III-G Structure and Properties of Carbon Nanotubes and Nanohorns

Our research on single-wall carbon nanotubes (SWNTs) and single-wall carbon nanhorns (SWNHs) have been extending toward two directions, the analysis of nanometer-scaled structures and the application. Developing new types of transmission electron microscopes (TEM), we could, for the first time, clearly observed holes opened on the tube walls. Also Gd atoms attached at the open end of the tubes and single-carbon-atom defects on the tube walls became observable. Even the determination of chiralities of SWNTs was possible. With aids of these TEM techniques, several methods of encapsulation and de-encapsulation of various molecules and clusters in liquid phase at room temperature have been developed, which assure the future application of SWNTs and SWNHs particularly in biological use.

Application of SWNTs was greatly enhanced by the progress of growth method, that is, site-selective growth by chemical vapor deposition. A top-gate transistor was fabricated and its performances has been ranked at the world top record for some time. For practical realization of SWNT-devices, we need to develop highly refined growth-methods, which we are currently engaging in.

III-G-1 Direct Evidence for Atomic Defects in Graphene Layers

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[*Nature* **430**, 870–873 (2004)]

Atomic-scale defects in graphene layers alter the physical and chemical properties of carbon nanostructures. Theoretical predictions have recently shown that energetic particles such as electrons and ions can induce polymorphic atomic defects in graphene layers as a result of knock-on atom displacements. However, the number of experimental reports on these defects is limited. The graphite network in single-walled carbon nanotubes has been visualized by transmission electron microscopy (TEM) and their chiral indices have been determined. But the methods used require a long image acquisition time and intensive numerical treatments after observations to find an 'average' image, which prevents the accurate detection and investigation of defect structures. Here we report observations in situ of defect formation in single graphene layers by high-resolution TEM. The observed structures are expected to be of use when engineering the properties of carbon nanostructures for specific device applications.

III-G-2 Selective Deposition of a Gadolinium (III) Cluster in a Hole Opening of Single-Wall Carbon Nanohorn

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[*Proc. Natl. Acad. Sci.* **101**, 8527–8530 (2004)]

As has been amply demonstrated in chemistry by way of metal-catalysis, metal-complexation should immensely widen the scope of carbon cluster science. Thus, metal-containing hollow carbon clusters such as endohedral metallofullerenes and carbon nanotube filled with metal atoms have been suggested as promising materials. However, the methodology to rationally control the size and the location of the metal clusters as well as to ensure high yield production of the material on a large scale has been lacking. Herein we report a method for forming a one- to multi-atom metal cluster specifically at the hydrophilic hole opening of a carbon nanotube as demonstrated by deposition of $Gd(OAc)_3$ in single-wall carbon nanohorns. The hole-selective deposition of the Gd atoms allows atomic scale detection of the structural defect in the graphitic materials, and, on a bulk scale, controls the permeability of molecules through the holes. The result would find use for modulation of the electronic properties of carbon nanotubes.

III-G-3 Material Storage Mechanism in Porous Nanocarbon

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[*Adv. Mater.* **16**, 397–401 (2004)]

Carbonaceous materials, such as activated carbon and charcoal, have long been known to possess "nanospaces," where a variety of materials can be accommodated. Their structures and chemical properties, however, have never been optimized for any specific purpose, because their mechanism of storing objects is not yet fully understood. We have therefore attempted to visualize how materials is stored in the inner spaces of nanocarbon materials in order to verify the storage mechanism. We used "single-walled carbon nanohorns" (SWNHs) for this purpose. This porous nanocarbon material, composed of single layer/crystal/atom graphite walls, is known to possess completely enclosed nanoscale spaces, and is therefore quite suitable for these experiments.

III-G-4 Structural Evolutions of Carbon Nano-Peapods under Electron Microscopic Observation

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[*Chem. Phys. Lett.* **390**, 462–466 (2004)]

Supramolecular assemblages made of single wall carbon nanotubes (SWNT) filled with fullerenes or metal doped fullerenes exhibit promising electronic structure variations at a nanometer scale. Nevertheless, the knowledge about the structural defects of these systems is still very limited. Here, we report structural evolutions under high-resolution electron microscopic observation at the sensitivity of a single atom detection for Ca@C$_{82}$ molecules encapsulated within SWNT.

III-G-5 Nano-Extraction and Nano-Condensation for C$_{60}$ Incorporation into Single-Wall Carbon Nanotubes in Liquid Phases

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[*Chem. Phys. Lett.* **380**, 42–46 (2003)]

We have established two new methods that enable incorporation of guest molecules into single-wall carbon nanotubes in liquid phases; nano-extraction and nano-condensation methods. To make SWNTs that have incorporated C$_{60}$ ((C$_{60}$)$_n$@SWNT) through nano-extraction, we put C$_{60}$ and SWNTs in ethanol for 1 day during which the C$_{60}$ molecules deposited themselves inside the SWNTs. The incorporation mechanism appears to be that the C$_{60}$ molecules dissolved slightly in the ethanol, diffused toward the SWNTs, and eventually deposited themselves at the most stable sites—that is, inside the SWNTs. In the case of nano-condensation, we formed thin layers of C$_{60}$-toluene saturated solution on SWNT surfaces, and then obtained (C$_{60}$)$_n$@SWNT within a few seconds. A reasonable explanation is that the C$_{60}$ molecules migrated through the thin layers of the toluene-C$_{60}$ mixtures on the SWNT surfaces and finally deposited themselves inside the SWNTs.

III-G-6 Preferential Deposition of Pt Nanoparticles inside Single-Wall Carbon Nanohorns

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[*Adv. Mater.* **16**, 1420–1423 (2004)]

Many types of materials can be incorporated into one-dimensional (1D) spaces of carbon nanotubes (CNTs). CNTs having fullerenes in their insides, “peapods,” are well known, and ionic salts, Ga, and organic molecules are also successfully incorporated. This 1D ordering is unique and fascinating but it is too simple to cope with a variety of application demands. Therefore we propose to use three-dimensional nanospaces of single-wall carbon nanohorns (SWNHs. Here, we report that our strategy is promising, that is, Pt nanoparticles could be placed inside this space. Furthermore, a curious size-mismatch is noticed, that is, the Pt particle diameters are large, but no holes with such diameters can be seen, which remind us ships-in-bottles. The formation mechanism of the Pt particle reveals that the starting materials are first incorporated into the SWNHs perhaps through the small wall-holes, and they construct the Pt-particles inside the SWNHs.

III-G-7 Support Materials Based on Converted Aluminum Films for Chemical Vapor Deposition Growth of Single-Wall Carbon Nanotubes

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[*Chem. Phys. Lett.* **380**, 158–164 (2003)]

We systematically studied the support materials for chemical vapor deposition of single-wall carbon nanotubes (SWNTs). Four support materials with iron catalysts were investigated: silicon dioxide, aluminum film, boehmite, and g-alumina. The boehmite and the γ-alumina were progressively converted from evaporated aluminum film. The iron catalysts on the aluminum film, the boehmite, and the γ-alumina produced a good SWNT yield in the growth temperature range of 650–800 °C, while the catalysts on silicon dioxide produced a poor SWNT yield. The X-ray diffraction patterns suggested that the catalyst particle sizes were kept small on these aluminum-based support materials.

III-G-8 Fe-Sapphire and C-Fe-Sapphire Interactions and Their Effect on the Growth of Single-Walled Carbon Nanotubes by Chemical Vapor Deposition

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[*J. Nanosci. Nanotechnol.* **4**, 1–5 (2004)]

We previously reported that the quantity of single-walled carbon nanotubes grown on Fe-coated sapphire by chemical vapor deposition depended on the crystallographic faces of sapphires. In this report, we show that the interaction of Fe, sapphire, and carbon depended on the sapphire faces. We deduce that the quantity of Fe available to catalyze the growth of single-walled carbon nano-tubes was suppressed by the formation of Fe-Al alloys and whether the Fe-Al alloys were formed on Fe-coated sapphire or not depended on the sapphire-surface structure.

III-G-9 Carbon-Nanotubes Field-Effect Transistors with Very High Intrinsic Transconductance

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[*Jpn. J. Appl. Phys.* **42**, L1288–L1291 (2003)]

We investigated intrinsic transconductance of carbon-nanotube field-effect transistors (CNT-FETs) with carbon nanotubes (CNTs) grown by chemical vapor deposition. The measured transconductance at a drain voltage of –1 V was 8.7 μS for a CNT with a diameter of 1.5 nm. Very high intrinsic transconductance of 20 μS was estimated by considering the contribution of parasitic resistance. Apparent and intrinsic transconductance per unit channel width were 5800 μS/μm and 13000 μS/μm, respectively, which are enormously larger than those for the state-of-the-art Si-MOSFETs. The parasitic resistance is dominated by the resistance of CNT in the region between the gate and contact. We expect the performance of CNTFETs will further advance by improving CNT quality and by optimizing device structures.

III-G-10 Raman Scattering Study on Fullerene Derived Intermediates Formed within Single-Wall Carbon Nanotube: From Peapod to Double-Wall Carbon Nanotube

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[*Chem. Phys. Lett.* **384**, 320–325 (2004)]

By heating of C_{60} peapods at 900 °C in vacuum, eight or more Raman peaks associated with the inner tubes were observed in the frequency range of the radial breathing mode vibration. An analysis of time traces of the peak intensities led to the growing mechanism of double-wall nanotubes: inner tubes with $\approx$ 0.7 nm diameters are first formed and then increase their diameters. To explain these phenomena, we propose a model based on formation of short achiral zig-zag nanotubes in the beginning of C_{60} coalescence.

III-G-11 Evidence for Substantial Interaction between Gd Ion and SWNT in (Gd@C_{82})@SWNT Peapods Revealed by STM Studies

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[*Chem. Phys. Lett.* **379**, 340–344 (2003)]

A metallofullerene, Gd@C_{82}, encapsulated in the inside of single walled carbon nanotube (SWNT) has been identified as an STM image of a carbon cage and a Gd atom by a measurement of the tunnel currents onto the SWNT surface. This fact indicates that there is a substantial local interaction between the wall of SWNT and the Gd ions close to the wall. The origin of this interaction is not yet clear, but its existence has also been supported by the results of axially- and peripherally-resolved STS measurements around the Gd ion sites in the peapod.

III-G-12 Structure Changes of Single-Wall Carbon Nanotubes and Single-Wall Carbon Nanohorns Cued by Heat Treatment

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[*Carbon* **41**, 1273–1280 (2003)]

Raman spectra and transmission electron microscope images showed that diameter enlargement of HiPco, a kind of single-wall carbon nanotubes, accompanied by tube-wall corrugation was caused by heat treatment (HT) at 1000 to 1700 °C. Further enlargement accompanied by straightening of the tube walls and incorporation of carbon fragments within the tubes became obvious after HT at 1800 to 1900 °C. The transformation of some single-wall carbon nanotubes into multi-wall nanotubes was observed after HT at 2000 °C, and most single-wall tubes were transformed into multi-wall ones by HT at 2400 °C. What influence the Fe contained in the HiPco tubes had on these structure changes was unclear; similar changes were observed in single-wall carbon nanohorns that did not contain any metal. This indicates that thermally induced changes in the structure of single-wall carbon nanotubes can occur without a metal catalyst. Heat treatment increased the intengrity of the nanotube-papers, and this increase may have been due to tube-tube interconnections created by HT.

III-G-13 Diameter Enlargement of Single-Wall Carbon Nanotubes by Oxidation

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[*J. Phys. Chem. B* **108**, 149–153 (2004)]

The diameter of high-pressure CO (HiPco) single-wall carbon nanotubes (SWNTs) has been enlarged by treating them with nitric acid and oxygen, and the diameter enlargement is related to the nitric acid refluxing time. Raman spectra (exciting wavelength 488 nm) and transmission electron microscopy showed that the 0.8–1.2 nm diameter distribution of HiPco SWNTs could be narrowed to one centered around 1.2 nm when the nitric acid treatment time was 1 h. Significantly, SWNTs of 1.37–2.4 nm in diameter were discovered when the nitric acid treatment lasted more than 2 h.

III-G-14 A Theoretical Study on the Geometrical Features on Finite-Length Carbon Nanotubes Capped with Fullerenes Hemisphere

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[*Chem. Phys. Lett.* **386**, 38–43 (2004)]

The structures of the finite-length (5,5) and (9,0) carbon nanotubes capped with fullerene hemisphere are analyzed by quantum chemical calculations at the B3LYP DFT level of theory. DFT calculations demonstrate that the geometries of the armchair tubes depend on the number of cyclic *cis*-polyene chains lined up along the tube axis, whereas the zigzag tubes consist of Kekulé-type networks in the cylinder, the geometries being independent of the number of component cyclic *trans*-polyene chains.

III-G-15 The Role of Fullerene Hemisphere in Determining the Geometrical Features of Finite-Length Carbon Nanotubes

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[*J. Phys. Chem. B* **108**, 11426–11434 (2004)]

Geometrical and electronic features of the armchair C_{40+20n} and zigzag C_{42+18n} nanotubes, in which n is the number of cyclic *cis*- and *trans*-polyene chains involved in the nanotubes, are analyzed from density functional theory (DFT) calculations. To illuminate the role of the fullerene hemispheres in their structures, $C_{20n}H_{20}$, and $C_{18n}H_{18}$, are also studied in terms of orbital interactions. Although there are various bond-deformation patterns within the *cis*-polyene chains in the $C_{20n}H_{20}$ series, the C_{40+20n} series always have similar bond-length alternate patterns. The geometrical change in the capped nanotubes is a consequence of orbital interactions in the cylindrical segments with the fullerene hemispheres. Accordingly, the fullerene hemispheres play a dominant role in determining the geometrical and electronic properties of the capped nanotubes. DFT calculations also demonstrate that the geometries of the armchair series exhibit an oscillatory behavior as the chain width with a periodicity of 3.

III-G-16 A Catalytic Chemical Vapor Deposition Synthesis of Double-Walled Carbon Nanotubes over Metal Catalysts Supported on a Mesoporous Material

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[*Chem. Phys. Lett.* **380**, 496–502 (2003)]

Double-walled carbon nanotubes (DWNTs) have been synthesized by catalytic chemical vapor deposition (CCVD) over supported metal catalysts decomposed from $Fe(CH_3COO)_2$ and $Co(CH_3COO)_2$ on mesoporous silica. Bundles of tubes with relatively high percentage of DWNTs, in areas where tubular layered structures could be clearly resolved, have been observed by transmission electron microscopy (TEM). In other areas, crystal-like alignment of very uniform DWNTs was observed for the first time, suggesting that mesoporous silica might play a templating role in guiding the initial nanotube growth. In addition, compatible with nanoelectronics research, bridging of catalytic islands by DWNTs has also been demonstrated.

III-G-17 Controlled Opening of Single-Wall Carbon Nanohorns by Heat Treatment in Carbon Dioxide

BEKYAROVA, Elena[1]; KANEKO, Katsumi[1]; YUDASAKA, Masako[2]; KASUYA, Daisuke[2]; IIJIMA, Sumio[2,3,4,5]; HUIDOBRO, Ana[6]; RODRIGUEZ-REINOSO, Francisco[6]
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[*J. Phys. Chem. B* **107**, 4479–4484 (2003)]

The opening of *bud*-type single-wall carbon nanohorns (SWNHs) by heat treatment in CO_2 was studied by TEM and nitrogen adsorption (77 K). The adsorption isotherms indicate that oxidation by CO_2 at 1273 K provides a sufficient nanohorn opening. The pore parameters of the open nanohorns can be controlled by varying the treatment conditions; the size of the generated nanopores increases with the temperature and time of treatment. In addition, TPD experiments indicate a significant decrease of the oxygen content in SWNHs opened by heat treatment in CO_2. This is in contrast to the procedures reported in the literature for opening of carbon nanotubular structures, typically introducing oxygen functional groups.

III-G-18 Interstitial Nanopore Change of Single Wall Carbon Nanohorn Assemblies with High Temperature Treatment

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[*Chem. Phys. Lett.* **389**, 332–336 (2004)]

Single-wall carbon nanohorns (SWNHs) were treated in vacuum at different temperatures of 473 to 1073 K. The nanostructural change due to the heat-treatment was studied by adsorption of N_2 at 77 K and H_2O at 303 K. The determined particle density showed that gas is not adsorbed in internal pores, but in interstitial pores. The high temperature treatment (HTT) in vacuo changed water adsorption, but it gave almost no influence on N_2 adsorption. The maximum nanopore volume from H_2O adsorption was observed at 673 K, indicating the interstitial nanopore change due to a local orientational change of SWNH particles.

III-G-19 Direct Thermal Fluorination of Single Wall Carbon Nanohorns

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[*J. Phys. Chem. B* **108**, 9614–9618 (2004)]

Single wall carbon nanohorns (SWNHs) were fluorinated to form more attractive nanohorns that have the characteristic structural and adsorptive properties. Nitrogen adsorption, XPS, TEM studies elucidated the surface states and the morphologies of fluorinated SWNHs (F-SWNHs). The XPS results of F-SWNHs showed that the nature of C–F bonds changed from semi-ionic to covalent with increase of the fluorination temperature. The N_2 adsorption isotherm indicated that the total amounts of N_2 adsorption on SWNHs fluorinated at 303 and 373 K was smaller than that of pristine SWNHs. After fluorination at 473 K, nano-order windows were produced on the sidewalls of SWNHs without change in the shape of each horn and aggregate. Therefore, the SWNHs fluorinated at 473 K can adsorb N_2 molecules on the internal surfaces of nanohorns through the nanowindows.

III-G-20 Synthesis of Carbon Nanohorn Particles by Simple Pulsed Arc Discharge Ignited between Pre-Heated Carbon Rods

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[*Chem. Phys. Lett.* **389**, 181–185 (2004)]

Single-wall carbon nanohorn (SWNH) particles were generated by simple pulsed arc discharge between pure carbon rods in the atmospheric pressure of air. Purity of SWNHs was reached higher than 90%, and the heating in dry air at 500 °C was useful for removal of amorphous carbon. The mean size of SWNH particles was ≈ 50 nm, which is smaller than those prepared by the CO_2 laser method. Pre-heating of the carbon rod up to 1000 °C, conducted just before ignition of arc, improved the quality of SWNHs. Transmission electron microscopy, scanning electron microscopy and Raman spectroscopy were used to characterize these SWNH particles.

III-G-21 Solvent Effects on Hole-Edge Structure for Single-Wall Carbon Nanotubes and Single-Wall Carbon Nanohorns

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[*J. Phys. Chem. B* **108**, 10732–10735 (2004)]

To extend the application fields of single-wall carbon nanotubes (SWNTs) and single-wall carbon nanohorns (SWNHs), their chemical modification is essential. Since their graphene-sheet-based structures are chemically robust, only the edges of the graphene sheets, more specifically the oxygen-containing functional groups at hole edges, are useful sites for chemical modification. However, not much is known about the hole-edges, so the phenomenon reported here, that the hole edges easily react with conventional reagents, was previously unknown. We observed a lowering of the combustion temperature of SWNTs and SWNHs immersed in water; this lowering was induced as a result of the hydrolysis of oxygen-containing functional groups (anhydrides and/or lactones) at the hole edges. We also found that the reactivity of hole edges can be easily controlled through an appropriate choice of solvents. We believe that this study is helpful to our understanding of hole-edge chemistry and will help to enable the production of well-designed carbonaceous materials with high functionality.

III-G-22 Evidence for the Intermolecular Motion of Gd Atoms in a $Gd_2@C_{92}$ Nanopeapod

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[*Nano Lett.* **3**, 1395–1398 (2003)]

Atoms in a confined space can be regarded to represent a completely new phase because it should behave differently than the atoms in a solid or in a free-space. The metallofullerene provides an ideal case of the confined atoms since a number of metal atoms are imprisoned in a subnanometer void of the carbon cage. Here we give direct evidence of the dynamic behavior for the confined atoms in metallofullerenes by observing individual atoms using the high-resolution transmission electron microscopy. Rapid movement of Gd atoms in $Gd_2@C_{92}$ peapod is identified for the first time. By comparison with simulation, the amplitude of the motion is roughly quantified as 0.2 nm at room temperature and is reduced to almost half at 100 K.

III-G-23 Laser Vaporization Synthesis of Polyhedral Graphite

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[*Appl. Phys. A: Mater. Sci. Process.* **77**, 69–71 (2003)]

Polyhedral graphite (PG) particles have been synthesized by CO_2 laser vaporization of graphite in high-pressure Ar gas (8×10^5 Pa). Faceted PG particles, ranging in size from 110 to 150 nm, have a turbostratic structure. The yield of PG is more than 90%. This synthesis is based on the condensation of hot carbon species confined by an Ar-gas atmosphere.

III-G-24 Direct Observation of 3D Mesoporous Structure by Scanning Electron Microscopy (SEM): SBA-15 Silica and CMK-5 Carbon

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[*Angew. Chem., Int. Ed.* **42**, 2182–2185 (2003)]

Mesoporous silica has attracted much attention in recent years, due to new possibilities for advanced applications in catalysis, separation technologies, electronic engineering, and manufacturing of optic devices. The highly nanoporous structures with good thermochemical stability are suitable for synthesis of new materials such as nano-particles, wires and networks of plantinum and carbon within the pore system. In the case of the carbon synthesis, the fabrication technique has been fully developed so that ordered mesoporous carbons exhibiting Bragg X-ray diffraction (XRD) lines similar to those of the MCM-41-type mesoporous silica can be obtained after the complete removal of silica template.

III-G-25 Study of the Growth of Boron Nanowires Synthesized by Laser Ablation

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[*Chem. Phys. Lett.* **385**, 177–183 (2004)]

Boron nanowires with different morphologies and diameters have been fabricated by laser ablation. The effects of the synthesis temperatures, intensities of the laser beams, the types of the metal catalysts and the addition of H_3BO_3 on the growth of the boron nanowires are studied. The systematic analyses show that the vapor-liquid-solid (VLS) model may play important roles in the growth of the boron nanowires.

III-G-26 Structure and Electronic Properties of a Nongraphitic Disordered Carbon System and Its Heat-Treatment Effects

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The heat-treatment effect on electronic properties is investigated in relation to structural change for pulsed-laser-deposited amorphous carbon thin films having sp^2/sp^3 ratio ≈ 9. The heat treatment at temperatures 200–400 °C increases conductivity and modifies the hopping conduction mechanism at low temperatures, resulting in the generation of a Coulomb gap at E_F. In the heat-treatment temperature region above 600 °C, considerably small positive thermoelectric power is suggestive of carrier compensation by the competition of hole and electron carriers that originate from the inhomogeneous charge. In the high-heat-treatment-temperature region 800–1100 °C, the formation of an infinite percolation path network of the graphitic sp^2 domains induces an insulator-to-metal transition, where the electron transport in the sp^2-rich metallic state is featured by weakly temperature-dependent conductivity.

III-G-27 Compression of Polyhedral Graphite up to 43 GPa and X-Ray Diffraction Study on Elasticity and Stability of the Graphite Phase

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The crystal structure of polyhedral graphite particles (“*G balls*”) has been investigated under pressure up to 43 GPa and at room temperature by x-ray powder diffraction measurements. The polyhedra maintain the graphite phase under pressure higher than 40 GPa. A 29% compression in volume at 43 GPa involves an unusual decrease in the interlayer distance of 25%. The polyhedra recover their original crystal structure by releasing the pressure. A closed and solid structure of the polyhedra, suppressing a transition into another phase, causes them to become metallic under pressures higher than 20 GPa.