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Polygon Building Block Route to sp^2 -Carbon-Based Materials**

By Chi-Young Lee,* Hsin-Tien Chiu,* Chih-Wei Peng, Ming-Yu Yen, Yu-Hsu Chang, and Chao-Shiuan Liu

Elemental carbon exists in two classes, sp^3 -hybridized, such as diamond, and sp^2 -hybridized, such as graphite, carbon nanotubes (buckytubes), carbon onions (buckyonions), and fullerenes.^[1,2] It is well known that diamond usually forms under high temperatures and high pressures. Preparation of the other classes of carbon materials requires high-energy processes too. In many examples, carbon nanotubes (buckytubes), carbon onions (buckyonions), and fullerenes were synthesized by high-temperature arc-discharge between graphite electrodes^[3] or laser ablation of a graphite target.^[4] The processes are simple and are being used to produce most of the new materials for current research activities: they are inefficient and of low yield. Chemical routes have also been attempted; however, suitable precursors are difficult to obtain and the reactions are difficult to control. For example,^[5] it has been shown that strained cycloalkynes with high-energy content can be converted, with limited success, to fullerene-class materials. In another example,^[6] the formation of fullerene in low yield was observed from laser ablation of perchloroacetylene ($C_{12}Cl_8$). Other possible chemical routes, such as flame synthesis^[7] and chemical vapor deposition,^[8] can be utilized to generate carbon nanotubes, but in low quantities. Clearly, a simple high-yield route to these materials is needed if carbon-based technology is to be developed to its full potential.

Many growth mechanisms^[9,10] have been proposed to rationalize how these materials are formed but they do not provide pointers to new synthetic strategies. When we examine the basic constructions of the sp^2 -hybridized carbon materials, we find that graphite and carbon nanotubes are formed from repeating hexagon units of carbon atoms while carbon onions and fullerenes contain, in addition to the hexagons, pentagon units of carbon atoms. According to IPR (the isolated pentagon rule),^[3] twelve (and only twelve) non-adjacent pentagons are essential for the formation of spherically shaped carbon onions and fullerenes. For example, it is well known that the buckyball is composed of twelve non-adjacent pentagons and twenty hexagons. However, as suggested by Kroto and Walton several years ago,^[11] a buckyball could be constructed by using pentagons as the only building block, if their vertices were linked as shown in Figure 1a (linking six pentagons to generate a half-buckyball). No hexagons are needed; they are

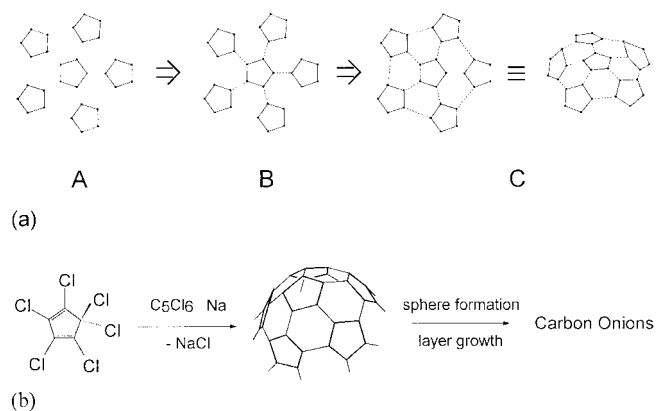


Fig. 1. a) Construction of C_{60} from pentagons only [11]. Two “C” fragments offer a C_{60} molecule. b) Reaction scheme for the formation of carbon onions.

generated as a natural consequence of the linking process. This suggests the possibility of employing pentagonal-shaped organic precursors as the “building blocks” to synthesize fullerene and buckyonions, while hexagonal-shaped precursors are needed to form graphite.

As shown in Figure 1b, letting hexachlorocyclopentadiene, C_5Cl_6 , react with Na through a Wurtz-type reaction at about 100 °C generated black powders containing carbon onions. Based on solid-state ^{13}C NMR (nuclear magnetic resonance) spectroscopy, more than 50 % of the carbon atoms are in an ordered environment.^[12] HRTEM (high-resolution transmission electron microscopy) images of the powder (Fig. 2) show that the sample consists of spherical and elliptical onion structures of various sizes. The number of shells of the onions is in the range 8–50. The smaller onions, such as the one shown in Figure 2a, have about 10 shells. The diameter of the innermost shell of such onions is about 2.5 nm. According to the projection method,^[2] a fullerene with I symmetry has a diameter of 1.985 or 2.779 nm, for C_{500} or C_{980} , respectively. This suggests that the innermost shell may be considered to be a buckyball with the number of carbon atoms in the range 500–1000. Also, this indicates that more C_6 hexagon units have been created than expected. The exact cause is not clear.

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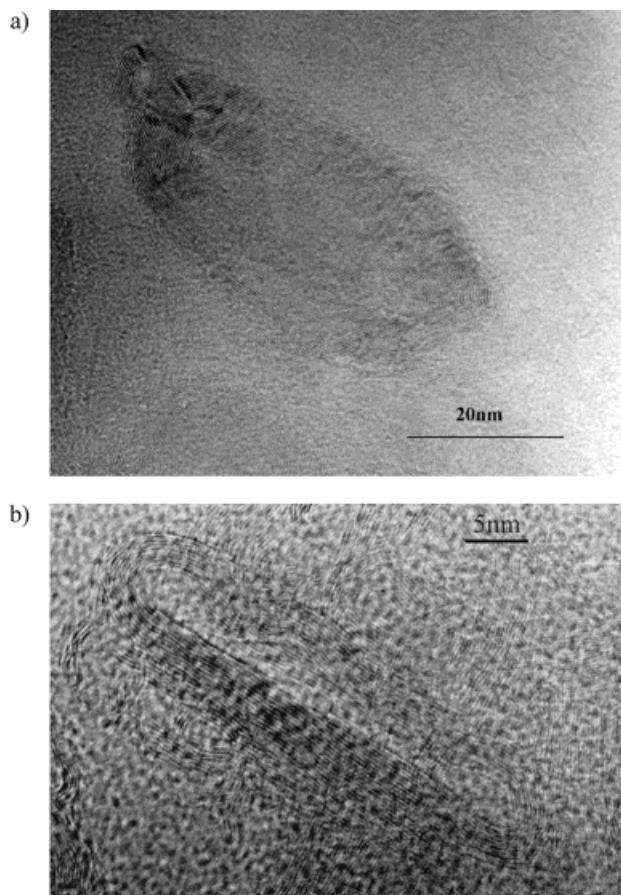


Fig. 2. a) HRTEM of spherical and elliptical carbon onions. b) HRTEM of a rod-shaped carbon onion.

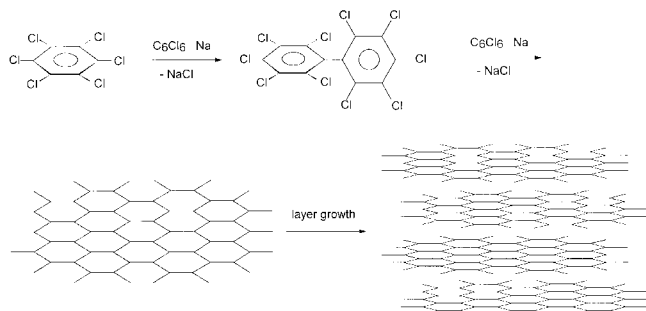


Fig. 3. Reaction scheme for the formation of graphite.

We speculate that a radical pathway may be responsible for the ring opening and the rearrangement of the carbon atoms. The distance between the layers is about 0.34 nm, close to the value of graphite.

In an analogous reaction employing C_6Cl_6 , a source of hexagonal building blocks of carbon atoms, nanosized graphite crystals were formed (Fig. 3) in nearly 70 % yield based on solid-state ^{13}C NMR. An HRTEM image is shown in Figure 4a. The micrograph reveals a nanocrystalline structure, as indicated by the Moiré fringe contrast patterns, with an average grain size in the range of 20 nm. The Moiré fringes arise from the lattice difference between the particles. An ED

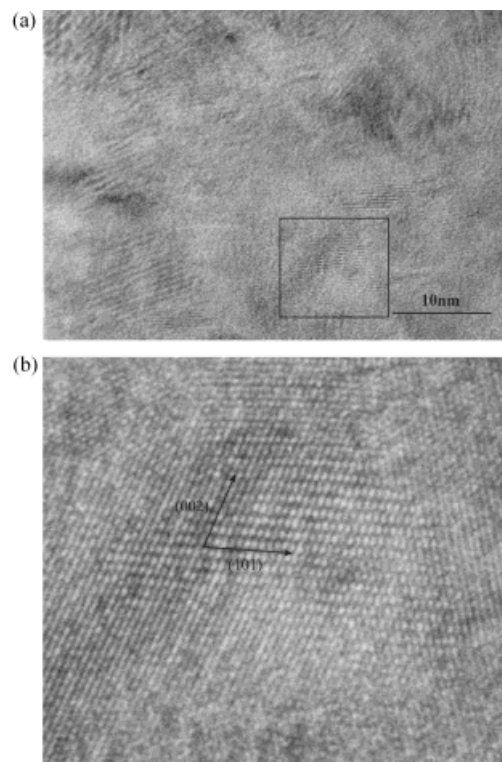


Fig. 4. a) HRTEM image of the graphite powder. b) Enlarged HRTEM image of the rectangular region shown in (a).

(electron diffraction) study shows ring patterns reflected from the randomly oriented graphite crystals. A magnified view of the marked area in Figure 4a is shown in Figure 4b. The pattern of the lines shown in Figure 4b identifies them to be (002) and (101) of graphite.

In conclusion, we have shown that carbon onions and nano-sized graphite can be synthesized employing carefully selected precursors, C_5Cl_6 and C_6Cl_6 , respectively, as the building blocks. It is promising that the “building block” strategy can be applied to prepare other carbon-based materials by selecting suitable precursors and reaction conditions.

Experimental

General Synthesis Steps of Carbon Onion and Graphite: The selected precursor, either C_5Cl_6 or C_6Cl_6 (both C_5Cl_6 and C_6Cl_6 are possible carcinogens and should be handled by trained personnel) was allowed to react with a stoichiometric amount of Na in a tube (allow extra volume for potential expansion of the vaporized precursors) sealed under vacuum at 100–150 °C. A dark gray powder was formed immediately from the highly exothermic reaction. After the reaction ceased, the byproduct NaCl was removed by washing with water. A black powder composed of carbon, as suggested by elemental analysis and EDS (energy dispersive spectroscopy), was isolated in nearly quantitative yield. Solid-state ^{13}C NMR spectra of the powders showed resonance signals at 130 and 178 ppm [12], which could be assigned to ordered and disordered carbons, respectively. The relative yield of the ordered carbon in the powders is 50 and 70 % for the reactions involving C_5Cl_6 and C_6Cl_6 , respectively.

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Photocontrol of the Basal Spacing of Azobenzene–Magadiite Intercalation Compound

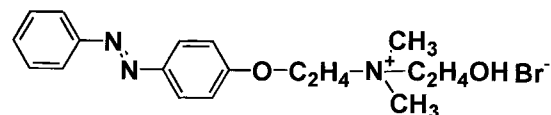
By Makoto Ogawa,* Takuma Ishii, Nobuyoshi Miyamoto, and Kazuyuki Kuroda

The synthesis of supramolecular materials incorporating a photochromic moiety is a topic of interest because of the possibility of creating novel photoresponsive materials and optical devices.^[1] Cis-to-trans photoisomerization of an azobenzene chromophore is a well-known phenomenon, which has been widely utilized as a trigger to induce the photoresponses due to the changes in the dipole moment, as well as the geometry, upon light irradiation.^[2] Accordingly, various azobenzene-containing supramolecular systems have been synthesized and the photoresponses of their physicochemical properties, such as guest binding,^[1b] have been documented. An azobenzene monolayer deposited on solid substrates has been used to control the alignment of liquid crystals^[3] and polymer chains.^[4]

This communication reports the photochromic reactions of a cationic azobenzene in the interlayer space of a layered silicate, magadiite (the ideal formula is $\text{Na}_2\text{Si}_4\text{O}_{29}\cdot n\text{H}_2\text{O}$), for controlling the microstructure by photoirradiation. Intercalation of organic guest species into layered inorganic solids is a way of producing inorganic–organic supramolecular assemblies with unique microstructures controlled by host–guest and guest–guest interactions.^[5] The organization of photoactive species on the surface of layered materials has been investigated

with a view to constructing photofunctional supramolecular systems.^[6] In order to utilize the photoisomerization of azobenzene as a trigger for controlling the physicochemical properties of intercalation compounds, efforts have been made using various layered materials and azobenzene derivatives.^[7] Although the intercalated azobenzene isomerizes effectively in the sterically limited interlayer space of layered materials, the photoresponses of the physicochemical properties of intercalation compounds are yet to be studied.

In this communication, we describe the intercalation of a cationic azo dye, *p*-(ω -dimethyl-hydroxyethylaminoethoxy)-azobenzene bromide; abbreviated as Az^+Br^-),^[8] into magadiite and the photochemical reactions of the intercalated dye that induce the change in the microstructure of the intercalation compound. The change was monitored by measuring the



change in the basal spacing after the photochemical reactions. The dye used consists of a photoisomerizable azobenzene unit and a cationic dimethyl hydroxyethyl aminoethoxy group. Magadiite is a layered silicate that is capable of incorporating guest species in the interlayer space to form intercalation compounds.^[9] Magadiite possesses some unique properties for organizing guest species.

1) The density of the cation exchange sites on the layer surface is about 2.2 meq/g, which is higher than that of smectites.

2) It can conveniently be prepared in a laboratory by hydrothermal synthesis.

Magadiite was synthesized by a hydrothermal reaction as described previously.^[9] Intercalation of the Az^+ into magadiite was carried out by the conventional ion-exchange reaction (see Experimental). The X-ray diffraction pattern of the product is shown in Figure 1B with that of original magadiite. After the ion-exchange reaction, the basal spacing increased to 2.69 nm. The interlayer expansion (gallery height) was determined to be 1.57 nm by subtracting the thickness of the silicate layer of magadiite (1.12 nm)^[10] from the observed basal spacing. Two possible orientations of the intercalated dye cations were proposed from the gallery height and the size of Az^+ ions (1.86 nm for the long axis). One is an interdigitated monomolecular layer and the other is a bilayer coverage of the dyes with the molecular long axis inclined to the silicate sheet (Fig. 1A).

The visible absorption spectrum of the Az^+ –magadiite embedded in PMMA film is shown in Figure 2a. In the absorption spectrum, an absorption band due to the *trans*-azobenzene chromophore was observed at around 335 nm, which is shifted toward a shorter wavelength region relative to that of the monomeric Az^+ (342 nm) observed in a dilute ethanol solution of Az^+Br^- (1.0×10^{-5} M). It has been reported that the interactions between siloxane surface and π -electrons induce the spectral shifts (metachromism).^[11] In the present system, such kind of interactions seem to be less plausible as

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