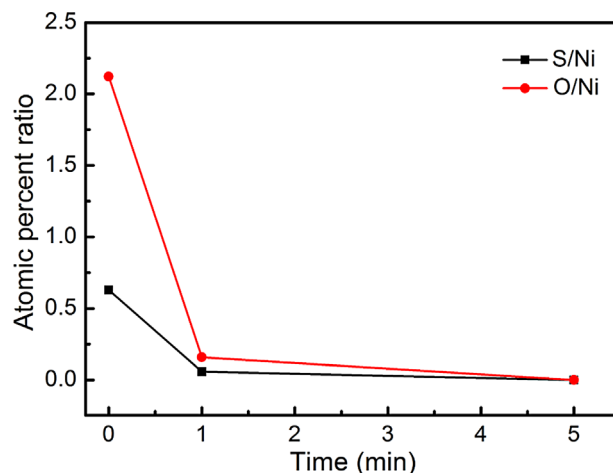
Fig. 4. Raman spectra for the $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ calcined at various temperatures.

Table 1. Raman shifts for the NiSO₄·6H₂O calcined at various temperatures.

Temperature (C)	Origin	550	650	750	850
	206.2				
		210.6	210.6	205.1	
	243.6				
	376.0				
	438.0				
	465.6	452.9	452.9	460.3	
		495.3	497.4	503.7	
Raman shift (cm-1)	603.1	610.3	610.3	610.3	501.6
	986.0	690.7	693.8	690.7	
	1086.9	986.9	987.9	987.9	
	1123.3				
		1130.9	1130.9	1130.9	
		1262.3	1262.3	1262.3	
Composition	NiSO ₄ ·6H ₂ O	NiSO ₄	NiSO ₄	NiSO ₄ & NiO	NiO

precursor for growing CMCs or CNCs, and has a destructive effect on the catalytic activity of NiSO₄ during the CVD process. Another question proposed is why the carbon materials obtained at growth temperatures of 550 and 650 °C are different, but the compositions of the catalyst are the same. It can be explained that the temperature can also affect the aggregation state of the NiSO₄ catalyst, which leads to a different size distribution of the catalyst. Therefore, the mixture of CMCs and CNCs can be synthesized at 650 °C.

Figure 5 shows the elemental percentage ratio changes of the NiSO₄ catalyst precursor with feeding acetylene at 650 °C for 0 to 5 min. It is observed that, with the increase of acetylene feeding time, both the ratio of O to Ni and S to Ni decrease rapidly, which suggests that NiSO₄ has been partially reduced by acetylene. During the reduction process H₂S is released and dissociates on the Ni surface, after which S from H₂S is adsorbed onto the Ni surface.^[25] For 5 min acetylene time, Ni contents decrease to approximately 0.5 at.-%, however S contents cannot be detected by energy dispersive X-ray (EDX) spectroscopy. This could be because of the low concentration of elemental S being below the EDX detection limit. Figure 6a to c show a series of SEM images indicating the morphological changes in the NiSO₄ catalyst precursor caused by feeding acetylene at 30 sccm for 1 to 5 min. For 1 min feeding time, carbon materials have been precipitated from the surface of NiSO₄ catalyst precursor and very few short and irregular CNFs have been grown, as shown in Figure 6a. In Figure 6b, some CMCs and CNCs are grown out after feeding acetylene for 3 min. When the feeding time reaches 5 min, almost 100% yield of CMCs and CNCs is observed to be grown on the catalyst surface as shown in Figure 6c, and their lengths reach up to several hundreds of micrometers. For comparison, the morphological changes of the NiO catalyst precursor have been investigated by feeding acetylene for a short time, as shown in Figure 6d - f. Similar to NiSO₄, highly irregular CNFs have been grown


 Fig. 5. Dependence on the acetylene feeding time of elemental percentage ratio changes in the NiSO₄ catalyst.

from the surface of a NiO catalyst precursor by feeding acetylene for 1 min (Fig. 6d), however for the feeding time of 3 min, no CMCs or CNCs are observed, but only some CNFs with large fiber diameter are grown. The catalyst particles are observed on the tips of these CNFs, indicating a tip growth mechanism, as shown in Figure 6e. The continuous feeding of acetylene up to 5 min leads to an increase in length of grown CNFs without formation of helical carbon fibers (Fig. 6f), which is totally different from the grown structures using the NiSO₄ catalyst precursor.

3. Conclusion

A mixture of CMCs and CNCs is successfully synthesized at a growth temperature of 650 °C using NiSO₄ as the catalyst precursor. Furthermore, the effect of growth and calcination temperatures on the synthesis of CMCs/CNCs has been investigated. For different growth temperatures, varieties of carbon deposits are grown. At 650 °C, a mixture of CMCs/CNCs is produced, while at 550 °C, only CMCs, together with some straight carbon fibers, are obtained. Higher growth temperatures, up to 750 °C, result in only the growth of some irregular CNFs. Calcination temperatures ranging from 550 to 650 °C yield pure NiSO₄, which is found to be an effective catalyst precursor for growing CMCs/CNCs, while no CMCs or CNCs are synthesized using NiO as the catalyst precursor. EDX analysis shows that a trace amount of elemental S exists in the catalyst during growth, indicating that S is crucial for the helical growth of CMCs/CNCs. In the grown carbon deposits, Ni grain catalyst is usually observed on the tip of the CMCs, indicating a tip growth mechanism for the CMCs, while absence of Ni grain for the CNCs is a possible indication of a bottom growth mechanism.

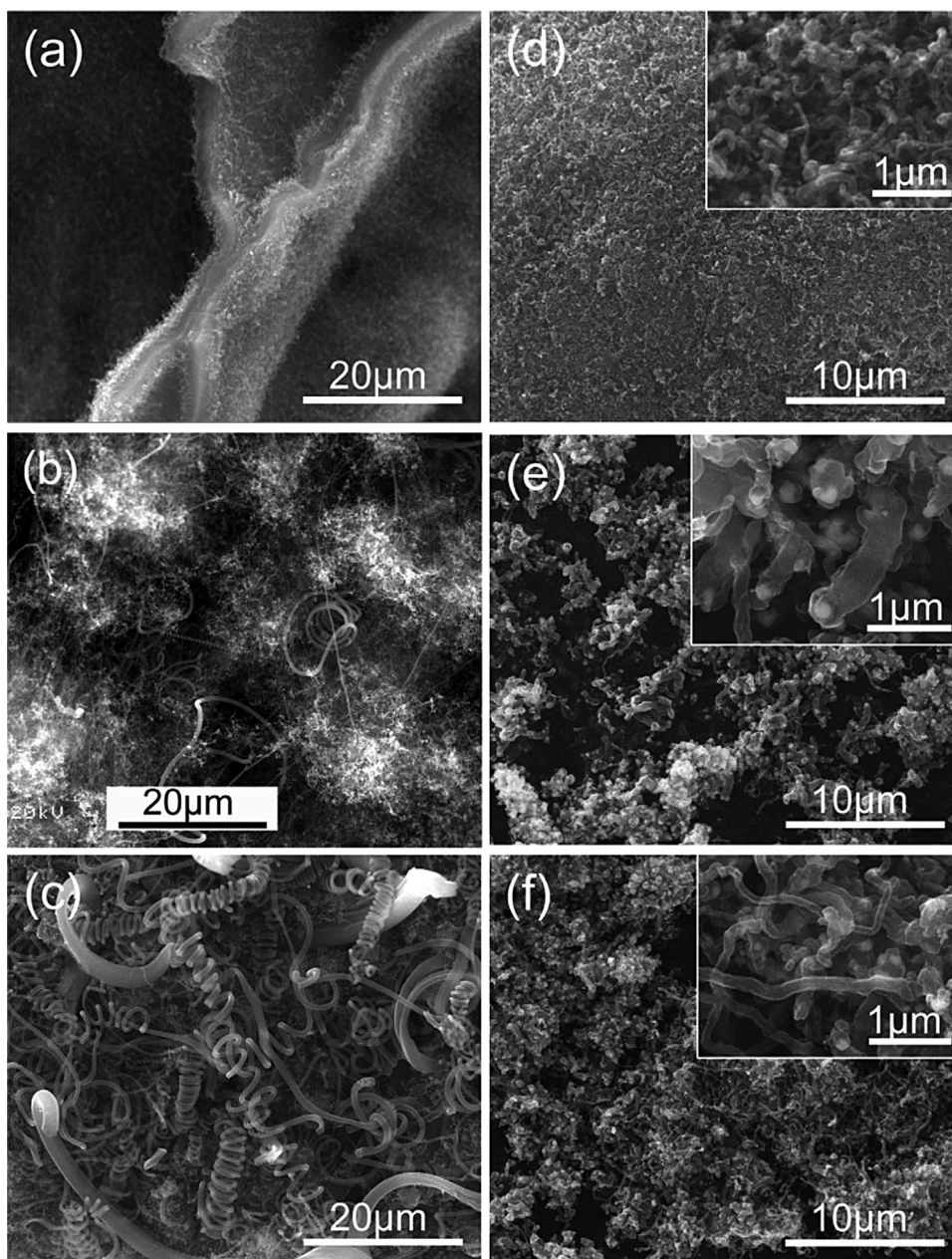


Fig. 6. SEM images of the NiSO_4 catalyst precursors after feeding acetylene at 650°C for a) 1 min, b) 3 min, and c) 5 min. SEM images of the NiO catalyst precursors after feeding acetylene at 650°C for d) 1 min, e) 3 min, and f) 5 min. Insets in parts (d - f) are the corresponding enlarged images.

4. Experimental

A 0.2 M solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was selected as the catalyst precursor. A drop, having $50\ \mu\text{L}$ volume of NiSO_4 aqueous solution, was dropped onto the SiO_2 substrates ($8\text{ mm} \times 8\text{ mm}$), and dried at 40°C for 10 min. Then the samples were calcined in air at temperatures of 650 to 850°C for 30 min. Carbon deposits were synthesized on these substrates by a thermal CVD system at 550 to 750°C for 30 min growth time by introducing acetylene and Ar gases with flow rates of 15 and 300 sccm, respectively. In addition, at the initial stage, we have investigated the morphological changes of carbon deposits synthesized at 650°C under constant gas flow rates but for reaction times ranging from 1 to 5 min.

The morphology and structure of the catalyst precursor and the synthesized carbon products were analyzed by SEM (JSM-6360LV), TEM (Tecnai G220, FEI, Eindhoven, Netherlands), RS (Renishaw inVia plus, He-Ne laser, 632.8 nm , 50% laser power, $50\times$ magnification, 10 s accumulations and twice accumulations).

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