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Carbon nanomaterials synthesized using a spray pyrolysis method

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ABSTRACT

Carbon nanomaterials were synthesized using a spray pyrolysis chemical vapor deposition system (SPCVD). By varying the reaction temperature or flow rate of the carbon source, the structure or morphology of the synthesized carbon nanocoils (CNCs) can be controlled. A vertical chemical vapor deposition (CVD) furnace with a three-stage heating zone was employed to synthesize carbonaceous nanomaterials using nano-Pd catalysts at growth temperatures of 600, 700, and 800 °C. The morphology of the synthesized carbon products and the relationship between the carbon source concentration and its yield were evaluated. The results showed that CNCs formed at a lower temperature (600 °C), whereas straight carbon nanotubes were obtained at a higher temperature (700 or 800 °C). The structure and morphology of the carbonaceous samples were observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Their graphite crystallinity was analyzed using Raman spectroscopy. When the three heating zones of the vertical CVD chamber were set to different temperatures, a unique nano-carbonaceous material with a special morphology similar to an octopus tentacle was formed.

1. Introduction

Carbon nanocoils (CNCs) and straight carbon nanotubes (CNTs) have attracted considerable attention in recent years because of their unique mechanical and electrical properties [1–9]. Due to their special helical structure, CNCs have the potential for applications in different fields such as hydrogen storage media [1], microwave absorbers [2], field emitters [3], microsensors [4], elastic materials [5], composite materials [6], electrode materials [7], and catalyst supports [8,9].

CNCs were first synthesized by Motojima and coworkers [10]. Using a nickel substrate or nickel powder as a catalyst, they synthesized coiled carbon microfibers [11] and suggested a growth mechanism based on the anisotropic extrusion of carbon over a catalyst particle [10,11]. Tang et al. synthesized helical CNTs and helical carbon nanofibers (HCNFs) on Fe nanoparticles and performed systematic experiments to investigate the specific effect of catalyst particle size on the selective growth of CNCs [12]. In 2001, Wen et al. successfully used acetylene as the carbon source and Ni–P–Cl composite catalysts to grow helical CNCs; they fabricated several CNC structures including solid and hollow coils [13]. Qin et al. used copper nanocrystals as a catalyst and acetylene as the source gas at a low temperature of 195 °C [5].

According to the literature, CNCs were generally synthesized using thermal chemical vapor deposition (TCVD) with metal particles as catalysts, methane or acetylene as the carbon source, and argon as the carrier gas. The common metal catalysts used for growing CNCs include iron (Fe) [12], nickel (Ni) [13], cobalt (Co) [14], and copper (Cu) [5].

In recent years, precious-metal catalysts, such as silver (Ag) [15], gold (Au) [16], titanium (Ti) and palladium (Pd) [17], have also been used for growing CNCs. Chiu and coworkers used liquid-phase metallic K with Ag or Au as the catalyst to grow amorphous CNCs from acetylene on Si substrates; they proposed a vapor-liquid-solid-growth mechanism for explaining the CNC growth [15,16]. Nitze et al. used C_{60}-supported Pd-catalyst particles at 550 °C to grow HCNFs [17]. Using Pd nanoparticles, they could grow homogeneous CNCs with a highly periodic pitch and diameter.

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Although the traditional TCVD method is a simple and inexpensive process for producing high purity CNCs effectively, the CNC yield of this method is poor and unfavorable for industrialization. Baddour et al. have grown CNTs on stainless steel particles with CVD in a fluidized bed system (FBCVD) to increase the yield [18]. However, compared with the traditional TCVD methods and FBCVD, the spray pyrolysis method (SPCVD) has many advantages such as the possibility of a substrate-free, continuous reaction, and shorter heating or cooling time for the furnace [19–22]. This method can be easily applied for the mass-production of nanocarbonaceous materials and is therefore more favorable for industrialization.

Aguilar-Elguezabal et al. successfully used spray pyrolysis of a ferrocene/benzene mixture to produce aligned, multiwalled carbon nanotubes (MWCNTs) [22]. Su et al. demonstrated a simple technique that involved dissolving ferrocene in alcohol and sprayed the solution into the reaction zone for the continuous production of high-purity, single-walled carbon nanotubes (SWCNTs) [20]. Zhang et al. used spray pyrolysis of ethanol to synthesize carbon nanofibers from carbon particles [23].

However, using the SPCVD method to produce pure CNCs has yet to be reported. In this study, we used poly(styrene-co-NIPAAm)/Pd nanoparticles [24] as a catalyst to synthesize carbonaceous samples with the spray pyrolysis method in a vertical CVD reactor. The morphologies of the synthesized carbon products were observed and their yield was evaluated.

2. Experiments

2.1. Spray-liquid preparation

We added a typical poly(styrene-co-NIPAAm)/Pd catalyst solution into ethanol and sonicated the mixture for 10 min to disperse the Pd catalysts homogeneously. The Pd nanoparticles then exhibited satisfactory dispersion in the ethanol without any surfactant.

2.2. Synthesis of carbonaceous samples by using spray pyrolysis chemical vapor deposition

Fig. 1 shows the schematic of our SPCVD reactor, which comprises a spray nozzle, a vertical heating furnace, a quartz tube, and a powder collector. The Pd/C_2H_5OH-mixed liquid was pumped into the vertical CVD chamber with compressed argon gas, hydrogen, and acetylene, to grow carbonaceous products at a temperature of 600–800 °C. The synthesis period was 1 h. The synthesized nanocarbonaceous products on the Pd catalysts were then observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Their graphite crystallinity was analyzed using Raman spectroscopy.

3. Results and discussion

3.1. Effect of growth temperature on the morphology of synthesized CNCs

Fig. 2 shows the SEM and TEM images of the carbonaceous products synthesized on Pd nanoparticles at various temperatures (i.e., 600, 700, and 800 °C). The gas flow rates of Ar, H_2, and C_2H_2 are 5000, 100, and 25 sccm, respectively. The samples synthesized at 600 °C is mainly CNCs (Fig. 2a), with very few straight CNFs, as indicated by the arrows. The CNCs grown at 600 °C have a solid helical structure and their diameter is approximately 100–150 nm, as shown in Fig. 2a, b. By contrast, the curly CNTs grown at 700 °C have a hollow structure and a diameter of approximately

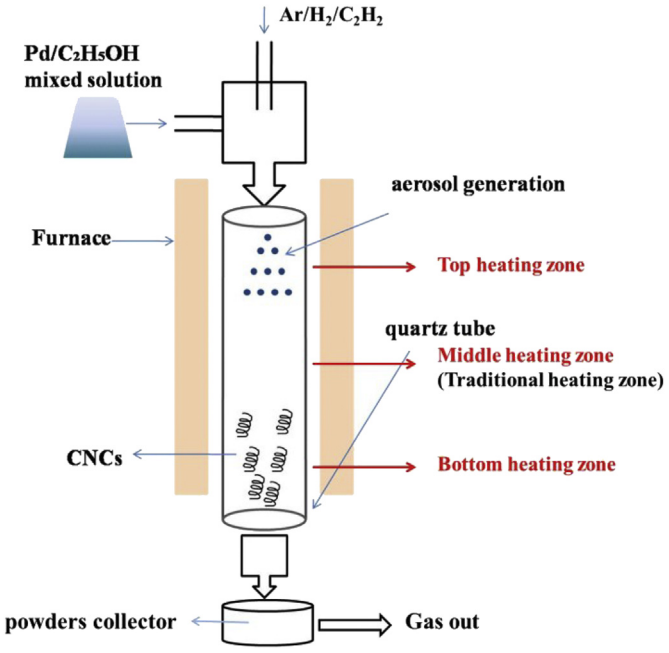

Fig. 1. Schematic of our vertical spray pyrolysis CVD reactor.

20–30 nm, as shown in Fig. 2c, d. When the growth temperature was increased to 800 °C, thinner CNTs with a diameter of approximately 15–20 nm were obtained, as shown in Fig. 2e, f.

According to Baker's theory [25], carbon atoms decomposed from a carbon source gas diffuse into the catalyst particles and precipitate on the surface to form carbon fiber, due to the

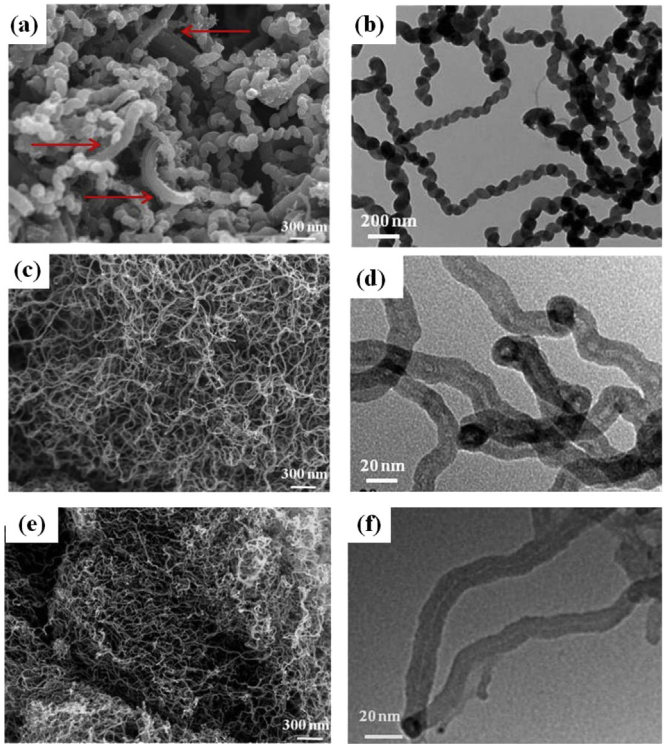

Fig. 2. SEM and TEM images of the nano-carbon samples synthesized at different growth temperatures: (a) (b) 600 °C, (c) (d) 700 °C, and (e) (f) 800 °C with vertical SPCVD reactor. The arrows in (a) indicate the few CNFs as the minority type of material.