Soft materials with graphitic nanostructures

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This review article focuses on our recent studies on novel soft materials consisting of carbon nanotubes. Single-walled carbon nanotubes, when suspended in imidazolium ion-based ionic liquids and ground in an agate mortar, form physical gels (bucky gels), where heavily entangled bundles of carbon nanotubes are exfoliated to give highly dispersed, much finer bundles. By using bucky gels, the first printable actuators that operate in air for a long time without any external electrolyte are developed. Furthermore, the use of polymerizable ionic liquids as the gelling media results in the formation of electroconductive polymer/nanotube composites with enhanced mechanical properties. The article also highlights a new family of nanotubular graphite, via self-assembly of amphiphilic hexabenzocoronene (HBC) derivatives. The nanotubes consist of a graphitic wall composed of a great number of π-stacked HBC units and are electroconductive upon oxidation. The use of amphiphilic HBCs with functional groups results in the formation of nanotubes with various interesting properties.

Keywords: graphene; nanotube; ionic liquid; hexabenzocoronene; self-assembly

1. Introduction

Graphene, a two-dimensional honeycomb network of sp²-hybridized carbon, is a fundamental structural element of carbon materials, and has attracted great attention. Recently, a single-layered graphene sheet has successfully been isolated and its electronic properties investigated (Novoselov et al. 2004, 2005; Zhang et al. 2005a,b). Carbon nanotubes are representative of graphene-based carbon nanoclusters, which are formed by rolling-up of a graphene sheet. Over the last decade, since the discovery of carbon nanotubes (Iijima 1991; Iijima & Ichihashi 1993), a great number of research activities have been devoted to the synthesis and physical properties of carbon nanotubes arising from their unique electronic structures (Dresselhaus et al. 2001) along with their potential application to electronic devices and structure-reinforcing materials (Baughman et al. 2002). Meanwhile, these rich aspects of carbon materials have also motivated organic chemists to synthesize polycyclic aromatic hydrocarbons...
PAHs as small fragments of graphene (Berresheim et al. 1999; Watson et al. 2001). As expected from the π-stacked architecture of graphite, PAHs are very likely to form, via π-stacking interactions, one-dimensional columnar structures, which display anisotropic charge carrier and energy transport pathways (Simpson et al. 2004). Therefore, PAHs are considered as promising components for electronic and optoelectronic molecular devices (Grimsdale & Müllen 2005).

For the last couple of years, we have been involved in supramolecular chemistry and materials science of carbon nanotubes and molecular graphenes. In this article, we will mostly highlight our past achievements on these topics with an emphasis of the development of novel soft π-electronic materials.

2. Soft composite materials of carbon nanotubes and ionic liquid derivatives

Owing to their extraordinary electronic and mechanical properties as well as unique structural aspects (Dresselhaus et al. 2001), carbon nanotubes offer numerous potential applications (Baughman et al. 2002). However, in a practical sense, the processing of commercially available carbon nanotubes suffers from essential problems arising from their poor solubility. Carbon nanotubes usually exist as bundles, which are heavily entangled with one another to form agglomerates. For a better processability along with chemical and physical modifications of nanotubes, adsorption of organic modifiers onto the nanotube surface via van der Waals and π-stacking interactions have been investigated (Vigolo et al. 2000; Barraza et al. 2002; Tasis et al. 2003). However, those methods are not yet sufficiently practical for the processing of nanotube-based materials and polymer composites.

(a) Carbon nanotube gels of imidazolium ion-based ionic liquids (bucky gels)

Recently, we happened to note that a suspension of single-walled carbon nanotubes (SWNTs) in an imidazolium ion-based ionic liquid, when set in an ultrasonic cleaner, gels within 1 h at room temperature (Fukushima et al. 2003). This observation suggested that the imidazolium ion part of the ionic liquid sticks to the π-electronic nanotube surface via a so-called cation–π interaction (Ma & Dougherty 1997). However, since this interesting phenomenon was not reproducible, we extensively studied and confirmed after numerous trials that higher-powered ultrasound generators are necessary for the suspension to undergo gelation. More importantly, we later found that grinding of this suspension in an agate mortar results in gelation reproducibly. The gelation occurs in a variety of imidazolium ion-based ionic liquids (figure 1) upon grinding with 0.5–1 wt% (critical gel concentration) HiPco SWNTs. Ionic liquids, added in excess with respect to the critical gel concentration, can be removed by centrifugation from the resultant gels. ‘Bucky gels’ thus obtained can readily be processed. For example, via extrusion from a syringe, one can fabricate bucky gel cables, which are not easily broken even when suspended (figure 2a). Owing to the non-volatility of ionic liquids, bucky gels, in sharp contrast with ordinary organo- and hydrogels, are highly stable and can retain their physical properties even under a reduced pressure.
Interestingly, TEM microscopy revealed that the heavily entangled SWNT bundles, upon grinding in ionic liquids, are exfoliated to give much finer bundles (figure 2b). According to electronic absorption and Raman spectral profiles, we confirmed that SWNTs are not disrupted chemically, indicating that the gelation is triggered only physically. Together with DSC and X-ray diffraction profiles, rheological properties of the bucky gels suggested that the gelling system is more likely ruled by a great number of weak physical crosslinks among the SWNT bundles, for which molecular ordering of ionic liquids is considered responsible. Namely, SWNTs may orient imidazolium ions on their π-electronic surfaces via a possible cation–π interaction. Such a molecular ordering may trigger clustering of the surrounding imidazolium ions in the bulk solvent phase and interconnect neighbouring SWNT bundles to form a physical crosslink. The nanotube bundles are weakly interlocked with one another, and the system therefore behaves as a gel. Upon grinding, the large bundles of SWNT are exfoliated to give many finer bundles, which efficiently promote the ordering of ionic liquids.

(b) Carbon nanotube-reinforced polymeric materials derived from ionic liquids

Carbon nanotubes are taken as potential dopants for polymer materials to fabricate mechanically reinforced, electroconductive plastics (Ajayan 1999). A single piece of SWNT has been reported to possess Young’s modulus of

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approximately 1 TPa (Krishnan et al. 1998; Salvetat et al. 1999; Yu et al. 2000), which is as large as that of graphite in-plane. On the other hand, bulk SWNTs show extraordinary high electrical conductivities of the order of $10^2$–$10^3$ S cm$^{-1}$ (Kaiser et al. 1998). Despite these promising features, successful examples of such SWNT-based soft materials have been very limited, mainly owing to an extremely poor dispersibility of SWNT bundles in polymer matrices. For better dispersion of carbon nanotubes in polymer matrices, one may consider wrapping of nanotubes with appropriate organic modifiers that can interact with the nanotube surface. However, when such modified nanotube surfaces are unable to provide a good contact with polymer matrices, no large enhancements in mechanical and electrical properties are expected for the resulting composites. We anticipated that ionic liquids of polymerizable imidazolium ions, in conjunction with SWNTs, might be good candidates for the fabrication of reinforced, electroconductive polymer materials. In fact, in situ free-radical polymerization of acrylate- and methacrylate-appended ionic liquids (figure 1), gelling with SWNTs, resulted in the formation of polymer/SWNT composite materials (bucky plastics) with highly enhanced mechanical and conductive properties (Fukushima et al. 2006). For example, a bucky plastic film, prepared from the methacrylate-appended ionic liquid monomer at a 7 wt% content of SWNTs, displayed a conductivity as large as 1 S cm$^{-1}$ and a 120-fold enhancement of the Young’s modulus. Such a large enhancement of the tensile modulus by SWNTs has never been reported for SWNT-doped polymeric materials. Furthermore, the observed conductivity is one of the highest values reported so far for SWNT-doped polymers ($\sigma<10^{-2}$ S cm$^{-1}$) at comparable loading levels of SWNTs. By means of SEM and AFM (figure 2c) techniques, we confirmed that the bucky plastic film contains well-developed crosslinked networks consisting of finely dispersed SWNTs. Such nanotube networks may hamper slipping of entrapped polymer molecules via a strong interfacial interaction, and could also facilitate an intertubular charge carrier transport.

(c) Plastic actuators based on bucky gels

One of the interesting applications of bucky gels is in the fabrication of electrochemical devices (Katakabe et al. 2005; Zhang et al. 2005a,b; Zhao et al. 2005) such as actuators. There are indeed several examples of polymer actuators. However, all of them require deposition of metallic layers on their surfaces and are operative only in electrolyte solutions. By using bucky gels from imidazolium ion-based ionic liquids and SWNTs, we recently succeeded in the development of the first dry actuator, which can be fabricated by simple casting without any metallic layer deposition and operates in air without any support of external electrolyte (Fukushima et al. 2005). Our actuator adopts a bimorph configuration with a polymer-supported internal ionic liquid electrolyte layer, which is sandwiched by bucky gel electrode layers. The actuation motion was long-lived and quick in response to low applied voltages.

The actuator film can be readily fabricated by layer-by-layer casting of the electrode and electrolyte components in a gelatious 4-methyl-2-pentanone solution of a vinylidene difluoride–hexafluoropropylene copolymer (PVdF(HFP)).
A typical example described below is given by a bucky gel actuator composed of the electrode layers including 13 wt% of SWNTs, 54 wt% of BMIBF$_4$ and 33 wt% of PVdF(HFP), and the electrolyte layer including 67 wt% of BMIBF$_4$ and 33 wt% of PVdF(HFP). When an electric potential of $\pm 3.5$ V was applied to this actuator strip with a frequency of 0.01 Hz, the strip underwent a bending motion towards the anode side with a maximum displacement of 5 mm. The strain and stress generated in the bucky gel electrode layer were determined as 0.9% and 0.1 MPa, respectively. The actuation took place quickly and perfectly in response to an alternating applied voltage of $\pm 3.0$ V even at a frequency of 30 Hz. We also confirmed that the actuation ($\pm 2.0$ V, 0.1 Hz) could be repeated at least 8000 cycles in air without notable decay (20%). These performances are outstanding because no polymer actuators that demonstrate such a prominent overall performance in air have yet been reported.

Baughman et al. (1999) have reported that SWNT sheets, laminated together with a double-sided Scotch tape, show an electrochemical actuation in aqueous electrolyte solutions, where the SWNT sheets not only serve as electrodes but also undergo elongation/contraction upon charge injection into the nanotubes. However, taking into account the low loading level of SWNTs (13 wt%), such a large strain (0.9%) cannot be explained only by the elongation/contraction of SWNTs. We rather consider that volume changes of the electrode layers, caused by an interlayer ion transport, possibly contribute to the actuation. Such an interlayer ion transport could be facilitated by the seamless connection of the electrode and electrolyte layers in the actuator. We believe that the soft matter-based, easy processing allows for the fabrication of actuators with desired shapes and can be combined with printing technologies for patterning.

3. Graphitic nanotubes from amphiphilic molecular graphenes

Although carbon nanotubes are superb nanomaterials, they suffer from essential drawbacks arising from a difficulty in chemical functionalization without disruption of their $\pi$-conjugated structure. As an alternative to carbon nanotubes, we aimed to develop a new family of $\pi$-electronic nanotubes, which can provide chemically accessible surfaces for functionalization. Our basic strategy was to use self-assembly of chemically programmed molecular building blocks, since such a bottom-up, supramolecular approach has shown a great potential for the controlled synthesis of nanotubular objects (Schnur 1993; Bong et al. 2001; Shimizu et al. 2005). However, self-assembled nanotubes with tailored electronic functions were unprecedented.

We took note of hexa-$peri$-hexabenzocoronene (HBC) as the building block. HBC is regarded as a molecular graphene and is known to possess a strong tendency to stack together via $\pi$-electronic interactions. Clar et al. (1959) are the pioneers in the synthesis and characterization of HBC. Later, Müllen et al. have exploited a new family of modified HBCs with long alkyl chains and successfully obtained discotic liquid crystalline materials with high charge carrier mobilities (Simpson et al. 2004). On the other hand, we designed
an amphiphilic HBC with an expectation that it could anisotropically self-organize to give a bilayer tape, a potential precursor for tubular structures (Oda et al. 1999).

(a) Tubular assembly of an amphiphilic hexa-peri-hexabenzocoronene

Figure 3 shows the schematic structure of our engineered amphiphilic HBC (1), which is characterized by a Gemini shape carrying two triethylene glycol (TEG) chains on the other side of the HBC molecule having two dodecyl side chains (Hill et al. 2004). When a THF suspension of 1 (1 mg ml\(^{-1}\)) is once heated at 50°C, and the resulting homogeneous solution is allowed to cool to room temperature, 1 self-assembles to form nanotubes, which are characterized by a 3 nm thick graphitic wall consisting of a great number of the molecular graphene units stacked parallel to the longer axis of the tube. The self-assembled nanotubes are yellow-coloured with red-shifted absorption bands at 426 and 459 nm, and isolable without disruption by filtration. As shown by a TEM micrograph in figure 4a, the nanotubes have a uniform diameter of 20 nm, roughly one order of magnitude larger than SWNTs. This is one of the important aspects in supramolecular chemistry, since there have been reported only a few tubular assemblies in this size regime. According to the electron diffraction profile, the HBC units are \(\pi\)-stacked with a plane-to-plane separation of 3.6 Å, which is comparable with that of the (002) diffraction of graphite (3.35 Å). A SEM micrograph clearly showed that all the nanotubes are open at the end (figure 4b). We assume that the nanotubes are formed by rolling-up of a two-dimensional pseudo-graphite tape composed of \(\pi\)-stacked 1 (figure 5). Fortunately, this assumption was supported by TEM of self-assembled 1 in a mixture of THF/water (80/20 v/v), where both coiled and tubular objects were visualized. Considering the molecular structure and the dimension of 1, the wall thickness of the nanotube (3 nm) suggests a bilayer structure of the precursor tape (figure 5). This bilayer tape most probably consists of two single-layered graphitic tapes, each composed of bilaterally coupled one-dimensional HBC columns. Given that the precursor bilayer tape is 22 nm wide, a 10 μm long nanotube roughly consists of 2×16 unidirectionally aligned \(\pi\)-stacked columns, each composed of 5×10\(^4\) molecules of HBC. Such a discrete, defect-free, long-range molecular ordering is outstanding. Here, the long alkyl chains are interdigitated to hold the bilayer structure, while the hydrophilic TEG chains, located on the surface of the bilayer tape, should suppress the formation of multilayer structures in a polar solvent such as THF.

(b) Electrical properties of self-assembled graphitic nanotubes

The nanotubes of self-assembled 1 are substantially an insulator. Since HBC derivatives are redox-active (Rathore & Burns 2003), we expected that one can generate charge carriers in the nanotubes upon oxidation. For this conductivity measurement, a single piece of the nanotube was successfully positioned by chance across the Pt nanogap (180 nm) electrodes on a SiO\(_2\) substrate and its conductivity was measured after oxidation. As expected, we confirmed that the nanotube after oxidation with NOBF\(_4\) clearly shows a conducting \(I–V\) profile with an ohmic behaviour, where the resistivity at 285 K was determined as 2.5 MΩ. The conductivity decreased as the temperature was lowered, indicating

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that the oxidized nanotube is a semiconductor. The electrical conduction thus observed indicates the occurrence of a long-range intermolecular electronic communication through the graphitic molecular arrays (Yamamoto et al. 2006).

Figure 3. Molecular formulae of Gemini-shaped hexa-\textit{peri}-hexabenzocoronene (HBC) amphiphiles.
As described previously, the hexa-peri-hexabenzocoronene graphitic nanotubes consist of helically rolled-up bilayer tapes formed from bilaterally coupled columns of π-stacked HBC units. Hence, they possess a helical chirality as a structural element. Since 1 is achiral, the above consideration suggests that the nanotubes from 1 are actually a 1:1 mixture of left- and right-handed helical nanotubes. We expected that the incorporation of an appropriate stereogenic centre into the hydrophobic or hydrophilic side chains of 1 might give rise to a stereochemical bias to either the right- or left-handed helical HBC array in the resulting nanotubular assembly (figure 6a). Thus, we designed chiral HBC amphiphiles 2 and 3 (figure 3) that bear asymmetric carbon atoms in the hydrophilic and hydrophobic side chains, respectively.

Controlled self-organization of 2 took place in 2-methytetrahydrofuran (MeTHF) to form a nanotubular assembly with a size regime identical to that of the graphitic nanotube derived from 1. We also found that the point chirality of 2 is successfully translated into the supramolecular helical chirality, affording either the right- or the left-handed helical sense depending on the absolute configuration of 2 (Jin et al. 2005a,b). A hot MeTHF solution of (S)-2 (3 mg ml⁻¹), when
rapidly cooled to $20^\circ$C, showed a time-dependent spectral change profile, displaying red-shifted absorption bands at 398 and 421 nm, characteristic of graphitic nanotubes, with an isosbestic point at 382 nm. While the solution of $(S)-2$ at $50^\circ$C was silent in circular dichroism (CD) spectroscopy, cooling of the solution resulted in the appearance of positive CD bands at 389, 400 and 423 nm. As expected, the self-assembly of the enantiomer $(R)-2$ showed a CD spectral change profile that was a perfect mirror image of that observed for $(S)-2$. By applying a vapour-diffusion technique, we successfully obtained a mixture of nanotubes and helical coils. TEM analysis of the helical coils clearly demonstrated nearly 100% helical dominance. This observation allowed us to conclude the formation of one-handed helical nanotubes from enantiomerically pure 2. In sharp contrast, chiral HBC amphiphile 3 bearing branched asymmetric centres in the paraffinic side chains hardly gave nanotubular assemblies. The branched side chains of 3 likely prevent the formation of a bilayer tape, essential for the nanotube formation. Conductive polymers with helical architectures have attracted attention in view of the concept of molecular solenoids (Akagi et al. 1999; Tagami et al. 2003). However, this concept has not yet been realized because there are no molecular objects that fulfil certain requisites for conductivity and helicity.

In the course of the above study, we also found an interesting phenomenon that the $(S)$- and $(R)$-enantiomers of 2 co-assemble at varying mole ratios to give nanotubes. Even though the enantiomeric excess of 2 was changed over a wide range from 20 to 100%, the CD spectrum of self-assembled 2 changed only a little, displaying a sigmoidal response of the CD intensity (423 nm) against the enantiomeric purity of 2 (figure 6b). Such a nonlinear phenomenon is referred to as majority rule-type chirality amplification (Green et al. 1999; Nakano & Okamoto 2001; Yashima et al. 2004), where the major enantiomer incorporated into each nanotube determines the helical sense. Although chirality amplification following the majority rule is well known for covalent helical polymers, the majority rule in supramolecular systems is very rare (van Gestel 2004; van Gestel et al. 2005).
From non-covalent to covalent graphitic nanotubes

Although self-assembly of programmed molecular building blocks is useful for the synthesis of soft materials with a nanometric precision (Hoeben et al. 2005), the resulting non-covalent architectures in most cases lack sufficient structural robustness for use in practical applications. Hence, one eventually has to consider physical stabilization of self-assembled nano-objects through covalent bonds (Hartgerink et al. 2001; Clark & Wooley 2002; Mueller & O’Brien 2002). Along this line, we designed HBC amphiphile 4 (figure 3) bearing allylic functionalities at the termini of the oxyalkylene chains (Jin et al. 2005a,b). Since the hydrophilic chains cover both inner and outer surfaces of the graphitic nanotubes (figure 5), we initially expected that acyclic diene metathesis (ADMET) could covalently stabilize the preformed nanotubes (figure 7a). However, ADMET of the resulting

Figure 7. Schematic of the formation of graphitic nanotubes via (a) ADMET of 4 and (b) post-photodimerization of 6.
nanotubes from 4 using a Grubbs catalyst (Trnka & Grubbs 2001) was very sluggish and this approach was unsuccessful. After numerous trials, we happened to find that ADMET of 4 in its homogeneous CH2Cl2 solution spontaneously gives surface-polymerized nanotubes nearly quantitatively (figure 8a). We confirmed that the surface polymerization significantly enhances the thermal stability of the graphitic nanotube. The polymerized nanotubes possess a higher softening temperature (244°C) than that of the non-polymerized version (195°C). Furthermore, they can retain the hollow structure much longer upon heating. For example, even at 175°C, most of the polymerized nanotubes survived after 24 h, whereas the non-polymerized nanotubes were completely disrupted within 2 h. Our finding of the ADMET-triggered controlled self-assembly is remarkable, considering a general understanding that the polymerization of dynamic assemblies usually gives rise to irregular aggregates. The polymerized graphitic nanotubes, thus obtained, possess chemically accessible olefinic functionalities on their surface, which may allow further surface functionalization.

A combination of bottom-up supramolecular approaches with top-down post-processings enables interesting applications. We designed novel thiol- and coumarin-appended HBC amphiphiles 5 and 6 (figure 3), which can be stitched in a self-assembled state by post-polymerization via electrochemical and photochemical coupling reactions of these functional units, respectively (Motoyanagi et al. 2006a,b). Here, we highlight controlled self-assembly of 6 and a lithographic post-processing of the resulting graphitic nanotubes by their photoinduced solubility change. When an EtOH vapour was allowed to diffuse at 25°C into a CHCl3 solution of 6, a yellow suspension of nanotubes resulted. Upon exposure at 25°C to a light of λ > 300 nm, photochemical dimerization of the coumarin pendants of 6 took place in the tubularly assembled solid state. In sharp contrast, the coumarin units in a film cast from a homogeneous CHCl3 solution of 6 did not undergo photodimerization. By means of SEM and TEM, we confirmed that the size regime of the irradiated nanotubes remains unchanged upon immersion in CHCl3, a good solvent for intact 6. Hence, such photochemical stitching of the non-covalently assembled HBC monomers endows the nanotubes with an enhanced shape stability against solvents. Cyclobutane derivatives, formed upon dimerization of coumarins, are known to undergo photochemical cleavage upon irradiation with UV light, to regenerate parent coumarins. The photochemical
regeneration of coumarin actually took place on the nanotube surface upon irradiation at \( \lambda = 250-350 \) nm, and the resulting nanotubes turned soluble in CHCl₃. Thus, the photochemical stitching process in the nanotubes is reversible (figure 7b). By taking advantage of this reversible solubility change, both negative and positive patterns of the nanotubes were developed by a lithographic post-processing. For example, an EtOH suspension of the nanotubes was cast on a silicon substrate, and the resulting thin film, after being air-dried, was covered by a 400 mesh Cu grid with hole and bar dimensions of 30 and 33 \( \mu \)m, respectively. Then, the masked surface of the film was exposed perpendicularly to light of \( \lambda > 300 \) nm for 15 min. Subsequent rinsing with CHCl₃ resulted in the development of a negative grid pattern with a dimension identical to that of the photomask (figure 8b). On the other hand, for the positive patterning, a cast film of the nanotubes, once stitched photochemically, was exposed to UV light (\( \lambda = 250-350 \) nm) through the same photomask in a direction orthogonal to the substrate surface. Then, unmasked domains were rinsed off from the film with CHCl₃ (figure 8c). The successful lithographic patterning described above again indicates a high potential of amphiphilic HBC derivatives for the design of \( \pi \)-electronic soft materials.

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