

Hot-wire chemical vapor synthesis for a variety of nano-materials with novel applications

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Abstract

Hot-wire chemical vapor deposition (HWCVD) has been demonstrated as a simple economically scalable technique for the synthesis of a variety of nano-materials in an environmentally friendly manner. For example we have employed HWCVD for the continuous production of both carbon single- and multi-wall nanotubes (SWNTs and MWNTs). Unanticipated hydrogen storage on HWCVD-generated MWNTs has led insight into the adsorption mechanism of hydrogen on metal/carbon composites at near ambient temperatures that could be useful for developing a vehicular hydrogen storage system. Recent efforts have been focused on growing MWNT arrays on thin nickel films with a simple HWCVD process. New data suggests that these MWNT arrays could replace the gold black coatings currently used in pyroelectric detectors to accurately measure laser power. Finally, we have very recently employed HWCVD for the production of crystalline molybdenum and tungsten oxide nanotubes and nanorods. These metal oxide nanorods and nanotubes could have applications in catalysis, batteries and electrochromic windows or as gas sensors. A summary of the techniques for growing these novel materials and their various potential applications is provided.

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1. Introduction

Hot-wire chemical vapor deposition (HWCVD) has been employed for the continuous production of both carbon single- and multi-wall nanotubes (SWNTs [1] and MWNTs [2]). Employing methane as the carbon source and ferrocene as a gas-phase catalyst, low temperature syntheses are conducted between ~30 and 550 °C. Both single- and multi-wall nanotubes have potential for a wide variety of applications including the fabrication of strong composite materials as well as gas adsorption and separation. SWNTs may be either semi-conducting or metallic depending on their size and chirality. Consequently, they have potential applications as nano-wires and interconnects. Carbon single-wall nanotubes have also been demonstrated as

promising candidates for the replacement of gold black coatings currently used in detectors to accurately measure laser power [3]. Aligned arrays of MWNTs have unique field emission properties making them suitable for flat panel display applications [4].

In this report we show that as-synthesized HWCVD MWNTs stabilize hydrogen at slightly above room temperature [5]. The results are not anticipated as neither the MWNTs nor the iron nanoparticles used to catalyze their growth is expected to store hydrogen at near ambient conditions. HWCVD is also employed for the growth of MWNT arrays on various substrates coated with a nickel film catalyst. These nanotube arrays have been shown to be superior to SWNT coatings on pyroelectric detectors employed to measure laser power [6]. Furthermore, HWCVD has been employed for the production of tungsten and molybdenum oxide nanorods. Crystalline rods with ~10–20 nm diameters and ~40–60 nm in length are

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generated at high density. Thin metal oxide films of both of these materials have a host of applications including electrochromic (EC) windows, high-energy-density batteries, catalysis and gas sensing devices. The incorporation of nanorods or nanotubes with the correct crystalline structure should result in greatly enhanced overall performance in any of these applications.

2. Experimental

HWCVD is performed in a quartz tube reactor enclosed in a clamshell furnace. For continuous bulk carbon nanotube growth, two parallel 0.5 mm tungsten filaments ~ 6 ” in length are operated at ~ 20 A, 25 V and at 2000 °C as determined by an optical pyrometer. Ferrocene is employed to supply an iron catalyst by maintaining the powder source near the sublimation temperature (140 °C), and methane is the primary carbon source. Under optimal conditions, graphitic MWNTs with minimal carbon impurities are produced in 1:5 CH₄/Ar at 150 Torr at ~ 100 mg/h with the furnace at 400 °C in a static gas environment or at ~ 150 mg/h with gas flow rates of 20 (CH₄) and 100 (Ar) sccm and the furnace at 550 °C. Similar growth conditions are employed for MWNT growth on nickel-coated quartz, crystalline silicon and lithium niobate (LiNbO₃) substrates. The nickel films are deposited via RF magnetron sputtering at 40 W in an argon ambient at 15 Torr. Film thickness ranges between 50 and 100 Å. The MWNT arrays are characterized on a JEOL 6320 field emission scanning electron microscope (SEM) operating at 2 keV, and a working distance of 4–5 mm with 1–2 s exposures. A thin layer of gold is applied to non-conducting samples for enhanced imaging.

The crude bulk MWNT materials are purified with a 16 h reflux in 3 M nitric acid at 120 °C. The MWNTs are recovered via filtration on a hydrophilic polypropylene filter, rinsed with de-ionized water and dried at 60 °C for ~ 1 h. Thermal gravimetric analysis (TGA), in a TA SDT2960 with a heating rate of 20 °C/min in flowing “dry air” (80% N₂, 20% O₂) at 100 sccm, is employed to determine MWNT purity. The metal oxide nanostructures are deposited by the direct evaporation of either a single molybdenum or tungsten filament in an Ar/O₂ ambient. The partial pressure of the oxygen is varied from 4% to 8% with the absolute synthesis pressure ranging from 10 to 150 Torr and the synthesis temperature between ambient and 600 °C.

The temperature programmed desorption (TPD) apparatus employed to determine the hydrogen capacities of the various carbon-based materials has been previously described [7]. Briefly, carbon samples weighing ~ 1 mg are placed in a packet formed from 25 μ m thick platinum foil and mounted at the bottom of a liquid nitrogen cooled cryostat. The packet is resistively heated with a programmable power supply. The sample temperature is measured with a thin thermocouple spot-welded to the platinum packet. Pinholes in the foil enable gas diffusion into and out

of the packet. Room temperature H₂ exposures for ~ 1 min at 500 Torr saturate the hydrogen adsorption. The sample is then cooled to ~ 130 K prior to evacuation of the chamber to $\sim 10^{-8}$ Torr. A mass spectrometer measures species with an *m/e* up to 300 a.m.u. and insures that only hydrogen is observed during desorption. Prior to hydrogen adsorption studies the MWNT samples are degassed by heating in a vacuum of $\sim 10^{-7}$ Torr to 823 K at 1 K/s. The instrument was calibrated by thermally decomposing known amounts of CaH₂. The amount of evolved hydrogen was linear with the weight of decomposed CaH₂, and the calibrations were performed with amounts of CaH₂ that yielded a TPD signal similar to the SWNT samples. The TPD system was also calibrated with hydrogen desorption studies of TiH₂ and Pd that was charged in situ. All three hydrogen calibration methods were confirmed with an in-house volumetric technique within $\pm 3\%$.

3. Results and discussion

3.1. Hydrogen storage

It has been speculated that high-capacity H₂ adsorption at near ambient conditions on carbon nanotube materials is only observed if metal particles are also present. However, to date hydrogen adsorption capacities on various different samples are not highly reproducible [8]. A greater understanding of the carbon metal interaction that results in enhanced nanotube hydrogen storage capacity is clearly needed. An economically scalable, continuous HWCVD technique has recently been developed to generate multi-wall nanotubes that are virtually free from non-nanotube carbon impurities. Transmission electron microscopy (TEM) showed that the MWNTs are highly graphitic with the distance between layers measuring ~ 0.34 nm. The graphitic nature of the MWNTs was also confirmed macroscopically by employing Raman spectroscopy. Following purification with a 3 M HNO₃ reflux, MWNTs that are >99.5 wt.% pure with an ~ 75 wt.% yield are easily obtained as shown by TGA [2].

The as-synthesized HWCVD materials typically contain ~ 15 – 25 wt.% iron catalyst particles. Fig. 1(a) displays the TPD spectra of both crude and purified MWNTs following 500 Torr H₂ exposure at room temperature. Note that hydrogen is stabilized at near ambient conditions for the unpurified sample that contained ~ 15 wt.% iron catalyst particles, but not for the purified MWNTs that are virtually metal-free. Iron is not a known metal hydride and is not expected to store any hydrogen under the charging conditions of this experiment. Similarly, MWNTs are not expected to stabilize hydrogen at near room temperature. Further TPD studies revealed that the hydrogen is stabilized with a binding energy of ~ 50 kJ/mol. Although the maximum near ambient hydrogen capacity is only ~ 0.035 wt.%, the data indicates a unique synergy resulting in

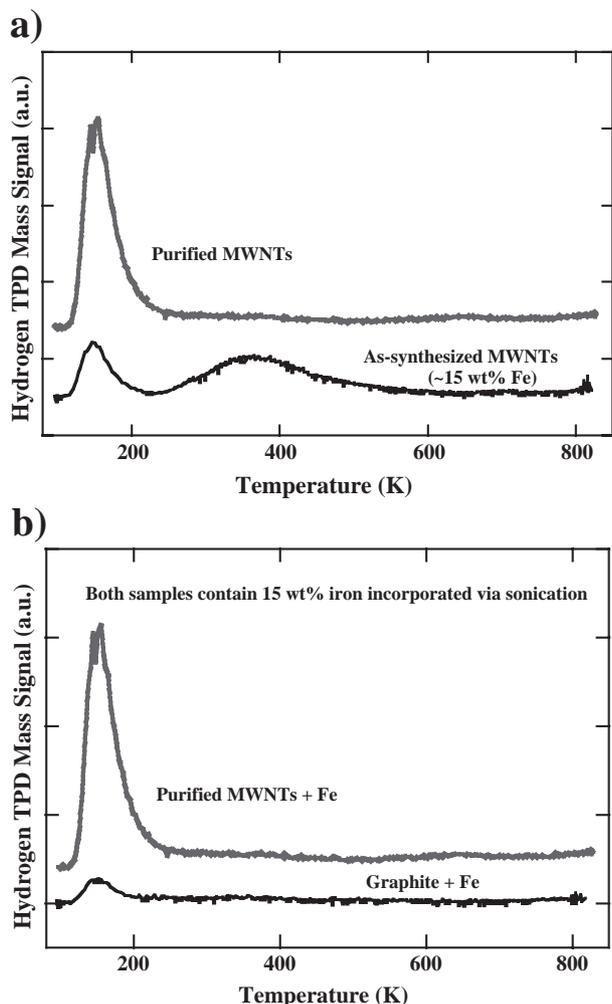


Fig. 1. Hydrogen TPD signals following room temperature H_2 exposures at 500 Torr for (a) as-synthesized and purified HWCVD-generated MWNTs and (b) purified MWNTs and graphite with 15 wt.% iron incorporated via sonication in toluene.

unanticipated hydrogen adsorption when metal and sp^2 -hybridized carbons are combined.

Fig. 1(b) displays TPD spectra of subsequent control experiments where ~ 15 wt.% iron particles (~ 40 nm to $1 \mu\text{m}$ in size) were introduced to both the purified MWNTs and to micron-sized particles of graphite via sonication in toluene and subsequent filtration on a hydrophilic polypropylene filter. Surprisingly, no hydrogen is stabilized at near ambient temperatures for either sample indicating that simple mixing is insufficient to observe hydrogen adsorption at near ambient temperatures. Further experimental and theoretical investigations indicate that atomic iron in highly intimate contact with the MWNTs may be necessary to observe the unique hydrogen adsorption properties.

3.2. MWNT arrays

Carbon single-wall nanotubes have been recently studied as the thermal-absorption coatings on a large area pyro-

electric detector used for the precise measurement of laser power. The responsivity of these thermal detectors depends on the variation of reflectance of the detector coating as a function of wavelength. Gold black coatings are capable of very low reflectance ranging from the $0.2 \mu\text{m}$ (UV wavelengths) to beyond $50 \mu\text{m}$ (infrared wavelengths). However, such coatings are vulnerable to damage at moderate power density, physical contact (they can be literally blown away), as well as aging and hardening at UV wavelengths [9]. Carbon nanotube-based coatings may be superior to present alternatives as carbon nanotubes are known to be lightweight inert materials with high thermal conductivities [10].

Carbon single-wall nanotubes were recently explored as replacements for the gold black coatings. Purified SWNTs were initially produced by a laser vaporization method [11] and dispersed onto a pyroelectric detector surface using a simple air brush technique [3]. A coating that was slightly more reflective than the currently used gold black coating was obtained for wavelengths up to ~ 1500 nm. Above this wavelength, however, the responsivity of the SWNT coated detector decreased dramatically. This may be due to the fact that metallic SWNTs are expected to have increased reflectivity at wavelengths greater than 900 nm. Alternately, non-uniformity in the nanotube surface could also affect the performance of the coating.

Arrays of MWNTs may be more promising as thermal adsorption coatings. The surfaces of the MWNT nanotube arrays should be relatively uniform, and the optical properties of the individual tubes should not vary dramatically. Fig. 2(a) displays a scanning electron microscope micrograph of an array of MWNTs deposited on a 50 \AA nickel film on a crystalline silicon substrate. For comparison an SEM image of the gold black coatings typically used in the fabrication of pyroelectric detectors is shown in Fig. 2(b). Recently, carbon multi-wall nanotubes were grown on a lithium niobate (LiNbO_3) pyroelectric detector coated with a nickel film catalyst [6]. The performance of this MWNT coating was compared with earlier results for purified bulk carbon single-wall nanotubes sprayed on a lithium tantalate (LiTaO_3) pyroelectric detector [3,6].

Fig. 3 compares the spectral responsivities of both SWNT and MWNT devices to that of a gold black coated detector. The responsivities are measured from 600 nm to 1800 nm and are normalized to the value of the gold black standard. Both nanotube coatings perform similarly to the gold black coating for wavelengths up to ~ 1500 nm. However, in the 1500 nm region the SWNT coating shows responsivity variations as large as 15%. The MWNT array is more spectrally uniform, with variations of only a few percent. For each of the thermal coatings represented in Fig. 3, incident light is converted to heat and conducted to the detector substrate. Photons incident on the coating may be reflected several times before being absorbed and converted to phonons. The percolation threshold depends on the size, depth, distribution, and topology of the coating. The

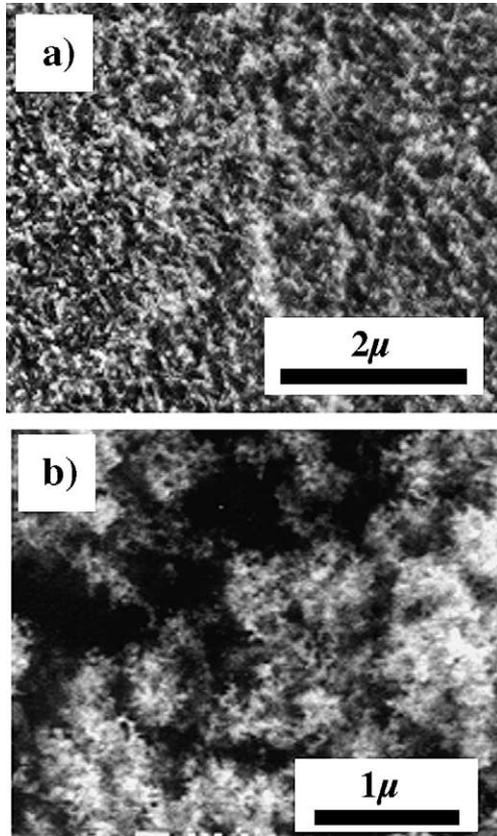


Fig. 2. SEM micrographs of (a) an aligned array of MWNTs deposited on a thin Ni film with HWCVD and (b) a gold black coating currently employed for laser power measurement with pyroelectric detectors.

HWCVD-deposited MWNTs may have a more uniform topology than the SWNT films improving their thermal diffusivity. The improved spectral uniformity of the MWNT coating compared to that of the SWNT coating suggests that HWCVD-deposited nanotubes warrant further study. In future investigations the growth conditions will be varied to achieve aligned arrays of precisely spaced MWNTs in order to obtain a nanotube coating with the optimal optical properties for this application.

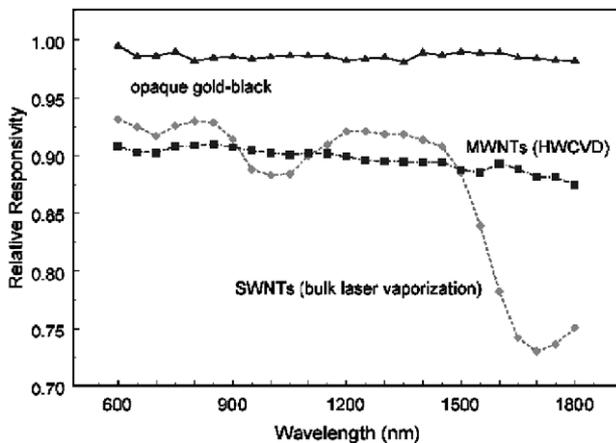


Fig. 3. Spectral responsivity of MWNT and SWNT coatings displayed relative to the responsivity of gold black.

3.3. Metal oxide nanorods

Fig. 4(a) displays a transmission electron microscope (TEM) image of HWCVD-deposited tungsten oxide nanorods and tubes. The crystalline nature of one of the nanorods is clearly depicted in the high-resolution TEM image of Fig. 4(b). X-ray diffraction (XRD) analysis revealed that the crystalline phase was WO_3 . The HWCVD-generated material was a fine powder consisting of predominantly nanorods or tubes with a few larger crystalline particles and a small amount of amorphous materials. Fig. 4(c) displays a high-resolution TEM image of molybdenum oxide nanotubes also grown by the HWCVD technique. Here the crystallite structure was shown with XRD to be MoO_3 . The density of nanotubes or nanorods was not as high in this particular material as that observed for the tungsten oxide. However, it is believed that the synthesis process may be further optimized.

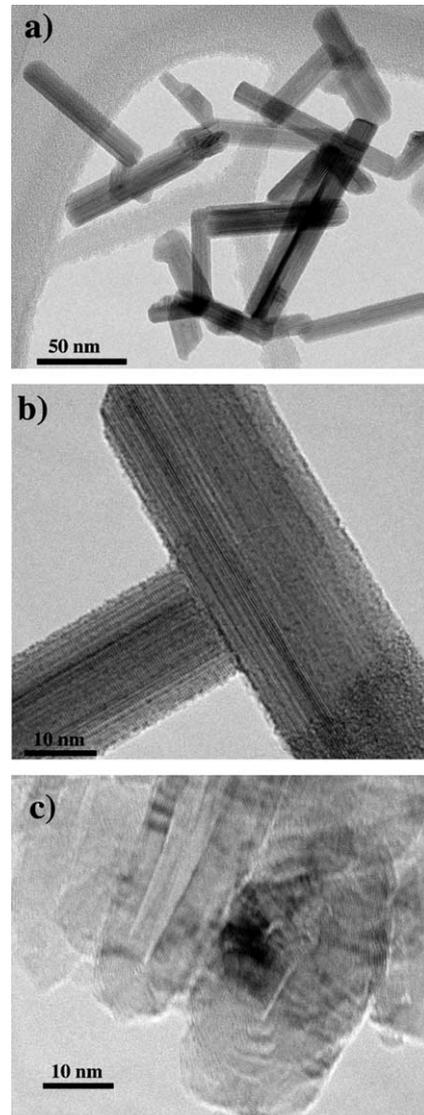


Fig. 4. TEM images of (a) WO_3 nanorods, (b) the same WO_3 nanorods at higher resolution revealing their crystallinity and (c) MoO_3 nanotubes.

Various transition metal oxides, including tungsten and molybdenum, have been investigated extensively as hosts for Li^+ and H^+ insertion. The accompanying changes in electrical and optical properties during ion insertion/removal processes are the basis for their applications as electrochromic (EC) materials and lithium battery cathodes [12]. The kinetics of the insertion reaction is often limited by the solid-state diffusion of the ions. The time constant of the process is determined by both the chemical diffusion coefficient and the length of the diffusion path. While the former depends on the chemical and crystal structure of the metal oxide, the later is determined by the microstructure [13]. In the case of a nanorod or nanotube, the radius of the rod represents the length of the diffusion path. Therefore, designing a crystalline nanorod structure with a small radius is key to a material with fast insertion kinetics and superior overall performance.

4. Conclusions

It is possible to produce a wide variety of nanostructured materials with a broad range of applications using the economically scaleable hot-wire chemical vapor deposition technique. Bulk SWNTs and MWNTs have both been synthesized with applications including gas storage and separation, nanoscale electronics and strong composite materials. Unanticipated hydrogen adsorption on as-synthesized MWNTs has led to a greater understanding of the hydrogen adsorption mechanism on metal/carbon composite materials. HWCVD growth of MWNT arrays has been performed with thin nickel film catalysts. These nanotube arrays have been demonstrated to be promising candidates for the replacement of gold black coatings on pyroelectric detectors employed for laser power measurements. Finally, metal oxide nanorods and nanotubes that have applications in batteries and electrochromic windows may be produced by a simple HWCVD technique.

Acknowledgments

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