MATERIALS



Nanocarbon Materials



Fullerenes

Carbon Nanotubes (CNTs) Graphene / Graphene Oxides (GOs) Nanodiamonds (NDs) Nanocarbon Unit Structures

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1. Fullerenes

Fullerene is a spherical carbon compound and is an allotrope of carbon such as diamond, graphite and carbon nanotubes. Fullerenes of C_{60} , C_{70} and C_{84} are well known. They are isolable carbon compounds in a sole molecular species. Among them, the C_{60} is a representative species. Kroto, Smalley and Curl *et al.* first observed the C_{60} in which the 60 carbon atoms consist of 12 five-membered rings and 20 six-membered rings.¹⁾ Kroto, Smalley and Curl won their joint Nobel prizes in chemistry in 1996 for their contributions. Osawa predicted existence of fullerene in 1970, earlier than the first observation of fullerene.²⁾

The most specific feature of fullerene is that it is an excellent electron acceptor. Any fullerenes are n-type semiconductors, which are suitable for organic electronic materials with electron carriers. Rubidium- and cesium-doped fullerenes can be superconductors with electron carriers. These superconducting transitions occur at more than 30 K.^{3,4}



Addition reactions and other chemical modifications of fullerenes easily produce fullerene derivatives. Precise structure analyses of these derivatives are possible because they are molecular species. Non-derivatized fullerenes are poorly soluble in similarity to the other nanocarbon materials. However, we can introduce soluble functional groups to form solution-processible electronic materials. Phenyl-C₆₁-butyric acid methyl ester ([60]PCBM [M2088]) and indene-C₆₀ bisadduct ([60]ICBA [10900]) are useful organic semiconductors for fabricating a solution-processible electronic device.^{5,6)} These fullerene derivatives are n-type organic semiconductors for organic photovoltaics (OPV) by mixing with a p-type conjugated polymer.⁷⁾ An application of a fullerene derivative for organic transistors was also reported.⁸⁾ A complexation of C₆₀ with tetrakis(dimethylamino)ethylene (TDAE) gives a

charge transfer complex (TDAE-C $_{60}),$ which is an organic magnet at low temperature. $^{9)}$

2. Carbon Nanotubes

A carbon nanotube (CNT) has a cylindrical structure with a nanoscale diameter that is like a rolled graphene sheet. Iijima first observed a CNT in 1991.¹⁰⁾ A CNT consists of only sp² carbons similar to fullerenes. There are diverse CNTs on the basis of their length, diameter of the nanotube, state of chirality, and number of the layer. The variety of these structures provides various band structures and metallic and semiconducting properties.^{11,12)} A normal synthetic procedure gives a mixture of semiconducting CNTs in 2/3 and metallic CNTs in 1/3, because rolling a carbon sheet occurs randomly. Since we need to obtain the semiconductivity, improved synthetic procedure and efficient purification of CNT are further required.¹³⁻¹⁵⁾

CNTs can enclose nanoscale molecules and atoms in the internal space, because of the cylindrical structure. For instance, there is a fullerene-enclosed CNT, the so-called 'peapod'.¹⁶⁾ In addition, CNTs can enclose metal, water, and molecular oxygen. Properties of the enclosed water in the CNT are different from those of bulk water.^{17,18)} An organic dye (eg. squarylium) can be easily enclosed within the internal space of CNTs in solution. In this case, the enclosed squarylium dye absorbs light and then an energy transfer (sensitization) to the outer CNT occurs.¹⁹⁾ Hydrogen storage using CNTs is expected to be used in the development of a fuel cell.²⁰⁾



3. Graphene / Graphene Oxides

Graphene, which is one of the nanocarbon materials, consists of all six-membered rings with sp^2 carbons having a twodimensional sheet structure. Graphene has been known for long time, since graphite is formed by combination of graphenes with van der Waals force. However, details of the properties were unclear until late years, because an isolation procedure of graphene from graphite was not well developed for long time. Geim and Novoselov *et al.* in 2004 successfully isolated a thinflake graphene by a simple procedure. They used a tape to peel off a graphene layer from highly oriented pyrolytic graphite (HOPG) and then the peeled graphene layer is stuck on a substrate. After this observation,²¹⁾ studies of graphene have proved the particular characteristics of electronic, mechanical, and chemical properties. Geim and Novoselov won their joint Nobel prizes in physics in 2010 for their contributions.

The most characteristic feature of graphene is its electrical property. The electron mobility in the graphene layer is 100 times greater than that of silicon.²²⁾ Accordingly, we can expect to develop a transistor with high-mobility and low-power consumption. Graphene may be promising for a next generation channel material that is useful for LSI (large-scale integration). In addition, the physical strength of graphene is 100 times greater than that of iron. The current density tolerance is much better than that of copper, thus it is expected to be an electrical wire transporting large currents.²³⁾

Electrons in the graphene behave as massless Dirac fermions as similar to neutrinos,²⁴⁾ and demonstrate a quantum Hall effect at room temperature.²⁵⁾ Graphene is an ideal material for spintronics, since there are small spin orbit interactions and the negligible nuclear magnetic moment of carbon. Hybridization of graphene and a ferromagnetic material is developed for the application of an information processor using the electron spin (spintronics device).²⁶⁾



[G0438] [G0441] [G0442] [G0499]



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The fabrication procedure for graphene is peeling off the layer from HOPG, a chemical vapor deposition (CVD)²⁷⁾ as well as reduction of a graphene oxide (GO).28) There are various synthetic methods of making GO, and the properties and applications depend on the degree of oxidation. GO disperses in water and several polar solvents, because the structure of GO normally includes hydroxyl, epoxy, and carboxyl groups on the graphene sheet. Accordingly, a GO thin film can be fabricated on a substrate by a solution-process. The reduction of GO provides a reduced graphene oxide (rGO), but it is not a perfect graphene. The rGO contains a few oxygen components and defects on the graphene structure. Although GO is an insulator because there are sp³ carbon atoms, rGO is conductive. Therefore the rGO is expected to be an electrode material. A water dispersion of GO is used as a lubricant to reduce friction on metal surfaces.²⁹⁾GOsupported metal catalysts were developed for a cross-coupling reaction and hydrogenation.^{30,31)} We can introduce several functional groups on GO because there are oxygen-based groups. These GO derivatives may be useful for luminescent materials and biosensors.32,33)

4. Nanodiamonds

Diamond, an allotrope of carbon, has excellent hardness,

coefficient of friction, thermal conductivity, insulation characteristics, and refractive index. Large and highly pure diamond is good for use as jewelry. Furthermore, the major industrial application of diamond is for cutting and polishing tools, because it is the hardest of natural products. However, diamond is not workable enough because of its hardness so there is a limitation for industrial use of a large diamond. Nanodiamond (ND) is a nanoparticle having the crystal structure of diamond, and it has excellent properties of normal diamond. ND is artificially synthesized and is useful for polishing tools and additives of engine oil.



We can modify the surface of ND by introducing carboxyl and amino groups. These groups are further converted by a chemical modification to functionalize the ND particle.³⁴⁻³⁶⁾ Non-modified ND can be dispersed in water, but coheres in organic solvents. On the other hand, a functionalized ND particle with alkyl groups can be dispersed in organic solvents. We can modify a glass surface with ND that is functionalized with a silane coupling reagent.³⁷⁾



An application of ND is extended for biology and medical use^{38,39)} because it is a harmless nanoparticle in-vivo. Since a diamond with a complex defect (NV) containing nitrogen (N) and vacancy (V) shows fluorescence,⁴⁰⁾ we can monitor movements and structural changes of a biological molecule on a microscope using the NV diamond as a fluorescent labeling reagent.41-43) We can easily detect fluorescent behavior in a complex atmosphere in-vivo, because ND is chemically publication stable. A described that functionalization of ND also showed fluorescent behavior without NV defects.44) Protein- and biotin-supported ND were reported in order to enhance affinity toward a biological molecule.45,46) These modified NDs are expected to be used for a drug delivery system.

5. Nanocarbon Unit Structures Cycloparaphenylenes (CPP)

Carbon nanotubes (CNT) have advanced chemistry, material science, life science and other research fields. CNTs can be

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prepared by physical methods such as arc discharge, laser furnace, and chemical vapor deposition techniques. One disadvantage of these physical methods is forming several kinds of CNTs with various diameters, thus uniform CNTs do not form.

Cycloparaphenylenes (CPP), the so-called carbon nanoring, have a cyclic structure formed by linkages of p-substituted benzenes. The CPP attracted researchers in fundamental chemistry and material science, because it is a unit structure of CNT. In fact, Itami *et al.* successfully synthesized uniform CNTs by a bottom-up procedure starting from CPP as a template compound.⁴⁷



Recently, this research was extended to synthesize a CPP of smaller diameters having a large distortion. Yamago⁴⁸⁾ and Jasti⁴⁹⁾ groups independently reported synthesis of the [5]CPP, which has been the smallest CPP so far. We can expect to synthesize the smallest diameter CNTs from [5]CPP. In addition, the electronic and physical properties of [5]CPP may be interesting, because [5]CPP is a unit structure of C₆₀ fullerene, too. CPPs of a specified diameter make an inclusion complex with a fullerene.⁵⁰

Corannulene and Truxene

Corannulene, the so-called [5]circulene, is one of the polycyclic aromatic compounds. It has a condensed structure of five benzene rings. The corannulene was first synthesized in 1960s,⁵¹⁾ and after that the bowl-type structure was observed.⁵²⁾ The corannulene is attractive as a nanocarbon material, because it is a unit structure of C_{60} fullerene.

Scott *et al.* synthesized a polyarene compound by a flash vacuum pyrolysis (FVP) starting from corannulene. This polyarene compound e corresponds to an end-capped CNT. An extension of the end-capped CNT may chemically produce a normal CNT.⁵³⁾ Itami and Scott *et al.* synthesized a grossly warped nanographene compound from corannulene.⁵⁴⁾



Truxene has star-shaped and rigid planar structures. Truxene is also a unit structure of C₆₀ fullerene. Truxene derivatives are useful for OLED materials because they easily form an amorphous structure.⁵⁵⁾ A chemical synthesis for C₆₀ fullerene was carried out starting from truxene. Otero *et al.* synthesized a polyarene compound formulated as C₆₀H₃₀ by three step reactions, and a thermal treatment of the polyarene on platinum surface gave C₆₀ fullerene all.⁵⁶⁾



Coronene

Coronene, the so-called [6]circulene, is another polycyclic aromatic compound. It has a condensed structure of six benzene rings. The coronene is a molecular compound in nanoscale, known as a representative nanographene compound that is smaller than graphene. The coronene can be an organic transistor material⁵⁷⁾ because it is a nanographene compound with a band gap, which is different from graphene. Furthermore, a bottom-up procedure of coronene fabricated a graphene nanostructure.58) After Kubozono et al observed superconductivity from an alkali-doped picene,59 studies on organic superconductors of polycyclic aromatic compounds recently received much attention.60,61) An alkali-doped coronene also showed superconductivity.62)



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