CONDUCTIVE AND NANOPOROUS SINGLE WALL CARBON NANOHORN EMBEDDED AEROGELS

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Introduction

With the recent development in nanoscience and nanothechnology carbons of nanostructures such as single-wall carbon nanotubes have attracted much attention (Hirsch, A., 2002). Single-wall carbon nanohorn (SWCNH) is one of the most attractive new forms of nanocarbons (Iijima, S. *et al.*, 1999). SWCNH is a graphitic tube that has a corn-shaped cap with a cone angle of 20˚ at one end. The individual particle of SWCNH has a typical diameter of about 2-3 nm, and SWCNH aggregates (SWCNHs) form a spherical colloid with diameters of 50-90 nm. Properties, such as high surface area, high thermal stability, high yield (> 95%) and purity, and conductive graphitic structures provide SWCNHs with specific properties that enable numerous potential applications, such as adsorbents, molecular sieves and ion sieves, catalyst support, and drug delivery (Bekyarova, E. *et al*., 2005; Urita, K. *et al*., 2006; Utsumi, S. *et al*., 2006; Yang, C. M. *et al*., 2007).

The Resorcinol-formaldehyde (RF) aerogel is a special type of low-density, open-cell structure derived from the polycondensation of resorcinol with formaldehyde. Since first synthesized by Pekala, RF aerogels have received considerable attention in commercial applications such as adsorbents, ion-exchange resins, gas diffusion electrodes in proton exchange membrane (PEM) fuel cells, and template synthesis (Moreno-Castilla, C. and Maldonado-Hodar, F. J., 2005; Tao Y. *et al*., 2005; Tao Y. *et al*., 2006).

In the present paper, we report experiments based on doping of SWCNHs in RF aerogels. The SWCNH embedded aerogels showed high conductivity and nanoporosity, allowing practical applications such as chemical vapor sensors and effective electromagnetic shielding materials.

Experimental

SWCNHs were prepared by laser ablation of graphite in an argon atmosphere at room temperature (Iijima, S. *et al.*, 1999). This method can produce SWCNHs in bulk quantities and without the need for a metal catalyst, thus SWCNHs have high purity. The RF aerogels were synthesized from a sol-gel polymerization process of resorcinol (R) and formaldehyde (F), followed by supercritical drying of RF gels with CO_2 according to the method proposed by Pakala (Pekala, R. W. and Alviso, C. T., 1992). SWCNHs were dispersed in toluene with a bath-type sonicator for 15 minutes. The mixture was then transferred to a reaction cell containing RF aerogels, which was evacuated at 383 K and 1 mPa for 2 h prior to use; the SWCNHs were introduced into the nanopores of RF aerogels.

Samples were studied with a field emission scanning electron microscope (FE-SEM) (JSM-6330F, JEOL), a transmission electron microscope (TEM) (JEM400FXII, JEOL), nitrogen adsorption/desorption at 77 K (Autosorb-1, Quantachrome), and direct-current (DC) volume electrical conductivity (Protek 603 Digital Multimeter) at room temperature.

Results and Discussion

Figure 1 shows the colloidal morphology of as-grown SWCNHs, and their unique internal nanopore structures and interstitial nanopore structures. The nitrogen adsorption isotherm of as-grown SWCNHs is of type II in IUPAC classification

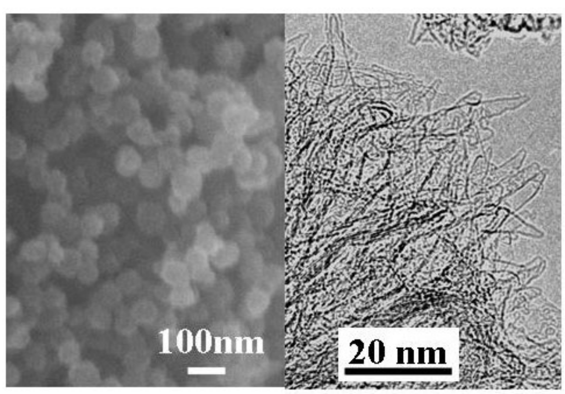

Figure 1. FE-SEM (Left) and TEM (Right) Images of as-gown Single-Wall Carbon Nanohorms.

without adsorption hysteresis. According to nitrogen adsorption, as-grown SWCNHs have surface area 308 m^2g^{-1} and interstitial micropore volume 0.1 cm^3g^{-1} (as-grown SWCNHs also have intrinsic micropores and its pore volume is 0.4 cm^3g^{-1}). Detailed porosity evaluation of SWCNHs can be found in the literature (Murata, K. *et al.*, 2000; Murata, K. *et al.*, 2001, Ohba, T. *et al*., 2001).

RF aerogels are composed of interconnected beads with continuous porosity. Adsorption and desorption isotherms of nitrogen at 77 K on the RF aerogels are IUPAC type IV, and from the nitrogen adsorption isotherm it was determined that the surface area was 860 m^2g^{-1}, a total nanopore volume was 4.4 cm^3g^{-1}. By nanopore filling of SWNHs in RF aerogels, we prepared the SWCNH embedded aerogels.

It was evidenced that SWCNHs were filled in the mesopores of RF-aerogels with the scanning electron microscopic and transmission electron microscopic observation. The nitrogen adsorption and desorption isotherms for the SWCNH embedded aerogels are IUPAC type IV. BET analysis and the DR method of the nitrogen adsorption isotherm of SWCNH embedded aerogels showed that the surface area was 380 m^2g^{-1}, the total pore volume was 0.5 cm^3g^{-1}. The mesopore sizes of SWNH/RFA were determined to be 2-10 nm widths using Dollomore-Heal (DH) method. Although RF aerogels are of typical electrical insulator, the SWCNH embedded aerogel shows high electrical conductivity (log sigma = -4 S/m), suggesting that an interconnected SWCNH structure lead to high electronic conductivity, Therefore, this SWCNH-embedded RF aerogels have new potential applications to be electrochemical sensor, electrode, energy storage, and gas sensor. Further exploration on the new fields of applications is currently underway.

In summery, conductive and nanoporous single wall carbon nanohorn embedded aerogels were prepared by nanopore filling of RF aerogels with SWCNHs. Such a nanoporous structure of SWCNH-filled aerogels can still show the same electrical conductivity as the carbon-nanostructure-filled polymer solid composites (Antonucci, V. *et al*., 2003). These materials are attractive, because the assembly form offers an additional advantage to SWCNHs in their applications in comparison with the as-grown colloidal form, and the significantly increased electrical conductivity, i.e. in the range of 10^{-4} S m^{-1} demonstrates the potential use of the conductive SWNH/RFA nanostructures.

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References

Antonucci, V.; K.- T. Hsiao; S. G. Advani. 2003. In G. O. Shonaike; S. G. Advani, Eds.; *Advanced Polymeric Materials: structure Property relationships*. Boca Raton, FL.: CRC Press.

Bekyarova, E.; A. Hashimoto; M. Yudasaka; Y. Hattori; K. Murata; H. Kanoh; D. Kasuya; S. Iijima and K. Kaneko. 2005. Palladium Nanoclusters Deposited on Single-Walled Carbon Nanohorns. *J. Phys. Chem. B*, 109:3711.

Hirsch, A. 2002. Functionalization of single-walled carbon nanotubes, *Angew. Chem. Int. Ed*. 41 (11): 1853-1859.

Iijima, S.; M. Yudasaka; R. Yamada; S. Bandow; K. Suenaga; F. Kokai and K. Takahashi. 1999. Nano-aggregates of single-walled graphitic carbon nano-horns. *Chem. Phys. Lett.* 309:165-170.

Moreno-Castilla, C. and F. J. Maldonado-Hodar. 2005, Carbon aerogels for catalysis applications: An overview, *Carbon* 43, 455-465.

Murata, K.; K. Kaneko; F. Kokai; K. Takahashi; M. Yudasaka; S. Iijima. 2000. Pore structure of single-wall carbon nanohorn aggregates. *Chem. Phy. Lett.* 331:14-20.

Murata, K.; K. Kaneko; W. A. Steele; F. Kokai; K. Takahashi; D. Kasuya; M. Yudasaka; S. Iijima. 2001. Porosity evaluation of intrinsic intraparticle nanopores of single wall carbon nanohorn. *Nano Letters*. 1 (7): 197-199.

Ohba, T.; K. Murata; K. Kaneko; W. A. Steele; F. Kokai; K, Takahashi; D. Kasuya; M. Yudasaka and S. Iijima. 2001. N_2 Adsorption in an Internal Nanopore Space of Single-Walled Carbon Nanohorn: GCMC Simulation and Experiment. *Nano Letters*, 1 (7): 371-373

Pekala, R. W. and C. T. Alviso. 1992. Carbon aerogels and xerogels. *Mater. Res. Soc. Symp. Proc.* 270:3-14.

Tao, Y.; Y. Hattori; A. Matumoto; H. Kanoh and K. Kaneko. 2005. Comparative study on pore structures of mesoporous ZSM-5 from resorcinol-formaldehyde aerogel and carbon aerogel templating. *J. Phys. Chem. B*, 109:194-199.

Tao, Y., H. Kanoh; L. Abrams and K. Kaneko. 2006. Mesopore-modified zeolites: preparation, characterization, and applications. *Chem. Rev.*, 106: 896-910.

Urita, K.; S. Seki; S. Utsumi; D. Noguchi; H. Kanoh; H. Tanaka; Y. Hattori; Y. Ochiai; N. Aoki; M. Yudasaka; S. Iijima and K. Kaneko. 2006. Effects of gas adsorption on the electrical conductivity of single-wall carbon nanohorns. *Nano Letters,* 6 (7): 1325-1328.

Utsumi, S.; K. Urita; H. Kanoh; M. Yudasaka; K. Suenaga; S. Iijima and K. Kaneko. 2006. Preparing a magnetically responsive single-wall carbon nanohorn colloid by anchoring magnetite nanoparticles. *J. Phys. Chem. B,* 110: 7165-7170.

Yang, C. M.; Y. J. Kim; M. Endo; H. Kanoh; M. Yudasaka; S. Iijima and K. Kaneko. 2007. Nanowindow-Regulated Specific Capacitance of Supercapacitor Electrodes of Single-Wall Carbon Nanohorns. *J. Am. Chem. Soc.* 129:20-21.