

# Synthesis of the Carbon Nano/micro Coils Applicable to the Catalyst Support to Hold the Tiny Catalyst Grain

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Carbon coils could be synthesized using  $C_2H_2/H_2$  as source gases and  $SF_6$  as an incorporated additive gas under thermal chemical vapor deposition system. The Ni layer on the  $SiO_2$  substrate was used as a catalyst for the formation of the carbon coils. The characteristics (formation densities, morphologies, and geometries) of the as-grown carbon coils on the substrate with or without the  $H_2$  plasma pretreatment process were investigated. By the relatively short time (1 minute)  $H_2$  plasma pretreatment on the Ni catalyst layered-substrate prior to the carbon coils synthesis reaction, the dominant formation of the carbon microcoils on the substrate could be achieved. After the relatively long time (30 minutes)  $H_2$  plasma pretreatment process, on the other hand, we could obtain the noble-shaped geometrical nanostructures, namely the formation of the numerous carbon nanocoils along the growth of the carbon microcoils. This noble-shaped geometrical nanostructure seemed to play a promising role as the good catalyst support for holding the very tiny Ni catalyst grains.

Keywords : Carbon coils,  $H_2$  plasma pretreatment, Geometry variation, Catalyst support, Thermal chemical vapor deposition

## I. Introduction

After Ijima's landmark report on the carbon nanotubes (CNTs), a tremendous research was focused on the synthesis of the various forms of the carbon nanomaterials, such as graphenes, horns, onions, helices, and so on [1-4]. Among the forms, the carbon coils have been noticed as the promising materials candidates for the diverse application field because of their spring-like helix-shaped geometry. The unique geometries of the carbon coils may induce an electrical current and consequently generate a

magnetic field. So, the carbon coils have been attracted as the high potential materials for the electromagnetic wave absorbers in the GHz to THz regions, nano/micro-sized tactile sensors, actuators, resonators, mechanical springs, and so on [5-7].

Recently many researchers have interest in the use of the one dimensional carbon nanomaterials (1D-CNMs), like the carbon coils, as the support for the high performance catalyst of the fuel cells because their use seemed to increase the catalytic capability [8-10]. For the direct alcohol fuel cells (DAFCs), the use of 1D-CNMs as the catalyst support was reported

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to greatly enhance the electro-catalytic activity for the alcohol oxidation [8,9]. The main cause for the enhanced catalytic activity by the support seemed to be associated with not only its noble hosting geometry for the metal catalyst particles but its protection ability from the degradation by the carbon monoxide poisoning [8–13]. Anyway, it is obvious that the geometrical nanostructures of the 1D-CNMs as the catalyst support would strongly influence on the catalytic capability.

Meanwhile, the surface area of the catalyst increases with decreasing the size of the catalyst. Consequently, it gives rise to the enhanced active sites for the catalytic performance. From the viewpoint of the catalyst size, therefore, the good catalytic capability of the catalyst should have the size as small as possible. Accordingly, the preparations of the 1D-CNMs for the good catalytic support would require the novel-shaped geometries for holding the catalyst having the size as small as possible.

In this work, we introduce the method for the noble-shaped geometrical nanostructure of the carbon coils as the 1D-CNMs for the good support of the catalyst. Indeed, the noble-shaped geometrical nanostructures for holding the very tiny catalyst grain in this work were composed by the formation of the numerous carbon nanocoils along the growth of the carbon microcoils. To make the noble-shaped nanostructures, we adopted the  $H_2$  plasma pretreatment process prior to the carbon coils deposition reaction. The pretreatment processes on the Ni-layered  $SiO_2$  substrate were varied according to the  $H_2$  plasma pretreatment times, namely the relatively short (1 minute) or long (30 minutes) time. The different Ni thicknesses and the surface state on the substrate due to the different  $H_2$  plasma pretreatment process were employed during the reaction. Among the various techniques to synthesize carbon coils, the incorporated additives, a trace of the sulfur-related species [14–16], was regarded as the promising meth-

od for the formation of carbon coils. We chose  $SF_6$  as a sulfur impurity and tried to reduce the amount of the used  $SF_6$  gas by shortening the injection time [17–19]. In this way, the formation of the carbon coils having the noble-shaped geometrical nanostructures could be obtained. The characteristics of the as-grown carbon coils were examined and discussed. Based on these results, we suggested and discussed the formation and the cause for the formation of the numerous carbon nanocoils along the growth of the carbon microcoils as the noble-shaped geometrical nanostructures.

## II. Experimental

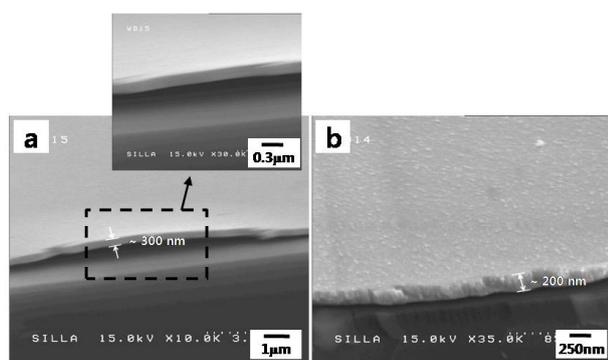
$SiO_2$  /Si substrates in this work were prepared by the thermal oxidation of the  $2.0 \times 2.0 \text{ cm}^2$  p-type Si (100) substrates. The thickness of the silicon oxide ( $SiO_2$ ) layer on Si substrate was estimated about 300 nm. To form the Ni catalyst layer, about 0.01 g of Ni powder (99.7%) was evaporated for 1.5 minutes on the substrate using the thermal evaporator. The estimated Ni catalyst layer on the substrate was about 400 nm.

For  $H_2$  plasma pretreatment, Ni-coated substrate was placed in the radiofrequency (13.56 MHz, 25 W) plasma enhanced chemical vapor deposition (PECVD) system prior to the carbon coils deposition reaction.  $H_2$  gas was introduced into the PECVD chamber. The flow rate for  $H_2$  was fixed at 17 standard  $\text{cm}^3$  per minute (sccm). The substrate was pretreated for 1 or 30 minutes using  $H_2$  plasma at 0.5 Torr total pressure. To improve the etching characteristics by  $H_2$  plasma, we used the protruded substrate holder.

For the carbon coils formation, thermal chemical vapor deposition system was employed.  $C_2H_2$  and  $H_2$  were used as the source gases.  $SF_6$  was injected as the additive during the initial deposition reaction stage. We fixed  $C_2H_2$ ,  $H_2$ , and  $SF_6$  flow rates as 15,

**Table 1. Experimental conditions for the deposition of carbon coils on the substrates.**

C <sub>2</sub> H <sub>2</sub> flow rate (sccm)	H <sub>2</sub> flow rate (sccm)	SF <sub>6</sub> flow rate (sccm)	Total pressure (Torr)	Total deposition time (min)	Source gases flow time (min)			Substrate temp. (°C)
					C <sub>2</sub> H <sub>2</sub>	H <sub>2</sub>	SF <sub>6</sub>	
15	35	35	100	90	90	90	5	750



**Figure 1.** The cross sectional FESEM images for the Ni catalyst-layered substrate after (a) 1 and (b) 30 minutes H<sub>2</sub> plasma pretreatment process. Inset shows the magnified FESEM image of the square area of Fig. 1(a).

35 and 35 sccm, respectively. The overall injection time for C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> was 90 minutes, while the injection time for SF<sub>6</sub> was 5 minutes merely during the initial reaction stage. The detailed reaction conditions for the formation of the carbon coils were shown in Table 1.

Detailed morphologies of CNFs-deposited substrates were investigated by using field emission scanning electron microscopy (FESEM). Ni chemical composition in the catalyst grain located in the head of the carbon nanocoils was analyzed using Energy Dispersive X-ray Spectroscopy (EDS).

### III. Results and Discussion

Fig. 1 show the cross sectional FESEM images for the Ni catalyst-layered substrate after (a) 1 and (b) 30 minutes H<sub>2</sub> plasma pretreatment process, respectively. Compared to the Ni layer thickness (~300 nm)

of the substrate after 1 minute H<sub>2</sub> plasma pretreatment process, the Ni layer thickness was reduced to ~200 nm by the long time (30 minutes) H<sub>2</sub> plasma pretreatment process. As the previous reports [20–23], the hydrogen plasma etching rate for Ni–SiO<sub>2</sub> substrate seems to be comparable to the conventional wet etching or halogen atom plasma etching case. Furthermore, the surface states of the sample in Fig. 1(b) seemed to be much more deteriorated by the long time (30 minutes) H<sub>2</sub> plasma pretreatment process. These results indicate that the long time (30 minutes) H<sub>2</sub> plasma pretreatment process can give rise to not only the reduction of the Ni catalyst layer thickness but the deterioration of the surface state of the substrate.

Two substrates having the different H<sub>2</sub> plasma pretreatment times (1 or 30 minutes) were prepared and they were simultaneously mounted on the substrate holder in the reaction chamber. So, the carbon coils formation reaction on the different substrates would have an identical experimental condition.

Fig. 2(a) shows FESEM images revealing the formation of the as-grown carbon coils on the substrate having the 1 minute H<sub>2</sub> plasma pretreatment process. Fig. 2(b) and (c) show the magnified FESEM images for Fig. 2(a) and (b), respectively. As shown in these Figures, we can see the well-developed carbon microcoils. Diameters of the microsized carbon coils are in the range of one micrometer to several micrometers. The length ranges of the coils are between a few micrometers and a few millimeters.

The details of the micro-sized carbon coils were investigated by the high-magnified FESEM image as shown in Fig. 3. Their individual carbon nanofila-

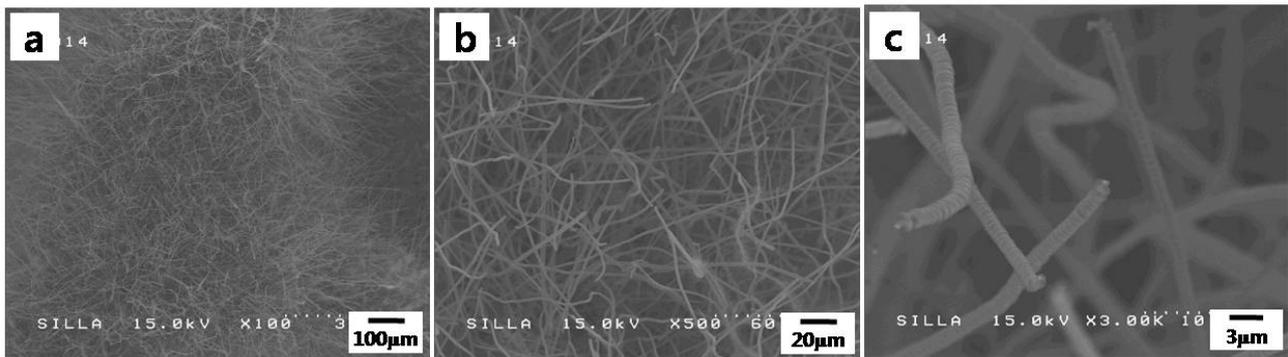


Figure 2. (a) FESEM images for the formation of the as-grown carbon coils on the substrate having the 1 minute  $H_2$  plasma pretreatment process, (b) the magnified FESEM image for Fig. 2(a), and (c) the magnified FESEM image for Fig. 2(b).

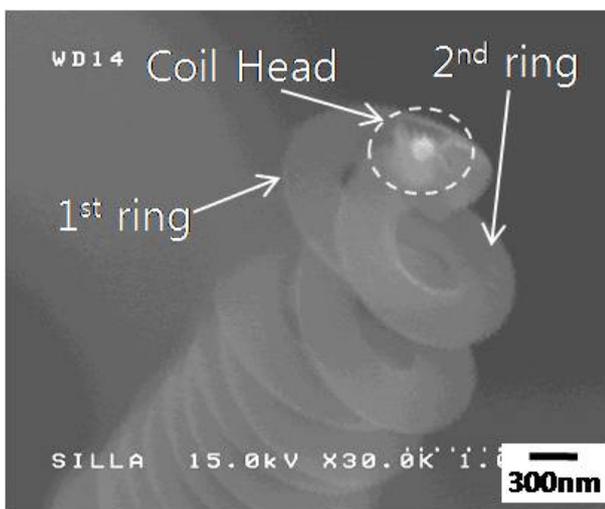


Figure 3. The high-magnified FESEM image for the micro-sized carbon coils. The double helix structure and the ending points of the rings constituting the coils could be clearly observed.

ments constituting the coil have the several sub-micrometers-sized diameters. First and second ending points of the rings could be clearly observed (see the rings in Fig. 3). It indicates that the formation of the micro-sized carbon coils in this work follows a typical double-helix structure for the geometry. For the shape of the rings constituting the coils, circular-type morphology could be observed. The head of the coil could be clearly observed as shown in the arrow head in Fig. 3. As our previous report, the head

of the coil seems to be the initiation point for these two rings [24].

Fig. 4(a) shows FESEM images revealing the formation of the carbon coils having the noble-shaped geometrical nanostructures on the substrate having the 30 minutes  $H_2$  plasma pretreatment process. Fig. 4(b) and (c) show the magnified FESEM images for Figs. 4(a) and (b), respectively. As shown in Fig. 4(c), the noble-shaped geometrical nanostructures for holding the very tiny catalyst in this work were composed by the formation of the numerous carbon nanocoils along the growth of the carbon microcoils.

Fig. 5(a) shows the magnified FESEM images of the formation of the carbon coils having the noble-shaped geometrical nanostructures. The bright spot, regarded as the Ni catalyst, could be shown in the several points, especially in the bent points, of the carbon nanocoils (see the head points of the arrow in Fig. 5(a)). Fig. 5(b) shows the high-magnified image focusing the carbon nanocoils area along the carbon microcoils. As shown in Fig. 5(a), the numerous carbon nanocoils seemed to be interconnected with one another and eventually forming the nanocoils network like the bush (see the bottom area of the carbon microcoils in Fig. 4(c)). The bright spot was also shown in Fig. 5(b) and it seemed to be composed by  $Ni_3C$  as the previous report [25]. The estimated sizes

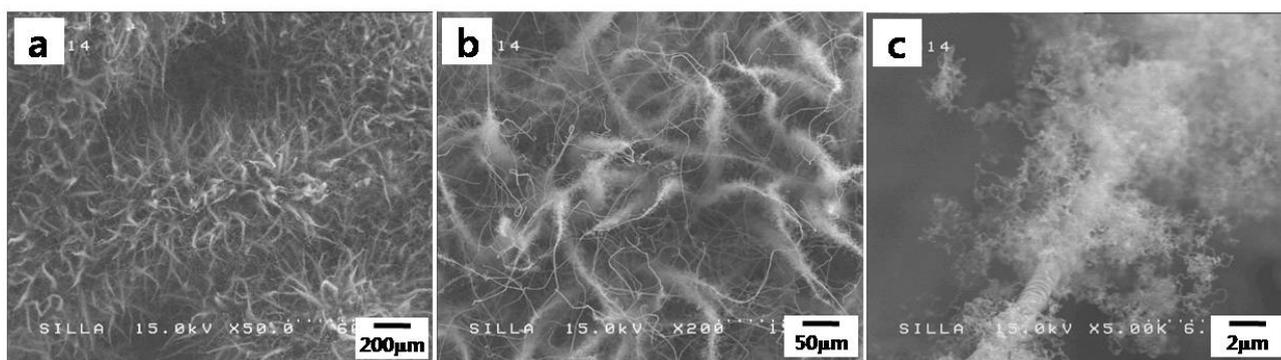


Figure 4. (a) FESEM images for the formation of the as-grown carbon coils on the substrate having the 30 minutes H<sub>2</sub> plasma pretreatment process, (b) the magnified FESEM image for Fig. 4(a), and (c) the magnified FESEM image for Fig. 4(b). The numerous carbon nanocoils network like the bush type could be clearly observed.

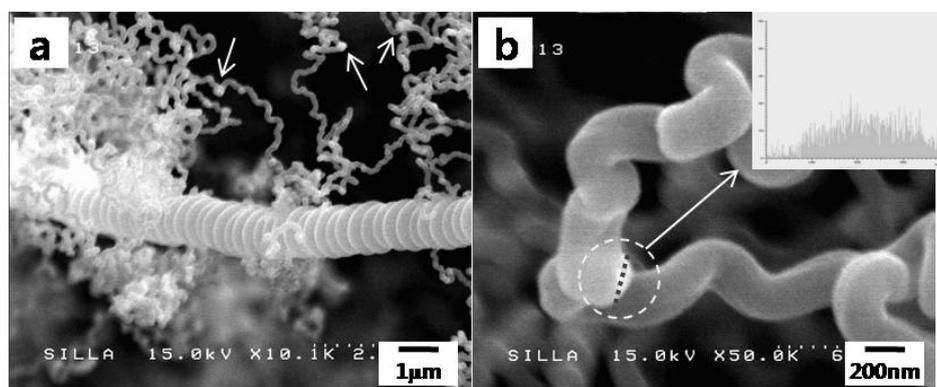


Figure 5. (a) The magnified FESEM images of the formation of the carbon coils having the noble-shaped geometrical nanostructures and (b) the high-magnified image focusing the carbon nanocoils area along the carbon microcoils. Inset shows the line (see the dotted line in the circle of Fig. 5(b)) mapping examining for the Ni component.

of the spots diameters are around 200 nm.

For the component investigation of the bright spot in Fig. 5(b), EDS line mapping examining for the Ni component was carried out. As shown in the inset of Fig. 5(b), the EDS result clearly confirms that the bright spot located in the bent points of the carbon nanocoils has a lot of the Ni component. This result reveals that lots of Ni catalyst grains spread out in the numerous carbon nanocoils along the carbon microcoils. Consequently, we are sure that the noble-shaped nanostructures in this work could hold a large number of the Ni catalyst grains having around

200 nm in diameter.

Based on the results from Figs. 1~5, it is understood that altering the characteristics of the nickel catalyst layer by the long time H<sub>2</sub> plasma pretreatment prior to the carbon coils synthesis reaction could form the noble-shaped geometrical nanostructures. For the SiO<sub>2</sub> substrate, the long time H<sub>2</sub> plasma pretreatment seems to etch the Ni catalyst layer thickness from ~300 nm to ~200 nm. In addition, it deteriorates the surface state of the substrate. Consequently, it may increase the stress between the pre-deposited Ni catalyst layer and SiO<sub>2</sub> substrate.

The cause for the stress between the metal layer and the substrate may be explained as follows. As our previous report [26], the difference of the thermal expansion coefficient value between Ni catalyst layer and the different substrates was known to be higher for SiO<sub>2</sub> substrate compared with that for the other substrate, especially for Si substrate [27,28]. The higher difference of thermal expansion coefficient between the metal layer and the SiO<sub>2</sub> substrate may induce the higher stress between them. Due to the stress between the metal layer and the substrate, the long time H<sub>2</sub> plasma pretreated-Ni layer might be more easily peeled off and broken into very tiny nanosized Ni pieces and eventually scattered in surrounding area. So, the peeled-off tiny nanosized Ni pieces could be the seed of the carbon nanocoils. Consequently, the density of the as-grown carbon nanocoils would be higher on the substrate having the 30 minutes H<sub>2</sub> plasma pretreatment process.

Fig. 6 shows FESEM images indicating the situation of the cracked and the damaged Ni layers on the substrate with the long time H<sub>2</sub> plasma pretreatment process after cooling down the substrate from 750°C to 25°C under vacuum condition. As shown in this image, SiO<sub>2</sub> substrate with the long time H<sub>2</sub> plasma pretreatment seems to give rise to the partly cracked and the damaged state for the Ni layer,

which partly producing the nanosized Ni pieces during the reaction. Basically, the mechanism of the carbon coils growth was dependent on the metal size and shape [29]. The nanosized carbon coils were formed from the nanosized Ni pieces. This seems to be the reason why the long time H<sub>2</sub> plasma pretreatment gives rise to the formation of the numerous carbon nanocoils along the carbon micro coils.

#### IV. Conclusions

The long time (30 minutes) H<sub>2</sub> plasma pretreatment prior to the carbon coils synthesis reaction could form the noble-shaped geometrical nanostructure, namely the formation of the numerous carbon nanocoils along the growth of the carbon microcoils. A lot of Ni catalyst grains spread out in the numerous carbon nanocoils. So, we are sure that the noble-shaped nanostructures in this work could act as a good catalyst support for holding a large number of the Ni catalyst grains having around 200 nm in diameter. The increased stress between the pre-deposited Ni catalyst layer and SiO<sub>2</sub> substrate by the long time H<sub>2</sub> plasma pretreatment seemed to be the main reason for the formation of the noble-shaped geometrical nanostructures.

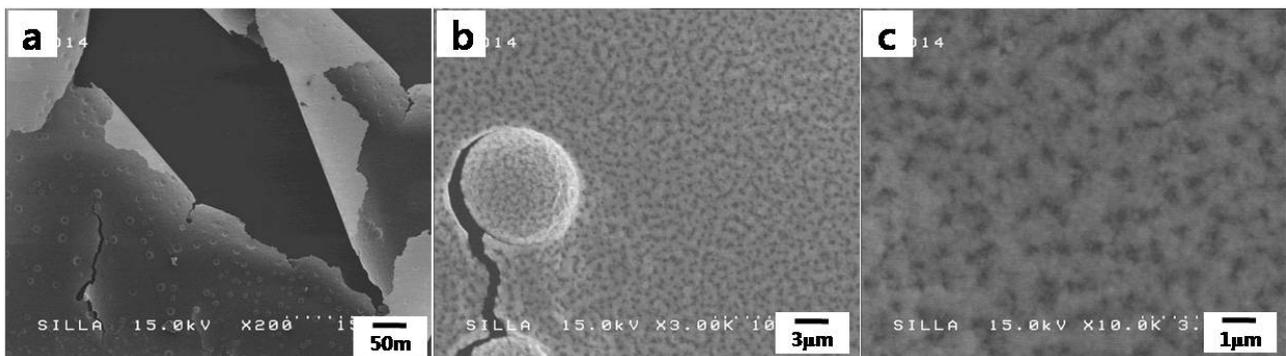


Figure 6. (a) FESEM images for the cracked and the damaged Ni layers on the substrate with the long time H<sub>2</sub> plasma pretreatment process after cooling down the substrate from 750°C to 25°C under vacuum condition, (b) the magnified images of Fig. 6(a), and (c) the high-magnified image of Fig. 6(b).

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# 매우 작은 크기의 촉매 알갱이를 지지하기 위한 촉매 지지대용 탄소 나노/마이크로 코일의 합성

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(2013년 9월 3일 받음, 2013년 10월 9일 수정, 2013년 10월 23일 확정)

아세틸렌과 수소기체를 원료기체로 하고 육불화황을 첨가기체로 하여 열화학 기상 증착하에서 탄소코일을 합성하였다. 이 때 산화실리콘 기판위의 니켈막을 탄소코일 성장의 촉매로 사용하였다. 성장된 탄소코일의 생성밀도, 형상, 기하구조 등을 수소 플라즈마 전처리의 유무에 따라 조사하였다. 상대적으로 짧은 시간(1분)의 수소 플라즈마 전처리는 탄소 마이크로 코일을 우세하게 성장시켰다. 긴 시간(30분)동안의 수소플라즈마 전처리는 탄소마이크로 성장 촉을 따라 수많은 탄소 나노코일이 들어붙어 있는 특이한 구조를 보였다. 이 특이한 구조는 매우 작은 니켈 촉매의 알갱이를 효과적으로 지지할 수 있는 촉매 지지대로서의 역할을 할 수 있을 것으로 예견되었다.

**주제어** : 탄소코일, 수소플라즈마 전처리, 기하구조 변화, 촉매 지지대, 열화학기상증착

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