

# Synthesis of platelet carbon nanofibers by an injection CVD method and their applications in hydrogen storage

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## ABSTRACT

An effective production of platelet carbon nanofibers (PCNFs) was obtained in the presence of sulfur in the catalytic solution by an injection chemical vapor deposition (CVD) method using alcohol as the carbon source, ferrocene as the catalyst, and thiophene as the promoter. Due to the simplicity of the present technique, the injection CVD method may be suitable for scale-up for mass production. Furthermore, the hydrogen storage capacity of the material was measured by volumetric method and the study was carried out at 77 K and the pressure up to 1 MPa. The result showed that the PCNFs can have a hydrogen storage capacity of more than 0.5 wt%. We believe that the material is potential for energy storage (hydrogen, methane).

**Keywords:** nanofibers, hydrogen storage

## 1 INTRODUCTION

Due to the environmental pollution and the energy crisis, hydrogen has become a promising energy substitute for fossil fuels in automotive applications. Since Dillon et al. [1] reported a 5-10 wt% hydrogen storage capacity in single-walled carbon nanotubes (SWCNTs), hydrogen storage in various carbon nanomaterials has been widely investigated experimentally and theoretically.

Among these materials, carbon nanofibers (CNFs) are a candidate for hydrogen storage because they exhibit a large amount of open edges and an interlayer spacing between the graphene sheets ( $\geq 3.35 \text{ \AA}$ ), acting like a slit-shaped pore to become an ideal configuration for hydrogen storage [2]. According to the literature reported [2-6], CNFs with graphene layers oriented perpendicularly or angularly to the fiber axis are most efficient for the adsorption of hydrogen. Storage capacities of CNFs ranging from less than 1 wt% to up to 15 wt% have been reported, and numerous factors have been used to describe the variability and inconsistency of these results, including experimental approaches, sample preparation, and processing conditions.

The mechanism of hydrogen storage in CNFs and the interaction between the graphene surface and hydrogen are not clear yet. Theoretically, hydrogen can be adsorbed onto

the surface and then incorporated/intercalated between the graphene layers or dissociated onto graphite edge sites [3,7]. Browning et al. [3] reported that the graphite edge sites in CNFs may play a role in the dissociation of hydrogen leading to high hydrogen capacity. Recently, Chen and Huang [8] reported that the defect structure of CNTs formed by KOH activation can enhance hydrogen storage capacity (4.47 wt%). Danilov et al. [9] also reported that the activation of CNFs with KOH results in a considerable improvement of the electrochemical characteristics of the hydrogen adsorbing electrode. As a result, increasing the defects and edge sites in CNFs can be an efficient method for increasing hydrogen storage capacity.

In this study, we demonstrate an effective method to fabricate platelet CNFs (PCNFs) by an injection chemical vapor deposition (CVD) method in the presence of sulfur using alcohol as the carbon source and ferrocene as the catalyst. In addition, the hydrogen storage capacity of the as-produced porous CNFs was also studied.

The PCNFs were characterized using high-resolution transmission electron microscopy (HR-TEM), field-emission scanning electron microscopy (FE-SEM), thermogravimetry analysis (TGA), and hydrogen uptake measurements using the volumetric method.

## 2 EXPERIMENTAL

### 2.1 Synthesis of PCNFs

The diagram of the apparatus for the synthesis of porous CNFs is shown in Figure. 1. The apparatus consisted of stainless steel gas flow lines, mass flow controllers (5850E, Brooks), stainless steel collector, a three-zone furnace (heating zone=900mm) equipped with a quartz tube (O.D.=75mm) and a syringe pump (KDS100, KD Scientific).

The CVD experiments started with passing nitrogen through the vertical tube when the furnace was heated to reach a desired reaction temperature. The reactant solution contained carbon source (alcohol), catalyst (ferrocene), and promoter (thiophene). Ferrocene and thiophene (molar ratio Fe/S = 1/2) were dissolved in alcohol and loaded into the syringe pump. The CVD experiments started with the

passing of nitrogen (100 sccm) through the vertical tube when the furnace reached the desired reaction temperature. The reactant solution was then injected (20 ml/hr) into the vertical furnace reactor from the top while nitrogen (500 sccm) and hydrogen (200 sccm) were admitted into the reactor at the temperature of 1100 °C for 30 minutes.

The morphology of PCNFs was examined by FE-SEM (Hitachi S-4800) while HR-TEM (Philips Tecnai-20 G-2, Philips Tecnai F20) was employed to understand the crystal structure and graphene layers arrangement of PCNFs. TGA was used to (PerkinElmer, Diamond TG/DTA) investigate thermal stability of PCNFs. The Pore characteristics were characterized by nitrogen adsorption using an ASAP 2020 system at 77 K.

## 2.2 Hydrogen storage experiment

The hydrogen storage capacity was measured using a pressure composition isothermal system (Micromeritics, ASAP 2050 Pressure Sorption Analyzer). The hydrogen storage capacity was measured using a pressure composition temperature (P-C-T) isothermal system manufactured by the Advanced Materials Corporation. During a typical experiment, approximately 100 mg of PCNFs were initially loaded into the sample chamber while heating under vacuum at 423 K for 4 h, removing any physisorbed water. The test started with the dosing of hydrogen into the manifold (up to 1 MPa) at 77 K for interaction with the samples. The amount of hydrogen adsorbed onto the carbon samples is presented in weight percentage (wt%).

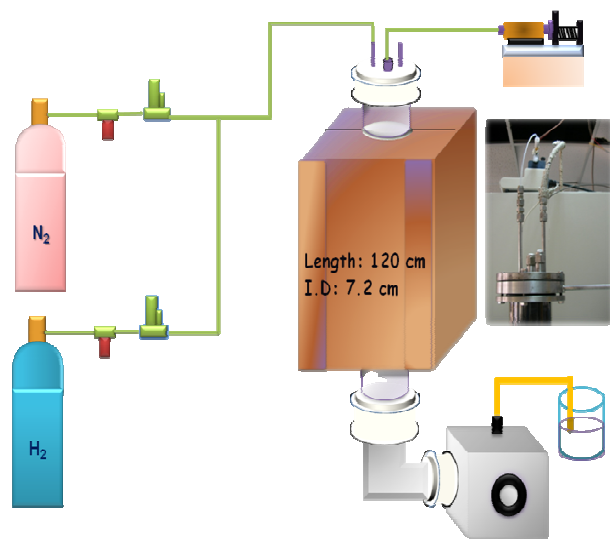
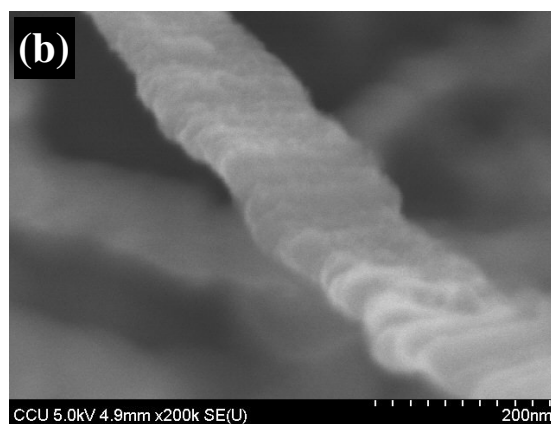
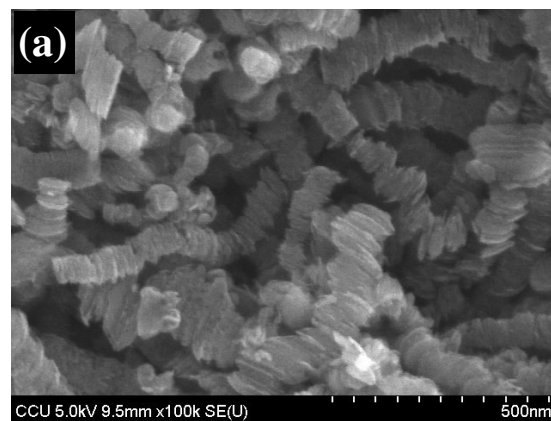


Figure 1: Diagram of the vertical reactor for the synthesis of PCNFs.

## 3 RESULTS AND DISCUSSION

### 3.1 Structural characteristics of the PCNFs

Figure 2 shows FE-SEM and HR-TEM images of the products after the synthesis. Figure 2(a) shows the SEM image of PCNFs formed at an Fe:S atomic ratio of 1:2. The PCNFs had a zigzag structure along their length direction with diameters ranging from 100 to 250 nm. Figure 2(b) shows that the PCNF had a rectangular transverse cross-section with a thickness of 40-50 nm and a washboard-like texture. The use of ferrocene and thiophene as catalytic precursors for the formation of PCNFs has not been previously reported in the literature. Figure 2(c) indicates that the PCNF had well arranged graphene layers and a high graphitization degree. As can be seen, the graphene layers were perpendicular to the growth axis. Figure 3 shows the TGA results of the PCNFs. Thermal oxidation of PCNFs occurs dramatically at the temperature about 650 °C. The PCNFs were burnt off at 750 °C, and the catalysts (about 2-5 wt %) remained. The production rate of as-produced PCNFs is approximately 0.8 g/hr in the collector. Some of the PCNFs were deposited on the quartz tube.



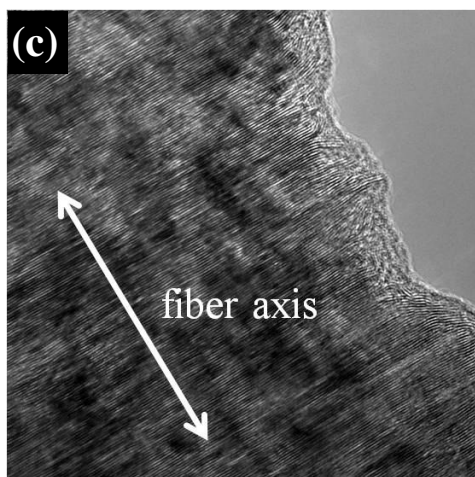


Figure 2. (a) SEM image of PCNFs, (b) HR-SEM image of the surface of PCNFs, and (c) HR-TEM images of PCNFs.

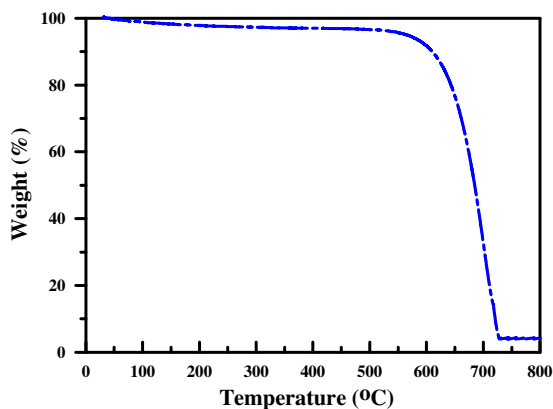


Figure 3. TGA results of the PCNFs.

Figure 4 shows the nitrogen adsorption/desorption isotherms of the PCNFs. The PCNFs represent the type-II adsorption/desorption isotherm, which can be considered as a non-porous surface (no hysteresis loop), with almost no micropores in the structure. The pore characteristics of the PCNFs are shown in Table 1.

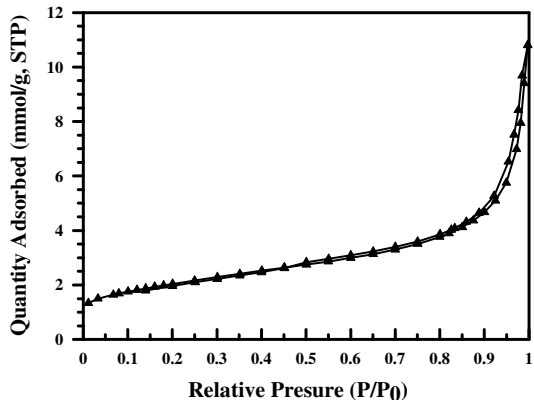


Figure 4. Nitrogen adsorption/desorption isotherms of PCNFs.

Table 1. Pore characteristics of the PCNFs.

	BET surface area (m <sup>2</sup> /g)	Pore volume fraction (%)		Total pore volume (cm <sup>3</sup> /g)
		Micropore	Mesopore	
PCNFs	113.28	3.71	96.29	0.213

### 3.2 Hydrogen storage test

PCNFs hydrogen storage was carried out using the volumetric method with the pressure up to 1 MPa at 77 K. Figure 5 shows the P-C-T isothermal curves of the PCNFs hydrogen storage capacity. The result shows that the PCNFs possess a 0.5 wt% hydrogen storage capacity. Some investigations reported that the hydrogen uptake of various carbon nanostructures at 77 K is correlated to their specific surface area. Zuttel et al. [10] reported that the theoretical value of potential hydrogen adsorbed was  $2.28 \times 10^{-3}$  wt% uptake for each square meter of surface area for the adsorption of a monolayer of hydrogen at the surface. This analysis requires a flat graphene sheet and ignores the microporosity contribution. Accordingly, in our study, hydrogen storage capacity was only 0.25 wt% when the as-produced PCNFs surface was covered with an atomic layer. However, surface areas accessible to nitrogen (kinetic diameter is 3.64 Å) may not necessarily be accessible to the hydrogen molecule (kinetic diameter is 2.89 Å) [3,5,11]. Thus hydrogen uptake does not always correlate to BET surface area, particularly for nanocarbons [3,5]. The difference between 0.5 and 0.25 wt% might be considered to be evidence of hydrogen intercalation within the graphene layers. The intercalant must initially find exposed graphene edges, which provide pathways for the intercalant to move inward and fill the space between the basal planes [7]. We think that the material is potential for energy storage such as methane and hydrogen.

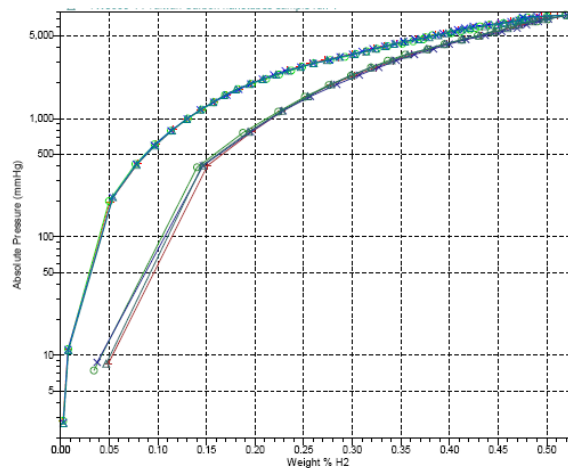


Figure 5. P-C-T curves of the PCNFs hydrogen storage capacity.

## 4 CONCLUCTIONS

A substrate-free and cost-effective method for continuous production of PCNFs using an injection CVD reactor was reported. SEM images showed that PCNFs with diameters ranging from 100 to 250 nm were successfully synthesized. Characterizations revealed that the PCNFs were constructed by well arranged graphene layers. Hydrogen storage in PCNFs, measured using the volumetric method with the pressure up to 1 MPa at 77 K, possessed a 0.5 wt% hydrogen storage capacity. We believed that the synthesis method (injection CVD) has a potential for large-scale synthesis of high-purity PCNFs.

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