

Polymerization of a Confined π -System: Chemical Synthesis of Tetrahedral Amorphous Carbon Nanoballs from Graphitic Carbon Nanocapsules**

By Cheng-Che Chu, Gan-Lin Hwang, Jau-Wern Chiou, Way-Faung Pong, Cheng-Lan Lin, Chien-Ying Tsai, Hsiu-Mei Lin, Yuan-Chih Chang, Chia-Seng Chang, Allen H. Hsu, Wu-Liang Huang, Jinghua Guo, Ping-Hei Chen, and Tien-Yau Luh*

Tetrahedral amorphous carbon films have been a subject of investigation during the past decade due to their unique properties, which are found to be between those of diamond and graphite.^[1] Most of the synthetic processes require relatively drastic conditions, and the carbon source may be obtained by ionization,^[2] ion sputtering,^[3] or laser ablation.^[4] In a graphitic structure, the 3.4 Å distance between each layer allows significant π - π interactions.^[5] As such, a radical species, which can be generated on the surface, may add onto the second graphene layer via a radical chain reaction process leading to carbon-carbon bond formation. The overall process can be considered as the conversion of the sp^2 hybridized carbons

into sp^3 hybridized carbons. This protocol might provide a useful procedure for the synthesis of tetrahedral amorphous carbon.

It is known that the pyramidal double bonds in C_{60} can easily react with an organic azide to yield the corresponding aziridino- or aza-adducts,^[6] and an aziridine ring can undergo thermolysis to generate a diradical or a zwitterion intermediate.^[7]

Carbon nanocapsules (CNCs) are polyhedral nanometer-scale particles that consist of a concentric graphene-layered structure with a cavity in the center.^[8] CNCs with diameters of tens of nanometers have been synthesized by a pulse plasma arc-discharge method.^[9] CNCs are a very robust allotrope of carbon which are stable up to 900 °C at ambient pressure under an inert atmosphere. A representative transmission electron microscopy (TEM) image of a CNC is shown in Figure 1. The spacing between each layer is 3.4 Å which is similar to the interval of graphite layers.^[5] Since CNCs have a ball-like structure, some of their double bonds might have

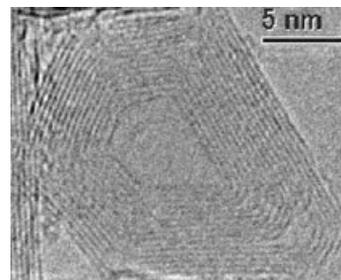


Figure 1. TEM image of a CNC.

pyramidal character and, therefore, are expected to be more reactive. The CNC itself may be considered to be a confined π -system constituted of layers of graphene structures. It is envisaged that the CNC could be readily derivatized by aziridination. Thermolysis of such aziridino derivatives may generate a radical species on the surface. The radical species on the surface may interact with the next graphene layer via a radical chain reaction process to transform the graphene-layered CNCs into a tetrahedral amorphous form. Here, we report the first chemical synthesis of tetrahedral amorphous-carbon nanoballs (CNBs) from graphitic CNCs.

A mixture of CNCs and an excess amount of azidobenzene in chlorobenzene was refluxed for 48 h under a nitrogen atmosphere. The solution was passed through a membrane filter. The recovered insoluble CNCs were utilized in a second derivatization reaction. The soluble portion was evacuated, and the residue was taken up in pentane. The precipitate was dissolved in chlorobenzene and the solution was spin-coated onto a quartz plate. Under a nitrogen atmosphere, the derivatized-CNC-coated quartz was placed in a tube furnace which was heated at a rate of 10 °C min⁻¹ to 700 °C. The sample was maintained at this temperature for 30 min. A second coating was applied by following the same procedure.

[*] Prof. T.-Y. Luh, C.-C. Chu
Department of Chemistry
National Taiwan University
Taipei 106 (Taiwan)
E-mail: tyluh@ntu.edu.tw

Dr. G.-L. Hwang
Union Chemical Laboratories
Industrial Technology Research Institute
Hsinchu 300 (Taiwan)

J. W. Chiou, Prof. W.-F. Pong
Department of Physics
Tamkang University
Tamshui 251 (Taiwan)

Dr. C.-L. Lin, H.-M. Lin
Institute of Chemistry
Academia Sinica
Nangang, Taipei 115 (Taiwan)

Dr. C.-Y. Tsai, Prof. P.-H. Chen
Department of Mechanical Engineering
National Taiwan University
Taipei 106 (Taiwan)

Y.-C. Chang, Prof. C.-S. Chang
Institute of Physics
Academia Sinica
Nangang, Taipei 115 (Taiwan)

A. H. Hsu, Prof. W.-L. Huang
Department of Geosciences
National Taiwan University
Taipei 106 (Taiwan)

Dr. J. H. Guo
Lawrence Berkeley National Laboratory
Berkeley, CA 94720-8226 (USA)

[**] This work was supported by the National Science Council of the Republic of China. Supporting Information is available online from Wiley InterScience or from the author.

X-ray diffraction (XRD) patterns of the CNCs, CNBs, and nanodiamond (ND) are displayed in Figure 2. The characteristic (111) peak of ND in Figure 2 suggests a polycrystalline

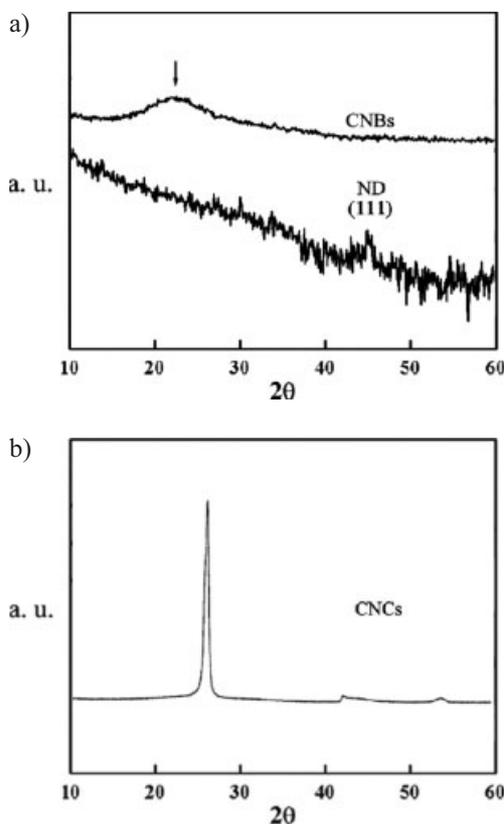


Figure 2. X-ray diffraction patterns of a) CNB and ND samples (the intensity is presented in log units), and b) CNCs.

nature, whereas the XRD spectrum of the CNBs implies an amorphous phase with broad features. The pyrolyzed sample was subjected to TEM analysis. Figure 3 shows a TEM image of the pyrolyzed sample on silicon wafer substrates prepared

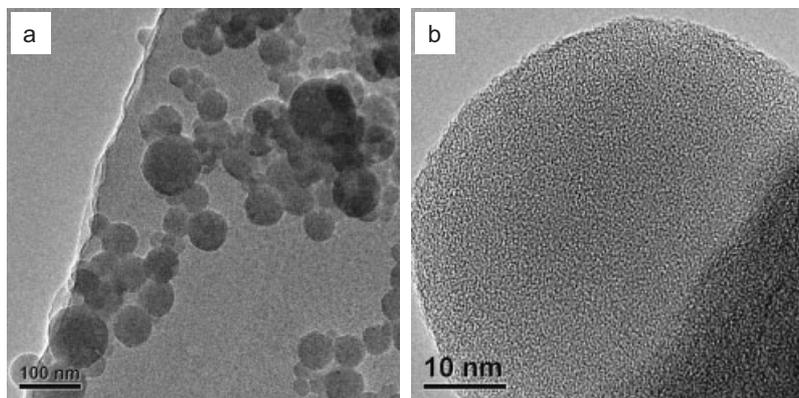


Figure 3. TEM images of the pyrolyzed sample on a silicon wafer substrate prepared by plane-milling: a) Low-magnification and b) high-magnification images.

by plane-milling. Consistent with the powder X-ray analysis, only amorphous structures were observed.

Figure 4 exhibits the C K-edge X-ray absorption near-edge structure (XANES) spectra measured at an incident angle of 45° for the CNBs and the references, ND and highly oriented pyrolytic graphite (HOPG). The spectra were normalized

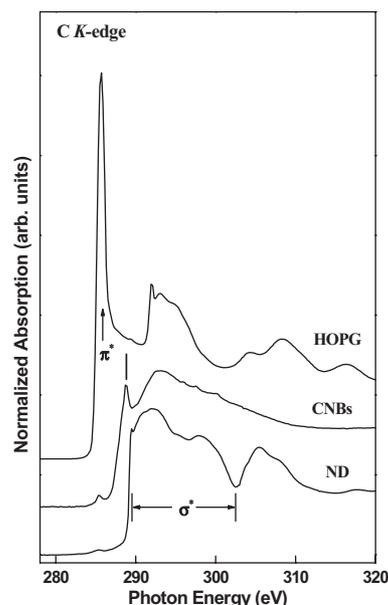


Figure 4. Normalized C K-edge absorption spectra of HOPG, CNBs, and ND.

using the incident-beam intensity I_0 , keeping the area under the spectra in the energy range between 315 and 330 eV fixed. According to the dipole-transition selection rule, the spectra in Figure 4 are a result of transitions from the C 1s core level to the p-like final unoccupied states above the Fermi level. The general shape of the C K-edge XANES spectra of the CNBs, which reflect local environments of the carbon atoms, seems to be different from that of the HOPG but fairly similar to that of ND. The XANES energy range for the CNBs is typically divided into two regions characterized by i) the spike of the C 1s core exciton resonance at approximately 288.7 eV (labeled by a vertical solid line), and ii) a relatively broad σ^* feature of the sp^3 -bonded carbon occurring between about 290 and 302 eV.^[10] A relatively weak peak at ≈ 285.4 in the CNB and ND spectra, which conversely is strong in the HOPG spectra, can be assigned to the π^* states of sp^2 -bonded carbon.^[11] Presumably, the residual phenyl group that arises from the *N*-phenylaziridine moiety may account for the π^* peak for the CNBs. The π^* peak in the CNB and ND spectra exhibits not only a lower intensity but also a slight shift

towards the lower-energy side by 0.2–0.3 eV relative to that in the HOPG spectrum. The lack of long-range order in the amorphous compound has long been understood to cause the excited electrons to be more localized near the core hole, resulting in a lower energy shift for the peak in the measured spectra.

A preliminary electrochemical examination indicated that CNCs spread onto an indium tin oxide (ITO) electrode gave a quasireversible cyclic voltammetry (CV) curve,^[12] whereas that of the CNBs showed no current response under the same conditions. This observation appeared to be consistent with the C sp³ structure of the CNBs.

In order to establish that such amorphous CNBs were obtained only from the pyrolysis of the derivatives of the CNCs, a pristine CNC sample was heated at 700 °C for 30 min: no morphological changes were observed. Even after the pristine sample was treated under 5 kbar (1 kbar = 10⁵ kPa) at 700 °C for 24 h, only slight changes at the corners of the CNC were observed in the TEM image, whereas the bulk of the graphene-like layers remained intact (Fig. 5). These results suggested that the conversion of the C sp² hybridization into C sp³ hybridization was facilitated when the CNC was modified

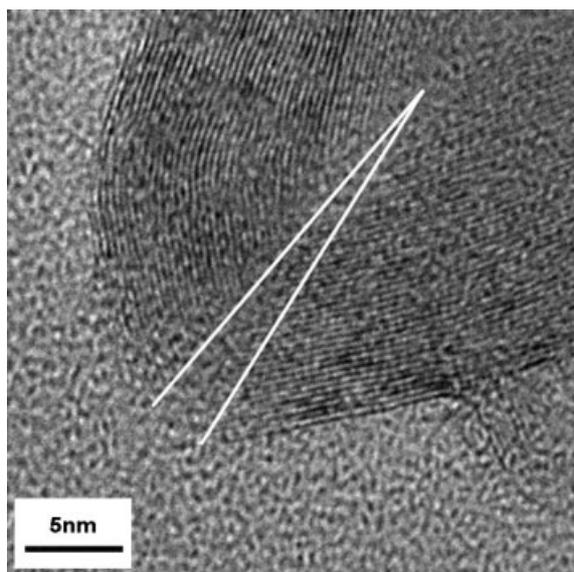
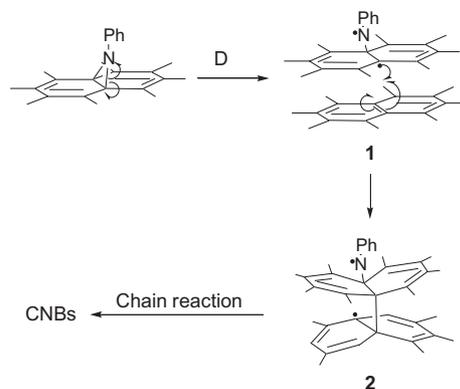


Figure 5. TEM image of a CNC treated under high pressure and temperature.

by the aziridine moieties. A plausible mechanism for the formation of amorphous carbon nanoballs is summarized in Scheme 1.

The radical species **1** generated by the homolysis of the C–N or C–C bond in an aziridine ring may undergo an addition reaction to a neighboring graphene layer to yield a new radical species **2**. The new radical may proceed to react further to precipitate a chain reaction that would result in the formation of an amorphous C sp³ network (Scheme 1). The



Scheme 1. Mechanism of formation of amorphous C sp³ network by a radical chain reaction, resulting in carbon nanoballs.

generation of the radical species would be crucial in this overall process, and this radical species would preferentially react with the π -system of the next graphene layer than revert to the starting aziridine moiety. Since the CNC is a rigid ball-like system, the overall reaction can be considered as a radical polymerization of π -bonds belonging to a three-dimensional confined system. The properties and potential applications of CNBs are under investigation.^[13]

Experimental

Cycloaddition of CNCs and Azidobenzene: CNCs (100 mg) were dispersed in chlorobenzene (200 mL) in a two-necked flask (500 mL). Air in the flask was removed under vacuum, and then the flask was filled with nitrogen. Azidobenzene (400 mg) in chlorobenzene (50 mL) was added dropwise into the above CNC slurry, and the mixture was refluxed for 48 h. After cooling, the solution was passed through a membrane filter (Advantec MFS Inc., PTFE, 0.5 μ m). The collected insoluble CNCs were again utilized in the derivatization reaction described above. The solvent of the filtrate was removed under vacuum (0.05 mm Hg, 1 mm Hg \sim 133 Pa). The residue was taken up in pentane (5 mL), and the precipitate was collected after centrifuging. The precipitate was dried under vacuum to afford the crude aziridino-CNCs as a brown powder (30.2 mg).

Synthesis of Amorphous CNBs: The crude aziridino-CNCs were taken up in chlorobenzene and 20 μ L of the solution (130 mg mL⁻¹) was spin-coated (spin rate: 3000 rpm for 20 s) onto a quartz substrate (10 mm \times 10 mm \times 2 mm) or a silicon wafer (10 mm \times 10 mm). The coated quartz was placed in a quartz tube (diameter = 2.54 cm, length = 60 cm). Air in the tube was expelled under reduced pressure, and the tube was filled with nitrogen. The gas-exchange cycle was repeated five times. The quartz tube was put in a tube furnace (Lindberg/Blue M, TF55035A-1), and the system was heated at a rate of 10 °C min⁻¹ to 700 °C and maintained at this temperature for 30 min. The sample was cooled to room temperature and subjected to analysis.

CV Experiments with CNCs: Cyclic voltammograms were obtained by using an EG&G (PAR 273A) potentiostat/galvanostat to control the potential applied to the working electrode. CV curves were measured in CHCl₂ with 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (TBAHFP) as the supporting electrolyte. A conventional three-electrode configuration was used for CV experiments. ITO glass (15 mm \times 40 mm) with CNCs physically adhered, a Pt wire, and a

Ag/Ag⁺ (0.1 M AgNO₃) electrode were used as the working, counter, and reference electrodes, respectively. Potentials were referenced to the ferrocene/ferrocenium ion (Fe/Fe⁺) couple, and the scan rate was 100 mV s.

Received: April 14, 2005
Final version: July 25, 2005
Published online: September 29, 2005

Oligomeric Phenylenevinylene with Cross Dipole Arrangement and Amorphous Morphology: Enhanced Solid-State Luminescence Efficiency and Electroluminescence Performance**

By Feng He, Hai Xu, Bing Yang, Yu Duan, Leilei Tian, Keke Huang, Yuguang Ma,* Shiyong Liu, Shouhua Feng, and Jiacong Shen

The electronic properties of photoluminescent oligomeric phenylenevinylene (OPV) derivatives, which serve as the model compounds for the corresponding poly(phenylenevinylene) (PPV), have recently attracted great interest.^[1] As active materials, OPVs are also widely used in device studies for their tunable electronic properties and well-defined chemical structures.^[2] The classic PPV oligomer, distyrylbenzene (DSB, **1**) and its derivatives,^[3] exhibit a nice blue fluorescence in dilute solution with a photoluminescence (PL) efficiency up to 90 %, but in the solid state the fluorescence is strongly quenched. This effect originates from intense crystallization characteristics and the pronounced π - π interaction encountered in the crystalline lattice of these planar conjugated molecules. This architecture leads to the formation of sandwich-type dimers (H-aggregates) in the ground state, and excimers in the excited state, which usually exhibit red-shifted fluorescence and a low PL efficiency.^[4] Much work has been done to prevent the aggregation of DSB, involving the tetrahedral linkage of four DSBs, referred to as tetrakis(4-*tert*-butylstyryl-stilbenyl)methane (C(BuSSB)₄),^[5] and the covalent assembly of four DSBs arising from a calyx[4]arene core.^[6] More re-

- [1] a) D. R. McKenzie, D. Muller, B. A. Pailthorpe, *Phys. Rev. Lett.* **1991**, 67, 773. b) Y. Lifshitz, *Diamond Relat. Mater.* **1999**, 8, 1659.
- [2] J. Ullmann, *Nucl. Instrum. Methods Phys. Res., Sect. B* **1997**, 127, 910.
- [3] a) Z. W. Deng, R. Souda, *Nucl. Instrum. Methods Phys. Res., Sect. B* **2001**, 183, 260. b) S. M. Mominuzzaman, K. M. Krishna, T. Soga, T. Jimbo, M. Umeno, *Carbon* **2000**, 38, 127.
- [4] G. Kovach, H. Csorbai, G. Z. Radnoczi, G. Vida, Z. Paszti, G. Peto, A. Karacs, *Mater. Sci. Eng.* **2003**, 414, 127.
- [5] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York **1988**, p. 237.
- [6] a) M. Prato, Q. C. Li, F. Wudl, V. Lucchini, *J. Am. Chem. Soc.* **1993**, 115, 1148. b) M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, J. R. A. Miller, A. T. Taylor, *Chem. Commun.* **1995**, 885. c) G. Schick, T. Grösser, A. Hirsch, *Chem. Commun.* **1995**, 2289. d) J. C. Hummelen, M. Prato, F. Wudl, *J. Am. Chem. Soc.* **1995**, 117, 7003. e) L.-L. Shiu, K.-M. Chien, T.-Y. Liu, T.-I. Lin, G.-R. Her, T.-Y. Luh, *Chem. Commun.* **1995**, 1159. f) C. K.-F. Shen, K.-M. Chien, C.-G. Juo, G.-R. Her, T.-Y. Luh, *J. Org. Chem.* **1996**, 61, 9242. g) A. B. Smith, III, H. Tokuyama, *Tetrahedron* **1996**, 52, 5257. h) J. Averdung, J. Mattay, *Tetrahedron* **1996**, 52, 5407. i) C. K.-F. Shen, H.-H. Yu, C.-G. Juo, K.-M. Chien, G.-R. Her, T.-Y. Luh, *Chem. Eur. J.* **1997**, 3, 744.
- [7] a) N. De Kamp, P. Sulmon, L. de Buyck, R. Vehre, N. Schamp, J. P. Declercq, M. van Meerssche, *J. Chem. Res., Synop.* **1984**, 82. b) T. Hudlicky, J. O. Frazier, L. D. Kwart, *Tetrahedron Lett.* **1985**, 26, 3523. c) W. H. Pearson, *Tetrahedron Lett.* **1985**, 26, 3527. d) C. Vogel, P. Delavier, *Tetrahedron Lett.* **1989**, 30, 1789.
- [8] H. Zeng, L. Zhu, G. Hao, R. Sheng, *Carbon* **1998**, 36, 259.
- [9] G.-L. Hwang, *Japanese Patent JP 2003 0910*, **2003**.
- [10] a) J. F. Morar, F. J. Himpel, G. Hollinger, G. Hughes, J. L. Jordan, *Phys. Lett.* **1985**, 54, 1960. b) Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P. D. Johnson, J. E. Rubensson, T. Boske, W. Eberhardt, S. D. Kevan, *Phys. Rev. Lett.* **1992**, 69, 2598.
- [11] J. Nithianandam, J. C. Rife, H. Windischmann, *Appl. Phys. Lett.* **1992**, 60, 135.
- [12] The CV curve for CNCs is shown in the Supporting Information.
- [13] Ball-like structures containing carbon and metal species have recently been described. See: S. Scholz, P. J. Leech, B. C. Englert, W. Sommer, M. Weck, U. H. F. Bunz, *Adv. Mater.* **2005**, 17, 1052.

*] Prof. Y. G. Ma, F. He, H. Xu, Dr. B. Yang, L. L. Tian, Prof. J. C. Shen
Key Laboratory for Supramolecular Structure and Materials
The Ministry of Education
Jilin University
Changchun 130012 (P.R. China)
E-mail: ygma@jlu.edu.cn
Y. Duan, Prof. S. Y. Liu
National Laboratory of Integrated Optoelectronics
Jilin University
Changchun, 130012 (P.R. China)
K. K. Huang, Prof. S. H. Feng
State Key Laboratory of Inorganic Synthesis
and Preparation Chemistry
Jilin University
Changchun, 130012 (P.R. China)

**] We are grateful for financial support from the National Science Foundation of China (grant numbers: 20125421, 90101026, 50303007, 20474024, 50473001), from the Ministry of Science and Technology of China (grant number: 2002CB6134003), and from PCRIIT. Supporting Information is available online at Wiley InterScience or from the author.