Self-Assembled Fullerene Nanostructures

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Abstract: This review briefly summarizes recent developments in fabrication techniques of shape-controlled nanostructures of fullerene crystals across different length scales and the self-assembled mesostructures of functionalized fullerenes both in solutions and solid substrates.

Key words: fullerene, self-assembly, nanostructures, liquid-liquid interfacial precipitation, nanowhiskers, nanotubes, nanosheets

1 INTRODUCTION

Design of nanostructured materials whose properties can be tailored across different length scales so that they can be utilized in different functional systems and nanodevices fabrication is a current topic of great interest in the field of materials nanoarchitectonics. Self-assembly is one of the special techniques applied for the organization of functional molecules such as fullerenes, amphiphiles, proteins and peptides with molecular level precision in the preparation of functional systems. This technique enables the arrangement of building blocks into a variety of nanostructures on the micro to macroscopic length scales. Using the concept of materials nanoarchitectonics in combination with self-assembly, various building units have been assembled or organized/reorganized into hierarchic functional nanostructures. Assembly of the ideal zero-dimensional building block fullerene (C60) into higher dimensional crystalline nanostructures and assembly of functionalized fullerenes into different mesostructures are good examples of the materials nanoarchitectonics concept.

Soon after its discovery in 19851, C60 received tremendous attention due to its unique structure and properties. After several years of intensive research activity, C60 has regarded as a molecule having tremendous potential as a building block for molecular engineering, novel materials synthesis, supramolecular chemistry, and also medicinal chemistry2, 3. The 20 hexagonal and 12 pentagonal rings compose an icosohedral (Ih) symmetric closed cage structure of the C60 molecule (diameter ~ 0.8 nm). In C60, each carbon atom is bonded to three other carbon atoms through sp2 hybridized bonds with the tendency for double bonds not to be present at the pentagonal rings resulting in poor electron delocalization, i.e. C60 is not a superaromatic molecule. As a result, it behaves as an electron deficient molecule. The electron-accepting capability of C60 both in solid state and solution have permitted special uses in the formation of charge-transfer complexes and bulk heterojunctions with suitable donors for the production of photocurrent. The formation of charge-transfer salts with a number of donor groups or doping with metals has led to ferromagnetic4 or superconducting materials5. C60 exhibits strong absorption bands in the UV region and weaker but significant bands in the visible region. Functionalized C60 retains these characteristics but, in addition, the absorption of the derivatives extends further into the near-IR region demonstrating that C60 and its derivatives are very easily excited by low-energy light. This, combined with the fullerenes’ high electron affinities, makes these materials appealing for use in photoinduced electron transfer6, and also for applications in medicinal chemistry7. Guldi and Prato8 have recently reviewed the excited-state properties of C60 derivatives.

C60 has also demonstrated excellent capabilities in the quenching of various free radicals compared to conven-
tional antioxidants. Many fullerene-based compounds have shown tremendous practical values biological systems, although the highly hydrophobic character of C₆₀ (it is water insoluble) limits its application in biomaterials’ field. This problem has been addressed by many materials chemists and water soluble fullerenes have been produced by appropriate substitution or functionalization with ionic and nonionic functional groups. Furthermore, amphiphilic fullerene derivatives have also been produced that can self-assemble into different mesostructures in solution or on a substrate. Water-soluble fullerene derivatives led to the discovery of the interactions between organofullerenes and DNA, proteins, and living cells. C₆₀ can also be encapsulated in supramolecular structures containing a host moiety, such as cyclodextrin, surfactants, gels, or polymers.

Needless to say significant advances in fullerene chemistry have led to a number of interesting developments including carbon nanotubes (CNTs). This functional molecule requires assembly into well-ordered one dimensional (1D) or two dimensional (2D) forms to promote its electronic and optical properties and to construct electronic or photonic devices. It is therefore essential to know the intermolecular ordering of C₆₀ molecules at the micro and macroscopic level for the production of dimension-controlled nanostructures of C₆₀.

In this review, we briefly summarize the recent developments of the production of low to higher dimensional nanostructured fullerene (C₆₀) crystals over different length scales and focussing on solution-based approaches and different self-assembled mesostructures of functionalized fullerenes.

2 NANOSTRUCTURED CRystALLINE FULLERENES

Nano-sized C₆₀ crystals have received much attention and are considered to be intermediate states between molecules and bulk materials. Hierarchical assembly of C₆₀ into nanocrystals (or nanoparticles) offers unique properties with potential to be used in device fabrication. Bulky particles without any unified shape of pristine C₆₀ have the interesting property of forming crystalline assemblies of various well-defined morphologies and sizes depending on the method of molecular assembly. Various synthetic approaches have been explored to make 1D or 2D nanostructures of C₆₀. Templating, slow evaporation, and vapor-solid processes are the commonly employed methods to produce C₆₀ crystals. Similarly other processes, such as layer-by-layer assembly and electrophoretic deposition have also been applied to assemble fullerene nanoparticles.

In addition to the aforementioned methods, precipitation either in the bulk or at interface is also important and is the most extensively employed method used for the production of tailored nanostructured crystalline C₆₀. Miyazawa and coworkers have developed a liquid-liquid interfacial precipitation (LLIP) method for growing low dimensional nanowhiskers or hollow tubular structures from solution under ambient conditions. It should be noted that if diameters of the 1D rod structure is in the range of hundreds of nanometers then they are referred to as C₆₀ nanowhiskers. In contrast to CNTs, C₆₀ nanowhiskers do not contain any internal hollow spaces. Rather, whiskers are composed of many C₆₀ molecules bonded through a combination of van der Waals interactions and chemical bonds. Miyazawa et al. have also extended this method to produce 2D hexagonal and polygonal shaped nanosheets. Very recently, we extended this method to produce giant microcrystals with macro pores at their surfaces and also succeeded in fabricating, for the first time, hexagonal-shaped crystalline fullerene with bimodal pore structures. Furthermore, we utilized this method for the unusual formation of 3D highly crystalline cubic-shape crystals of C₆₀ fullerene-Ag(I) organometallic heteronanostructure [C₆₀ |AgNO₃]., which showed irreversible structural rearrangement upon gentle washing with aliphatic alcohols resulting in the formation of uniquely structured formations of well-oriented C₆₀ microcrystals.

In solution-based crystal formation methods, the crystal formation mechanism is suggested to be driven by supersaturation related to the low C₆₀ solubility in alcohols (known as an antisolvent or a poor solvent for C₆₀). Therefore, the solubility of C₆₀ is a key parameter for good and poor solvent selection. Rods or needles grow in arbitrary directions through the LLIP process at the interface of saturated C₆₀ in toluene and isopropyl alcohol (IPA). In depth investigations on the production of structure controlled crystalline fullerene have confirmed the fact that the morphology and size of crystalline assembly of C₆₀ largely depend on the synthetic route, concentration of C₆₀ in solution, crystallization temperature, and mixing ratio of antisolvent and solvent particularly in the precipitation method. Formation of 1D rods and 2D plate-like morphologies from slow evaporation of C₆₀ solution and vapor deposition, respectively, can be taken as a good example. In the following section, we discuss recent advances for the lower to higher dimensional nanostructured crystalline fullerene by solution-driven assembly methods.

A very simple method for producing so-called zero-dimensional C₆₀ nanoclusters is the solvent-exchange method in which C₆₀ molecules dissolved in a good solvent assemble into particle type (pseudo sphere or irregular shape particles) upon solvent removal or during solvent exchange. Recently this method has been extended to the fabrication of higher dimensional C₆₀ nanocrystals by optimizing synthetic conditions. Work of Deguchi et al. can
be taken as a good example of the formulation of stable aqueous dispersions of fullerenes (C_{60} and C_{70}) consisting of nearly spherical shaped nanoclusters by simply injecting a saturated solution of fullerene in tetrahydrofuran (THF) into water followed by THF removal by purging gaseous nitrogen. At that time, it was the first example of the stable dispersion of C_{60} in water. From transmission electron microscopy (TEM) observations they found fairly monodisperse clusters of C_{60} and C_{70} displaying low dimensional morphology (see Fig. 1). High resolution transmission electron microscopy (HR-TEM) revealed the polycrystalline nature of the clusters. They found that the dispersion is very easy to perform and exhibits excellent colloidal stability without any stabilizing agent. No precipitation was observed even after storage in the dark at room temperature over long periods (at least 9 months of preparation). It was found that the surface of the cluster is negatively charged and the electrostatic repulsion between the negatively charged cluster surfaces is important for the stability of the dispersions. The method proposed by Deguchi et al. is a simple route to produce stable dispersions of colloidal C_{60} and C_{70} in water, which are certainly suitable for the study of biomedical applications of fullerenes.

In solvent-exchange methods, THF is the most commonly employed solvent for the production of colloidal dispersions of C_{60} nanocrystals. Rapid mixing of a THF solution of C_{60} into water followed by evaporative removal of the THF controls the particle size by varying the liquid-phase addition rate. Various other solvents have been used with or without THF for the production of sub-100 nm low dimensional C_{60} nanoclusters. Other examples can be found elsewhere^{37, 38}. Recently Park et al.^{39} investigated the critical effect of solvent geometry on the morphology of C_{60} prepared by a drop-drying process at room temperature. They found a critical correlation between the solvent geometry and the geometry of the self-assembled C_{60} crystals. Although a clear mechanism of such crystal formation was not clear, they found that pseudo 0D solvent guides C_{60} molecules to self-assemble into α-1D morphology. That is, pseudo 3D (p3D) solvents guide C_{60} molecules to self-assemble into p2D hexagonal disk structures, and that p2D and p1D solvents result in p1D C_{60} wire and p0D C_{60} dot structures, respectively. They found that when a C_{60} solution in p3D tetrahydrofuran carbon tetrachloride was dropped and dried, 2D hexagonal nanosheets were observed. On the other hand, when a C_{60} solution in linear chain α-hexane (p1D structure) was drop-dried, spherical 0D C_{60} crystals were observed.

We noticed that morphology of fullerene crystals fabricated using solvent-exchange method is not very well defined in particular for lower or 0D morphology. Most reported examples have been mostly particle type and were not of perfect 0D morphology. Masuhara and coworkers^{40} have recently reported fine fullerene crystals with unique shapes including perfect 0D fullerene nanoballs using a reprecipitation method. The 0D spherical nanostructures having average size ~100 nm were fabricated by injecting 200 μL of 1 mM C_{60} solution in m-xylene into 10 mL of IPA solution at 353 K and aging the mixture at room temperature (see Fig. 2a). On the other hand, nanoballs having sizes in the range of 300-500 nm were fabricated by injecting 200 μL of C_{60} solution in pyridine (0.3 mM) into 10 mL ethanol solution at room temperature (Fig. 2b). The nanospheres and nanoballs were apparently monodisperse.

Herein, we discuss 1D fullerene nanowhiskers and nanotubes. Fullerene nanowhiskers are generally rodlike or needlelike 1D crystals having diameters < 1 μm and length several tens of μm to hundreds of nm. These structures are the most investigated nanostructures of C_{60} and have been prepared by several different approaches. Slow evaporation is one of the methods used to produce 1D nanorods. In this method, C_{60} solutions in organic solvents are evaporated at a controlled rate at a particular temperature. The aspect ratio can be controlled by adjusting the solvent evaporation

![Fig. 1](image1.png)  Low dimensional fullerene nanocrystals fabricated by the so-called solvent exchange method: (a) TEM image C_{60} nanocrystal, and (b) the same for C_{70}. Reproduced with permission from Langmuir 17, 6013-6017 (2001). © (2001) American Chemical Society.

![Fig. 2](image2.png)  Schematic model demonstrating 0D fullerene nanostructures: (a) nanospheres obtained from IPA/m-xylene system, and (b) nanoballs fabricated from ethanol/pyridine systems.
kinetics, physical properties of solvents (vapor pressure, solubility of C_{60} etc.), temperature, etc. Usually, very long high aspect ratio 1D rods of C_{60} crystals can be synthesized using this method. Bulk precipitation and drop drying method also yields 1D crystal. Volume ratio of poor solvents with C_{60} solutions, concentration of C_{60}, and solvents nature have been pointed out as crucial parameters in the control of the dimensions of 1D rods prepared by the precipitation method. On the other hand, as mentioned earlier, in the drop-drying method solvent structure is crucial to control the geometry of C_{60} crystals produced. Drop-drying of C_{60} solution prepared in so-called p2D solvents usually results in the formation of p1D C_{60} wires. For example, 1D C_{60} wires were formed from a C_{60} solution prepared using m-xylene, a representative p2D benzene series solvent with methyl functional groups meta to each other. Similar 1D C_{60} wires were obtained upon drop-drying C_{60} solutions of mesitylene and 1,3-dichlorobenzene, which have similar structures to m-xylene, except for the multiplicity and type of functional groups. These results of Park et al.\(^{29}\) confirmed that C_{60} molecules are specifically guided to self-assemble into 1D morphologies upon evaporation of benzene series solvents, as long as they have functional groups 120° apart, regardless of the polarity, size and number of the functional groups. The method of Park and coworkers may provide guidelines for the production of multidimensional fullerene nanostructures required for nanodevice fabrication.

Recently, use of the LLIP method is becoming more widespread for the production of nanostructures of C_{60} particularly for growth of 1D nanowhisker of C_{60} crystals due to the ease of synthesis under ambient conditions. Furthermore, the possibility of doping various elements into nanowhiskers and easy production of multicomponent fullerene nanowhiskers composed of different kinds of fullerene molecules are another advantage of the LLIP method. The basic concept of the LLIP method is to use a liquid-liquid interface as nucleation site for crystals. Miyazawa et al.\(^{20}\) used an interface between a concentrated solution of C_{60} in toluene and isopropyl alcohol (IPA) to produce a needlelike morphology of C_{60} with single crystal-like structure having diameters of about 250 nm and lengths in the range of several tens of microns. The largest ratio of length to diameter reached 4000. It has been found that the intermolecular distance within C_{60} nanowhiskers is shorter along the growth axis than in pristine C_{60} crystals indicating the formation of strong bonding between C_{60} molecules. It was anticipated that the fullerene nanowhiskers polymerize via a "2+2" cycloaddition in the close-packed[110] direction\(^{20}\). An initial model of C_{60} nanowhiskers where the C_{60} molecules are chained by the "2+2" cycloaddition along the whisker growth axis was proposed by Miyazawa and is presented in Fig. 3. This model is based on the fact that the intermolecular distance of C_{60} mole-

![Fig. 3](image)

Fig. 3 A body-centered tetragonal (bct) model of 1D C_{60} nanowhisker polymerized via "2 + 2" cycloaddition of C_{60} molecules. Reprinted with permission from *J. Mater. Res.* 17, 83-88 (2002), © 2002, Materials Research Society.

C_{60} nanowhiskers was found to be shortened by a few percent along the growth axis than that of pristine C_{60} crystals based on a transmission electron microscope (TEM) observations. This shortening is anticipated to be caused by the polymerization of C_{60} caused by electron beam irradiation.

These C_{60} nanowhiskers usually have a face-centered cubic (fcc) crystal structure with growth direction parallel to [110] and the overall morphology of C_{60} crystals is found to depend on the combinations of antisolvent and solvent, their volume ratios, and also the presence of water\(^{40}\). However, the solvated hexagonal close packed (hcp) structure of C_{60} nanowhisker has also been occasionally observed depending on the combination of antisolvent and solvent. Solvated crystals grown at an interface of IPA with a saturated solution of C_{60} in m-xylene can be taken as one example\(^{40}\). These solvated hcp C_{60} nanowhiskers were transformed into fcc structure upon evaporation of solvent or heating the sample. Minato and Miyazawa pointed out that the kinetics of hcp-to-fcc structure transformation depend on vapor pressure of solvent; higher vapor pressures lead to more rapid transformation. For example, the hcp to fcc structural transformation occurred more rapidly in toluene than in m-xylene. Entrapment of solvent molecules in the crystals in the initial production stage is expected to be responsible for the formation of hexagonal solvated C_{60} nanowhiskers. Solvents could be easily removed by heat treatment.

Investigations have shown that fabrication of fullerene nanotubes is rather difficult compared to fullerene nanowhiskers. Generally, two types of tubular structures of fullerene crystals have been observed. One is partially hollow around the edge of 1D structures and the other is hollow throughout. Masuhara et al. found that, in addition to the crystal size, overall concentration of C_{60} also causes the formation of a hollow structure although the tubes were short ~2-5 μm. They observed hollow structures upon injecting 300 μL C_{60} solution in m-xylene (2 mM) into
10 mL of 2-propanol, otherwise, solid C₆₀ rods were observed upon injection C₆₀ solution below 300 μL. Ji et al. also observed single crystalline submicrometer C₆₀ tubes with highly uniform size by using a solvent-induced and surfactant-assisted self-assembly technique. Although they pointed out that length and length-to-width ratio of the tubes can be controlled by varying the concentration of C₆₀ in the stock solution and the mixing ratio of antisolvent and C₆₀ solution. Lengths of nanotubes were found to be in the range of a few microns (~5 μm). A major contribution to the production of long fullerene nanotubes came from Miyazawa and coworkers. They fabricated very long (length in the range of few hundreds microns) single crystalline nanotubes of not only C₆₀ but also of C₇₀ using LLIP method. They also found that the C₆₀ nanotubes sometimes grow to extreme lengths into the millimeter length scale with outer diameters of several hundreds of nanometers and inner diameters of several tens of nanometers to a few hundreds of nanometers. These nanotubes showed good uniformity and linearity. The same group succeeded to fabricate vertically aligned fullerene microtubes by slowly injecting IPA solution into a saturated solution of C₆₀ in toluene through an alumina membrane. The length of the vertically aligned C₆₀ microtubes reached about 500 μm and their planar density and diameter could be controlled by changing the growth conditions, such as the injection rate of IPA and the amount of the C₆₀ solution.

Regarding the dimensions of 1D nanostructures of C₆₀ crystals, usually volume ratio of antisolvent and C₆₀ solution and concentration of C₆₀ in the stock solution play a crucial role. At fixed volume ratio, increasing C₆₀ concentration decreases the length and width of derived C₆₀ rods and tubes. Ji et al. carefully addressed the effect of C₆₀ concentration and volume ratio of antisolvent and C₆₀ solution on the dimensions of 1D C₆₀ crystals using IPA and m-xylene systems. At fixed 1:1 volume ratio of IPA and C₆₀ solution in m-xylene, increasing C₆₀ concentration from 0.75 to 1.2 mgmL⁻¹ formed C₆₀ rods with average length ca. 25 to 3.0 μm and width 447 to 406 nm, respectively. On the other hand, at fixed concentration of 1.2 mgmL⁻¹ increasing volume ratio of IPA and C₆₀ solution in m-xylene from 1:1 to 1:3 modulated the shapes of C₆₀ crystal from rods to tubes. The lengths of rods and tubes were essentially the same at ca. 3 μm but their widths increased from 406 to 811 nm (see Fig. 4).

Miyazawa’s group proposed a modification of the LLIP method to produce fullerene nanowhiskers and nanotubes having lengths hundreds of μm in a relatively short period of time (~2 h). They divided nucleation stage and crystal growth stage. For nucleation stage, saturated C₆₀ solution was mixed with a small amount of alcohol and for the growth stage C₆₀ was precipitated in the nucleated solution by injecting alcohol to the bottom of the solution at a controlled flow rate using a syringe pump. The widths were found in the range 200-500 nm. They also succeeded to control the diameter of C₆₀ nanowhiskers by changing the area of the liquid-liquid interface, which could be done by simply altering the reaction glass bottle size. Increasing the internal diameter of the glass bottle, i.e., increase in the area of liquid-liquid interface, increases the overall diameter of nanowhiskers. For example, the mean diameter of C₆₀ nanowhiskers grown at an IPA and toluene interface found in the range 200-500 nm. They also succeeded to control the diameter of C₆₀ nanowhiskers by changing the area of the liquid-liquid interface, which could be done by simply altering the reaction glass bottle size. Increasing the internal diameter of the glass bottle, i.e., increase in the area of liquid-liquid interface, increases the overall diameter of nanowhiskers. For example, the mean diameter of C₆₀ nanowhiskers grown at an IPA and toluene interface

![Fig. 4](image-url) SEM images of C₆₀ rods (a-d) and tubes (e-g) at different concentration of C₆₀ in m-xylene and at different volume ratio of IPA and C₆₀ solution: (a) Typical SEM images of C₆₀ rods at 1:1 volume ratio and 0.75 mgmL⁻¹ C₆₀ in m-xylene, (b) C₆₀ rods from 1.0 mgmL⁻¹ C₆₀ in m-xylene, (c) low and (d) high magnification SEM images of from 1.2 mgmL⁻¹ C₆₀ in m-xylene, (e) SEM images of C₆₀ tubes obtained at volume ratio of 1:2 and 1.0 mgmL⁻¹ C₆₀, (f) tubular structure obtained at volume ratio of 1:2 and 1.2 mgmL⁻¹ C₆₀, (g) show a tubular feature obtained at volume ratio of 1:3 and 1.2 mgmL⁻¹ C₆₀, and (h) TEM image demonstrating tubular structure. Adopted with permission from J. Phys. Chem. C 111, 10498-10502 (2007) © 2007, American Chemical Society.
was increased from 222 to 579 nm upon increasing the internal diameter of the glass bottle from 17 and 32.4 mm\(^ {46}\). Details of the dimension controlled fabrications of C\(_{60}\) nanowhiskers or nanotubes from a variety of antisolvents and solvents and using different methods have been recently summarized elsewhere\(^ {47}\).

Next we briefly discuss 2D crystals. Fabrication of a 2D plate like morphology of fullerene crystals particularly by solution based methods has been sparsely reported in comparison to the 1D structures. Physical vapor deposition methods have been mostly used to make 2D thin films of C\(_{60}\)\(^ {48}\). Highly selective disk-shaped 2D single crystalline C\(_{60}\) reported by Shin et al.\(^ {49}\) is another good example of vapor deposition processes for synthesis of 2D crystals of C\(_{60}\). A C\(_{60}\) solvate formed upon storing C\(_{60}\) solution in trichlorobromomethane (BrCCl\(_3\)) in dark for a week, which showed interpenetrated hexagonal shape single crystals of C\(_{60}\)-2BrCCl\(_3\), may be the first example of fabrication of 2D C\(_{60}\) crystals based on a solution method\(^ {50}\). The average size of the hexagonal shaped 2D crystals was about 100 \(\mu\)m with thicknesses of a few microns. The group of Miyazawa reported the first example of very thin (so called transparent) hexagonal shaped C\(_{60}\) nanosheets by the LLIP method at an IPA and carbon tetrachloride (CCl\(_4\)) interface\(^ {31}\). They could tailor the average size of the nanosheets by simply changing the type of alcohols though thickness remained essentially unchanged. For example, hexagonal shape nanosheet with a diameter \(\sim 7.5\) \(\mu\)m was observed in the IPA/CCl\(_4\) system, whereas the diameter decreased to \(\sim 2.5\) \(\mu\)m and 500 nm, respectively with ethanol and methanol. The same group also fabricated polygonal shaped 2D crystals including hexagons and rhombuses by altering solvent molecular structures\(^ {52}\). As mentioned earlier, Park et al.\(^ {30}\) produced 2D crystals of C\(_{60}\) by a drop-drying method from a so-called pseudo 3D geometry solvent such as CCl\(_4\) and SnCl\(_4\), which also supports the results of Miyazawa and coworkers. Figure 5 shows representative SEM images of 2D crystals produced by using LLIP method.

Regarding the 3D morphology of fullerene crystals, Choi and coworkers\(^ {54}\) recently reported high-definition cube-shaped crystals of C\(_{70}\), which were synthesized by the LLIP and precipitation methods from a mixture of a solution of C\(_{70}\) in mesitylene and IPA. Formation of local mesitylene cavities, which are instantaneously generated when IPA is added to the C\(_{70}/\)mesitylene solution, was expected to be the key factor for C\(_{70}\) cube formation. Due to the low solubility of C\(_{70}\) in IPA, the local concentration of C\(_{70}\) in the mesitylene cavities is increased upon addition of IPA in C\(_{70}/\)mesitylene solution. Therefore, instant nucleation of C\(_{70}\) occurs in the mesitylene cavities. This mixed-solvent-mediated nucleation phenomenon is similar to the traditional recrystallization process and the synthesis of various self-crystallized C\(_{60}\) structures. Once C\(_{70}\) molecules are localized in the cavity of mesitylene, which is surrounded by IPA, mesitylene guides C\(_{70}\) molecules to self-crystallize into cubes. They found that the average size of the C\(_{70}\) cubes decreases with increasing the amount of IPA and the concentration of C\(_{70}\) in the starting solution. Their results support the hypothesis that the addition of IPA induces local cavities of mesitylene in which C\(_{70}\) molecules are localized and their self-crystallization is guided. It should be noted that the size of the cavity should become smaller as the amount of IPA increases as a result; the average size of the resulting cube crystal is then also smaller. The decrease in the size of the cube with the C\(_{70}\) concentration is due to the increased number of nucleation sites. The average size of C\(_{70}\) cubes was ca. 2.05 \(\mu\)m.

Another contribution to the fabrication of cube-shape C\(_{70}\) crystals came from Yao et al.\(^ {52}\). They fabricated cube shape C\(_{70}\) microcrystals by using a fast solvent-assisted evaporation method by selectively using aromatic solvents with halogen radicals as a controller. The C\(_{70}\) cubes were of rather polydisperse sizes ranging from several hundred nanometers to tens of micrometers (\(>30\) \(\mu\)m). It was found that when the size of the cubic crystals was larger than \(\sim 10\) \(\mu\)m, the cube crystals formed usually have a concave pyramid and some of them have a polycrystalline flower-like shape.

To our knowledge, a perfect cubic shape 3D morphology of C\(_{60}\) crystal is still absent from the literature. However, assembly of 1D nanorods or nanotubes of C\(_{60}\) has been shown to yield 3D nanostructures\(^ {55}\). We have also found a similar aggregation of 1D nanorods or nanotubes into a flower-like morphology in the presence of surfactants in the antisolvent. These 3D flower-shaped C\(_{60}\) crystals have hexagonal close packed structure and show intense photo luminescence (PL) compared to pristine C\(_{60}\)\(^ {54}\). Our group very recently succeeded to fabricate highly crystalline cube-shaped crystals of C\(_{60}\)-fullerene-Ag(1) organometallic heteronanostructure[C\(_{60}\){AgNO\(_3\)}\(_{2}\)], which undergoes irreversible structural rearrangement upon exposure to low molecular weight aliphatic alcohols (in particular 1-butanol) yielding a uniquely structured formation of well-oriented C\(_{60}\) nano/microcrystals (‘bucky cubes’)\(^ {56}\). The mechanism of rearrangement represents a supramolecular analogue of topotactic processes more commonly associated with some purely inorganic materials, such as maghemite, where chemical changes can occur with addition or

Fig. 5  SEM images of 2D C\(_{60}\) crystals grown at liquid-liquid interface as typical examples. Adapted with permission from J. Am. Chem. Soc. 131, 6372-6373. © 2009 American Chemical Society
loss of materials. Hence, \( C_{60} | \text{AgNO}_3 \) \(_5\) undergoes a supertopotactic transformation from a crystalline organometallic complex to well-ordered cube-shaped arrays of needle-like \( C_{60} \) crystals which reflect the original cubic crystal morphology an internal structure.

### 3 SELF-ASSEMBLY OF FUNCTIONALIZED FULLERENES

Herein, we discuss the self-assembly of functionalized fullerences into different mesostructures in solution. As we have mentioned earlier, owing to its highly hydrophobic character, fullerene \( C_{60} \) is insoluble in water, which limits its practical applications. However, this extremely hydrophobic \( C_{60} \) molecule can be made water soluble by functionalizing with charged groups such as carboxylic acids or amines and, hence, its theoretical importance and potential applications are improved. \(^{[55, 56]}\) Ravi et al. \(^{[57]}\) recently reviewed several synthetic routes proposed to functionalize \( C_{60} \) to increase its solubility and processibility. Derivatizing \( C_{60} \) with different functional groups, solubilizing and encapsulating through the formation of complexes with surfactants, cyclodextrins, calixerenes, Tween-20, phospholipids, and liposomes, and producing charge-transfer complex with organic compounds bearing electron donat-

sulating through the formation of complexes with surfac-
tion of \( C_{60} \) into an amphiphilic molecule its self-assembly be-

havior in different solvent systems has been investigated in
detail with emphasis on its potential impact for the de-
velopment of functional materials. For example, Jeng et
al. \(^{[58]}\) observed monodisperse spherical type aggregates
having a radius of gyration of about 2.0 nm in dilute solu-
tions of starlike hexanionic fullerene derivatives, \( C_{60}^{[\text{CH}_2}_4\)
SO_4Na\(_4\) (star-ionomer). SAXS and SANS studies showed
that the interparticle interaction between the aggregates is
much weaker and insensitive to the temperature and con-
centration characteristics of hard-sphere type interactions
common in surfactant micelles. The hydrophobic behavior
of star-ionomer was expected to be responsible for the for-
mation of monodisperse aggregates. Sano et al. \(^{[59]}\) have
also synthesized novel amphiphilic \( C_{60} \) derivatives with two am-
onium headgroups (so called bola-amphiphilic \( C_{60} \): sche-
matic molecular structure is presented in Fig. 6a) and ob-
served self-assembled spherical vesicles with average
diameter in the range of 20-50 nm from the dilute aqueous
solution of this bola-amphiphilic \( C_{60} \) (3-10 mM) (see Fig. 6).
Vesicular dispersion was obtained by applying simple ultra-
sonication to the mixture. This novel aggregation was an-
ticipated to be caused by the hydrophobic interaction pro-
duced by the fullerene moieties exposed to water
molecules by the disordered alkyl tails. Wilson and cowork-

ers \(^{[60]}\) obtained experimental evidence of nanoscale aggre-
gates formed by e,e,e-tris-malonic acid-\( C_{60} \) (or \( C_{63} \)) in water,
which was commonly assumed to exist as discrete mole-
cules solubilized in aqueous solution. Figure 7 shows the
molecular structure of \( C_3 \) and electron micrographs of the
aggregates at different magnifications. The aggregates
were polydisperse having sizes in the range of 40-80 nm.
The size was independent of concentration and tempera-
ture, but strongly dependent on pH between pH 4-8. The
aggregates increased in size with decreasing pH. For in-
stance, the average hydrodynamic diameter of the aggre-
gates formed by \( C_3 \) increased from about 90 to 380 nm at a
fixed concentration 5 mgmL\(^{-1}\) at 25°C. This increase with
pH has been explained by considering the effect of proton
dissociation of the \( C_3 \) malonic acid groups. They also con-
firmed that it is the aggregates of \( C_{60} \), which are responsible
for their neuroprotective action in cells, not the individual
\( C_{60} \) molecules.

Geckeler et al. \(^{[61]}\) synthesized water-soluble mono-6-aza-
6-deoxy-\( \beta \)-cyclodextrin-\( C_{60} \) (or \( C_{63} \)) is covalently bonded to
\( \beta \)-cyclodextrin via a bridging nitrogen atom), which exhibited
unusual aggregation behavior in solution. The average
particle size increased from 0.55 to 3.255 μm with decreas-
ing concentration of the solution from 0.216 to 0.01 mM.
This unusual phenomenon was related to the diffusivity of

Fig. 6 (a) Molecular structure of bola-amphiphilic \( C_{60} \),
(b) schematic model of vesicle, and (c-f) electron
micrographs of the derived vesicles at different
magnifications. Adopted with permission from
American Chemical Society.
the particles. Dilution led to a reduction in the viscosity and a corresponding increase in the diffusivity of the particles, which facilitated the interaction between clusters leading to cluster-cluster aggregation. The group of Nakamura investigated association behavior of potassium salt of pentaphenyl fullerene (Ph₅C₆₀K) in water⁶⁰. Using a laser light scattering (LLS) technique they found that in aqueous solution the hydrocarbon anions Ph₅C₆₀⁻ associate into bilayers forming stable spherical vesicles with an average radius of gyration of about 17 nm. The critical aggregation concentration was found to be extremely low (≤10⁻⁷ moles per liter). However, the average aggregation number of associated particles in these large spherical vesicles was about 1.2 × 10⁵. The same group showed that the attachment of five aromatic groups to one pentagon of a C₆₀ molecule produces deeply conical molecules, which can stack into polar columnar assemblies⁶¹. The stacking was expected to be driven by attractive interactions between the spherical fullerene moiety and the hollow cone formed by the five aromatic side groups of a neighboring molecule in the same column. Interestingly they found that the packing pattern is maintained upon extending the aromatic groups by attaching flexible aliphatic chains, which thereby resulted in the formation of compounds with thermotropic and lyotropic liquid crystalline properties demonstrating the possibility of designing a range of new polar liquid crystalline materials. Liquid crystalline properties of selected self-assembled fullerene derivatives can be found elsewhere and in the references therein⁶²,⁶³. Nakamura and coworkers recently reported that fullerene anions featuring a nonpolar/polar/nonpolar ternary motif spontaneously form vesicles exposing their nonpolar fluorous chains to the aqueous environment. Average diameter of vesicles was ca. 36 nm⁶⁴. They found that these vesicles tightly yet noncovalently bind fluorous molecules on their surfaces. In contrast to lipid vesicles that easily lose their structural integrity upon removal from aqueous solution, their vesicles were very robust and retained their spherical shape even on a solid substrate under high vacuum. They looked like nanometer-sized hollow Teflon balls. When the vesicle solution was coated and dried on a hydrophilic surface (Indium tin oxide), it became water-insoluble and made the surface water-repellent (contact angle ca. 111.7°) similar to a Teflon surface demonstrating the possible utility of the vesicle surface as a scaffold for molecular display, the interior for molecular delivery, and the solution for macroscopic surface modification. In subsequent work, Nakamura and coworkers synthesized twenty potassium complexes of fullerene anion amphiphiles having overall structure nonpolar/polar/nonpolar and investigated their abilities to form bilayer vesicles in water⁶⁵. The complexes were penta[(4-substituted)phenyl] [60] fullerene anions, where the 4-substituents included alkyl groups ranging from methyl to icosanyl groups and perfluoromethyl, perfluorobutyl, and perfluoroctyl groups. They found that despite the hydrophobicity of the fullerene moiety (nonpolar part) and alkyl/perfluoroalkyl chains (second nonpolar part), all compounds except for the one with perfluoromethyl groups were soluble in water due to the centrally located fullerene cyclopentadienide (polar part) and spontaneously formed a vesicle of 25-60 nm diameter with a narrow unimodal size distribution. The vesicles were stable upon heating to 90°C or standing over a year in air, as well as on a solid substrate in air or in vacuum, maintaining their spherical form. The vesicle membrane consists of an interdigitated bilayer of the amphiphile molecules, in which the nonpolar fullerene part is at the interior and the other nonpolar part is exposed to water. Note that the exposure of nonpolar parts of an amphiphile to water is an unusual phenomenon in surfactant science and it is beyond common sense. However, this fact was well supported by experiments. These vesicles, in particular those bearing icosanyl chains, exhibited the smallest water permeability coefficient ever found for a self-assembled membrane in water. Figure 8 shows SEM images of vesicles on indium tin oxide (ITO) surface formed by the fullerene anion bearing five perfluoroalkyl chains (Rf8K) as a typical example. As can be seen in Fig. 8a, the Rf8K vesicles uniformly cover a wide area of the ITO substrate. A closer look at the SEM image (Fig 8b) reveals that the vesicles sit on the grain boundaries of the ITO surface to maximize contact with the surface. The 30°
Self-Assembled Fullerene Nanostructures

Fig. 8 (a) SEM images of Rf8K vesicles on ITO under ca. $10^{-5}$ Pa. (b) Magnified view of panel a, and (c) a different area of the same sample as viewed with a 30° tilt of the sample stage. Adopted with permission from J. Am. Chem. Soc. 133, 6364-6370 (2011) © 2011 American Chemical Society.

tilted side view (Fig. 8c) confirms this observation and also indicates that the vesicles largely retain their spherical structures under the rather harsh SEM conditions of $10^{-5}$ Pa, which demonstrates the unusual robustness of the fullerene vesicle. The average diameter of the Rf8K vesicle particles was ca. 35.6 nm. The attractive features of these vesicles are that they are morphologically stable, monodispersed, nanosized, spherical hollow objects, which can be prepared by a simple method without any purification. They can also be used to modify solid surfaces. It is anticipated that these nonpolar/polar/nonpolar type amphiphiles will open a new avenue in research on nano-sized compartment structures in solution and on solid surfaces.

In the study of supramolecular assemblies of fullerene derivatives, Georgakilas et al. found that ionic fullerene derivatives, which are relatively soluble in polar solvents, self-organize into different morphological nanostructures such as spheres, nanorods, and nanotubes in water depending on the side chain appendage of the fullerene spheroid. Guldi et al. discussed the organization of fullerene derivatives in bulk, at interfaces, and on substrates. They highlighted that the proper combination of the hydrophobic fullerene core with hydrophilic functional groups (both ionic and nonionic) potentially leads to organized structures whose sizes range from nanometer to micrometer length scales. The main driving force of such spontaneous assembly is the amphiphilic character of the fullerene derivatives. They pointed out that, similarly to the conventional surfactant systems, supramolecular assembly, dimensions and the functions of the fullerene derivatives depend on the following parameters: (a) hydrophilic-hydrophobic balance, (b) the effect of the environment, typically provided by solvents, (c) the interface at which the aggregation occurs, and (d) the solvation process. The influence of these effects on the fullerene supramolecular assemblies can be found elsewhere.

Nakanishi et al. reported 1D lamellae of fullerene derivatives bearing long alkyl chains. The 1D structure epitaxially oriented along the highly oriented pyrolytic graphite (HOPG) lattice. They could tune the distance between adjacent nanowires at the nanometer length scale by the molecular design. They presented an approach to directly assemble fullerene lamellae on graphite in a predictable way using alkanes as structure-directing components, covalently bonded to C60 and explored the polymorphism of fullerene assemblies by using the two different intermolecular forces, namely π-π interactions of C60 and van der Waals interactions of aliphatic chains. The same group also reported novel micron size flowerlike supramolecular assemblies of fullerene-based molecules bearing long alkyl chains. In the following work, Nakanishi and coworkers observed that a novel N,N-dimethylfulleropyrrolidinium iodide (ionic fullerene derivative derived from fulleropyrrolidinium) form a variety of functional and polymorphic self-assembled structures both from solution and on substrate. They observed that these ionic fullerene derivatives due to π-π, van der Waals, and electrostatic interactions hierarchically organized into flake-like microparticles with high water repellency, doughnut-shaped objects with rough surfaces, and long 1D C60 nanowires (≥1 μm). The flake-like microparticles due to surface roughness in nanometer length scale showed water repelling properties giving a static water contact angle of ~140°, which is about 10° lower than that observed from microflowers formed by the parent fullerene amphiphile, i.e. N-methylfulleropyrrolidinium. The authors mentioned that the difference in water repellency is due to different surface roughnesses. Figure 9 shows typical SEM

Fig. 9 Typical SEM and AFM images of flakelike microparticles and 1D nanowires of N,N-dimethylfulleropyrrolidinium iodide. Adopted with permission from Langmuir 27, 7493-7501 (2011). © 2011 American Chemical Society.
images of flake-like microparticles formed by \(N,N\)-dimethylfulleropyrrolidinium iodide by slow addition of excess methanol solution into its concentrated solution in dichloromethane and typical AFM images of nanowires of the \(N,N\)-dimethylfulleropyrrolidinium iodide obtained by spin-coating of its 10 \(\mu\)M solution in dichloromethane on HOPG substrate. As can be seen in AFM images, \(N,N\)-dimethylfulleropyrrolidinium iodide forms extremely large areas of 2D lamellar domains composed of the 1D C\(_{60}\) nanowires with lengths of over 1.0 \(\mu\)m. The periodic separation of the nanowires is ca. 7.3 nm, which is almost exactly twice the molecular length of \(N,N\)-dimethylfulleropyrrolidinium iodide in a fully extended conformation (3.7 nm). Moreover, a cross-sectional line analysis reveals that the average height difference within the lamellae is 0.38 nm, which is close to the difference between the diameter of C\(_{60}\) and the height of a flat-lying alkyl chain layer on the HOPG surface. These results indicate that the organization of \(N,N\)-dimethylfulleropyrrolidinium iodide within nanowires is similar to that of \(N\)-methylfulleropyrrolidine, with the C\(_{60}\) moieties organized in a zigzag conformation and the aliphatic chains localized in between\(^{70}\).

In the study of supramolecular assembly of fullerene glycoconjugates in aqueous solution, Kato et al.\(^{73}\) found small supramolecular aggregates (spherical micelles type) having particle size of about 4 nm. These spherical micelles with an extremely narrow size distribution represent supramolecular sugar balls, which have potential for biomedical applications. Nurmawati et al.\(^{74}\) outlined a synergistic self-assembly of fullerences (C\(_{60}\)) and functionalized poly(\(p\)-phenylene) (PPP) to develop nanofibers with high aspect ratios. Nanostructured PPP-C\(_{60}\) hybrids were prepared by direct casting of a dilute solution on solid substrates and on water under ambient conditions. When a solution of the mixture of C\(_{60}\) and PPP polymer (C\(_{12}\)PPPOH) (1:1, 0.5 mgmL\(^{-1}\)) in toluene was cast onto a solid substrate, unidirectional crystallization of nanohybrid material having nanofibrous morphology with high aspect ratios was observed (see Fig. 10).

Nanofibers that have an average diameter of about 35 nm and length of 30-50 \(\mu\)m aggregate to form whiskers. The observed high aspect ratio of 1050 is typical to aspect ratios of CNTs. The HR-TEM images shown in Fig. 10c, d shows regular lattice fringes in the nanoneedles spanning along the growth axis. They explained that planarization of the polymer backbone through potential O-H-O hydrogen bonds and optimum alkyl chain crystallization played an important role in the molecular level ordering of C\(_{12}\)PPPOH during the whisker formation. The first step of the multiscale assembly of the whisker formation involves a molecular level polymer C\(_{60}\) assembly driven by \(\pi\)-\(\pi\) stacking of the conjugated backbone of the polymer and the fullerene, resulting in the nanofibers. Murthy and coworkers\(^{75}\) have recently demonstrated first example of

4 CONCLUDING REMARKS

In this review we have briefly summarized recent developments in the production of shape-controlled fullerene nano/microcrystals by solution-based approaches. Facile syntheses of fullerene crystals having different morphology such as fullerene spheres, fullerene nanowhiskers and nanotubes, fullerene nanosheets, and assembly of fullerene nanorods or nanotubes in three-dimensional assemblies are discussed. Moreover, supramolecular assembly of functionalized fullerenes (fullerene derivatives) into different mesostructures (micelles, liquid crystals, and vesicles) both in solution and substrate was discussed.
ACKNOWLEDGEMENT

This work was also partly supported by World Premier International Research Center Initiative (WPI Initiative), MEXT, Japan and the Core Research for Evolutional Science and Technology (CREST) program of Japan Science and Technology Agency (JST), Japan.

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