above mechanism may also explain the influence of pyrolysis temperature. Increasing the pyrolysis temperature may destroy more complementary linkers and favor the partial-filling effect since the condensation and aggregation of PF resin may be more pronounced at high temperatures. Therefore, when compared P-K-1.0-950 with P-K-1.0-580, the former material shows more apparent bimodal pore size distribution and a deformed symmetry of $I \alpha_1$. Cycle voltammetry (CV) measurements have been conducted to investigate the electrochemical properties of the products. For samples prepared at different temperatures with the same loading amount ($X = 1$), P-1.0-780 exhibits the highest capacitance of 127 F/g, while P-1.0-580 and P-1.0-950 has a lower capacitance of 87 and 93 F/g, respectively. For P-1.0-780, the CV curves remain the rectangular shape even when the scan rate is increased to 40 mV/s. It is also important to note that at such a fast scan rate, the capacity has a loss less than 5% of that obtained at a scan rate of 5 mV/s, indicating a good rate capability and power ability.

In summary, highly ordered mesoporous polyacenes/carbon have been synthesized successfully via a simple nanocasting process. The influences of the loading amount and the pyrolysis temperature on the structure and the capacitance of the products have been studied. CV measurements show that the products have good capacitive behaviors and high specific capacitances (up to 127 F/g). Such materials are good candidates for the fabrication of electrochemical double-layer capacitors.

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References


Novel catalyst particle production method for CVD growth of single- and double-walled carbon nanotubes

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Chemical vapor deposition (CVD) is described as the most versatile method for the production of carbon nanotubes (CNTs). Typically metallic nanoparticle catalysts for the CNT synthesis by CVD are prepared by wet chemical routes [1–3], involving several intermediate stages, or by depositing thin metal film on substrates by sputtering [4] or evaporation [5]. Aerosol methods offer simple alternative for production and deposition of catalyst nanoparticles with controlled sizes. As an example, Sato et al. [6] have used size-selected Ni nanoparticles generated by laser ablation for the synthesis of diameter-controlled multiwalled CNTs by CVD. Similarly, Kohno et al. [7] used the same technique to create alloy particles for the synthesis of single-walled CNTs (SWNTs). Our group has recently reported on well size-controlled production of Fe and Ni aerosol catalyst particles using a resistively heated metal wire. Fe and Ni particles have been used successfully for the synthesis of SWNTs in the gas phase [8]. In our aerosol method, catalyst particles embedded in SWNTs were found to have a mean diameter from 1.4 to 2.0 nm depending on the growth conditions [9]. Furthermore, a method for the efficient homogeneous deposition of catalyst particles via thermophoretic forces was developed [10].

In this letter, we report a simple, ambient pressure substrate CVD method for the selective synthesis of single- or double-walled CNTs. The novelty of this method is in combining the aerosol synthesis of size-controlled catalyst particles and their direct deposition by thermophoresis for further utilization for CNT growth. Nanometer size particles are produced by metal vaporization, subsequent vapor cooling resulting in the particle formation due to nucleation and growth by condensation of the supersaturated vapor and cluster coagulation. Newly designed thermophoretic precipitators were used for the collection of the particles onto different substrates.

Fe catalyst particles were produced using a hot wire generator (HWG) [8] and collected via thermophoresis using two different approaches: ex situ and in situ. The HWG consists of a thin resistively heated iron wire (0.25 mm diameter). The size of the Fe particles can be controlled by the wire temperature, flow rate through the HWG and distance between the locations of the particle generation and their deposition. In the ex situ method, Fe nanoparticles were produced by the HWG located inside a glass bulb and were transported to a thermophoretic precipitator (TP) described elsewhere [10] and shown in Fig. 1(a). In order to improve the control on the catalyst particle size and to avoid the losses during their transportation, another thermophoretic precipitator, based on the in situ catalyst particle production and deposition was designed and constructed (Fig. 1(b)). It is comprised of an iron wire placed inside a ceramic tube (13 mm o.d., 9 mm i.d.) and a water cooled plate with an attached substrate. In this case, the Fe wire is not only the source of the catalyst particles, but also the heating element of the TP. The distance between the wire and the substrate was kept at 1.5 cm, providing a temperature gradient around 2800 °C/cm. The flow rate inside the TP was maintained at 560 cm³/min of Ar/H₂ gas mixture (mole component ratio 93.0/7.0).

For the growth of CNTs three different substrates were used. Si₃N₄ (50 nm thick) and SiO₂ window membrane grids (Structure Probe, Inc., PA, USA) were used for direct transmission electron microscopy (TEM) observations. For the growth of long and aligned CNTs, both flat (260 nm thick SiO₂ layer) and grooved (1 μm thick SiO₂ layer) Si substrates were employed.

The growth of CNTs was carried out in a vertical laminar flow reactor. It consisted of a stainless steel tube with an inner diameter of 2.2 cm inside a 44-cm long furnace. A stainless steel rod of 6 mm in diameter with a sample holder was designed for inserting different supports. Before the introduction of the carbon source, deposited Fe catalyst particles were reduced at 890 °C for 5 min under an H₂/N₂ (340/380 cm³/min) flow. Then, N₂ flow was replaced with CO (380 cm³/min), while the H₂ flow rate was lowered to 240 cm³/min. The substrate temperature was kept at 890 °C for 20 min. After the reaction, the flow in the reactor was switched to H₂/N₂ (240/380 cm³/min) flow. During this stage, the rod was moved downstream near to the cooling zone (porous tube dilutor with a 12 l/min N₂ flow rate). The morphology of the as-grown CNTs was examined by field emission scanning electron microscopy (SEM, Leo Gemini DSM982) and field emission transmission electron microscopy (TEM, Philips CM200 FEG). The nanotubes were further characterized by Raman spectroscopy (Horiba Jobin Yvon, model Lab AM). The 633 nm line from a He–Ne laser was used as excitation source.
TEM studies revealed that the nanotubes synthesized by the ex situ method were mainly double-walled CNTs (DWNTs). A few triple-walled CNTs were also found. Fig. 2 shows HR-TEM images of the as-grown nanotubes. They were clean and individual. Additionally, they were very straight without bends or kinks. DWNT diameters observed by TEM presented a distribution in the range of 5.9–7.5 nm and 5.0–6.8 nm for outer (o.d.) and inner (i.d.) diameters, respectively. The interlayer spacing varied between 0.37 and 0.44 nm, to our best estimate. Our results indicate that the DWNTs synthesized by the catalytic disproportionation of CO had larger diameters and broader interlayer spacing range than DWNTs formed by other carbon sources using CVD methods [1,2,11].

CNTs were also grown on both flat and grooved Si/SiO$_2$ substrates (Figs. 3,4). The tubes observed by SEM were ultralong with lengths up to 0.7 cm (Fig. 3) obtained for a synthesis period of 20 min. Thus, the estimated growth rate was 5.8 $\mu$m/s, higher than the previously reported (3 $\mu$m/s), for the synthesis of SWNTs in a CO/H$_2$ CVD sys-

![Fig. 2. HR-TEM images of CNTs grown using the ex situ particle production and collection method: (a) a closed particle-free end of an individual and large diameter DWNT; (b) DWNT with an outer diameter of 7.5 nm. Catalyst particles were collected on a 50 nm thick Si$_3$N$_4$ window membrane grid.](image1)

![Fig. 3. SEM images of long nanotubes of 0.50 (black arrows) and 0.24 cm (white arrows) on flat oxidized Si substrate. Starting from the bottom, images (a) 1–5, (b) 5–10 and (c) 10–14.](image2)
tem [12]. Moreover, the majority of CNTs grew horizontally aligned preferentially in parallel to the direction of the gas flow. Arrays of straight CNTs were especially observed when using flat substrates. It was also possible to find tubes with wavy segments in the middle or at the end, sometimes entangled, adjacent to straight ones. Increasing the collection time in the TP led to a higher particle deposition density and, as a result, to a higher density of synthesized CNTs (Fig. 4(a)). Thus, these results demonstrate the possibility to grow CNTs with different densities.

Fig. 4. SEM images of Si grooved substrate: (a) covered by high density ultralong and aligned CNTs and (b) nanotubes crossing the channels (~400 nm deep).

Fig. 5. TEM images of the CNTs produced by the in situ particle production and collection approach: (a) Bundle of SWNTs and a DWNT. (b) Individual SWNT. (c) Raman spectrum of the sample. Excitation wavelength was 633 nm.
by this method. SEM images of the CNTs grown on
grooved substrate (Fig. 4(a) and (b)) revealed that the tubes
continued to grow even when physical barriers (edges of
the channels of grooved substrates) are present. Moreover,
the growth orientation did not change. These observations
suggest that our nanotubes float above the substrate with
the gas flow during growth as it was previously reported
by Huang et al. [12].

The synthesis of DWNTs with large diameters is directly
related to the large catalyst particle size. In the ex situ
experimental setup, the size of the particles become larger
due to the long distance between the hot wire vapor source
and the substrate, and as a result, particles additionally
grow due to the catalyst cluster collisions. Another draw-
back is the large number of particle losses along the tubing
because of the high diffusivity of nanoparticles. The close
proximity of the hot wire and the substrate in the in situ
approach allowed us to reduce the excessive particle growth;
hence smaller particles can be collected. As expected, the
in situ grown nanotubes had smaller diameters. In fact,
mainly SWNTs were synthesized. Depending on the collection
conditions, i.e. the density of deposited particles, the
CNTs were aggregated into bundles (Fig. 5(a)) or individ-
ual (Fig. 5(b)) with diameters varying between 1.3 and
2.1 nm. A few DWNTs were also found. In Fig. 3(a), an
individual DWNT with o.d. and i.d. of 2.0 and 1.3 nm is
depicted. CNTs were characterized by Raman spectro-
scopy. Fig. 5(c) shows a typical spectrum with peaks at
around 1580 cm$^{-1}$ (G band) in the tangential mode and
143 cm$^{-1}$ in the radial breathing mode (RBM) range,
respectively. The D band at $\sim$1350 cm$^{-1}$ was not observed,
indicating the synthesis of good quality and clean SWNTs.
The diameter ($d$) of the SWNTs, calculated from the RBM
frequencies using the expression $w_R (cm^{-1}) = 248/d$ (nm)
[13], was 1.73 nm. This value is within the range of those
determined from TEM images.

In summary, a CVD method to selectively produce sin-
gle- or double-walled CNTs was described and demon-
strated using Fe and a mixture of CO and H$_2$ as the
catalyst and feeding gases, respectively. Catalyst particles
were produced by a physical vapor nucleation method
and ex situ and in situ deposited by thermophoresis onto
different substrates. The ex situ deposited particles led to
the synthesis of large diameter DWNTs (o.d.: 5.9–7.5 nm;
i.d.: 5.0–6.8 nm). In the in situ approach resulted in the for-
mation of smaller catalyst particles and, as a result,
SWNTs. Depending on the collection time, individual or
bundles of SWNTs with diameters from 1.3 to 2.1 nm were
grown. The possibility of producing ultralong (up to
0.7 cm) and high density aligned CNTs was demonstrated
on flat and grooved oxidized Si substrates. The estimated
growth rate of CNTs was 5.8 $\mu$m/s.

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