Various Surfactants for 0 – 3 Dimensional Nanocarbons: Separation, Exfoliation and Solubilization

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Abstract

Nanocarbons are carbon allotropes with nanometer scale and comprised mainly of 0 – 3 dimensional (0D – 3D) forms; fullerenes (0D), carbon nanotubes (1D), graphene (2D), and nanodiamond (3D). In our group, various surfactants with appropriate size and shape have been developed for the nanocarbons. In order to separate the fullerenes, bowl-shaped surfactants were designed and synthesized to accommodate the 0D spherical nanocarbon, giving C_{70} selectively as precipitates. On the other hand, gable- and bracket-shaped surfactants formed stable complexes with 1D tubular nanocarbons, dispersing carbon nanotubes with specific diameter, handedness and/or metallicity selectively in solution phase. The flat surfactants worked as an exfoliant and dispersant for graphite in both wet and dry processes; sonication and ball milling, respectively. They gave graphene composites with high concentrations and yield in aqueous solution and low-boiling point organic solvents. The hyper-branched polymer named polyglycerol coated the nanodiamond surface covalently through ring-opening polymerization of glycidol. The chemisorped polymer gave large hydrophilicity to the nanodiamond, dispersing it stably in aqueous solutions such as water and phosphate buffer as well as polar organic solvents such as methanol. Copyright © VBRI Press.

Keywords: Nanocarbon, fullerene, carbon nanotubes, graphene, nanodiamond, surfactant.

Introduction

Fullerenes, the first carbon allotropes with nanometer scale, were found by Kroto and Smalley in 1985 [**1**]. Since fullerenes have defined structures and good solubility in some organic solvents, many organic chemists started to work with fullerene after their synthetic process was established [**2**]. In 1991, Iijima found carbon nanotubes (CNTs) [**3**] and materials scientist who worked with fullerenes moved to CNT research. However, most of the organic chemists involved in fullerene research dropped out, because CNTs are not like fullerenes in terms of structural uniformity and physical properties. Graphene was found by Novoselov and Geim in 2004 [**4**]. Since graphene does not have uniform structure, organic chemists have synthesized graphene nanoribbon and short CNTs with defined structure, recently [**5-7**]. Nanodiamond via detonation process was found in Russia in 1960s. Organic chemists developed surface modification and characterization in 1990s [**8-9**].

As an organic chemist, the author has been dealing with 0 – 3 dimensional (0D – 3D) nanocarbons shown in **Fig. 1** from the viewpoint of their surface activation with various surfactants.
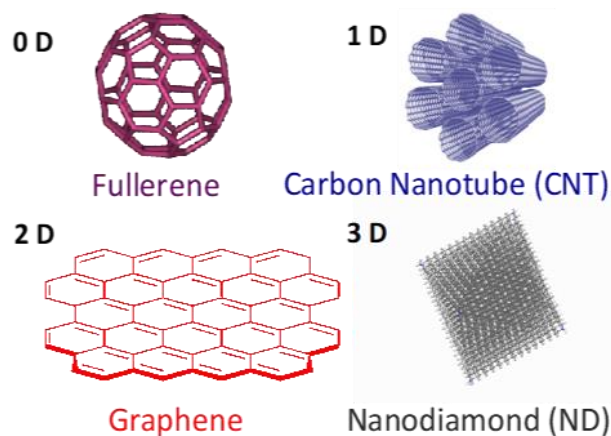

Fig. 1. Nanocarbons from 0 to 3 dimensions.

Physisorption of aromatic compounds and chemisorption of polymers have been applied to nanocarbons on the purpose of separation, exfoliation and solubilization as summarized in **Table 1** [**10**].

Table 1. The surfactants we used so far for 0 – 3 dimensional nanocarbons to be separated, exfoliated or solubilized.

Nanocarbon	Fullerene	CNT	Graphene	ND
Surfactant	Homooxacalix[3]arene	Nanotweezers Nanocalipers	Hexahydroxytriphenylene chlorine6	Polyglycerol
Purpose	Separation	Separation	Exfoliation	Solubilization

Homooxacalixarenes for separation of C₇₀

A large number of host molecules to encapsulate fullerenes have been reported so far [11-13]. Although most of the host molecules exhibited very large association constants toward C_{60} in organic solvents [14-15], the structural separation of fullerenes by molecular recognition has been rarely seen.

In 1997, the author and the coworkers found bismuth bromide-catalyzed reductive coupling reaction of carbonyl compounds in the presence of triethylsilane [16]. This reaction was extended to the preparation of homooxacalix [**3**] arenes (1_3R) through the reductive coupling of 4-substituted-2,5-diformylphenols as shown in **Scheme 1** [17]. Thus prepared 1_3I and 1_3Br having bowl-shape were found to precipitate C_{70} at the selectivity as high as 92% through physisorption (**Fig. 2**) [18].
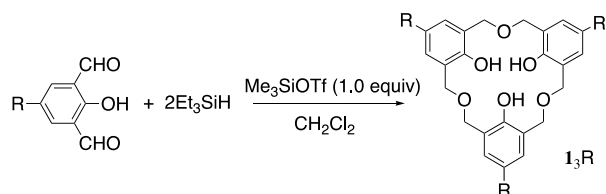
Scheme 1. Synthesis of homooxacalix[3]arenes (1_3R) by reductive coupling reaction of 4-substituted-2,5-diformylphenols.
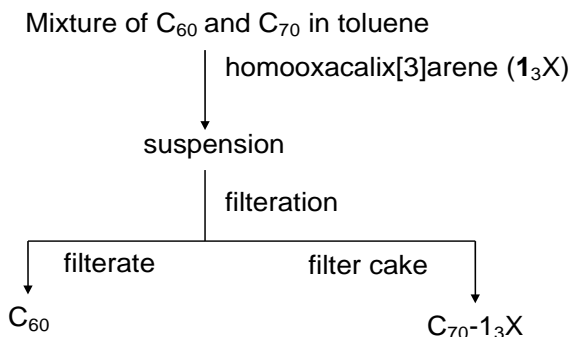

Fig. 2. Selective precipitation of C_{70} over C_{60} with trihalohomooxacalix [3] arene (1_3X).

Nanotweezers and nanocalipers for separation of carbon nanotubes

In the opposite sense to the selective precipitation of C_{70} mentioned above, selective solubilization of CNT was intended through physisorption [19-20]. While bowl-shaped trihalohomooxacalix [**3**] arenes 1_3X were applied to spherical nanocarbon (**Fig. 2**), tubular nanocarbon was encapsulated by gable- and bracket-shaped host molecules designated as nanotweezers and nanocalipers, respectively (**Fig. 3**). The syntheses and structures of chiral porphyrin-based nanotweezers **2** and nanocalipers **3** are depicted in **Scheme 2**. In addition to

the diameter discrimination by the cavity, the handedness of CNTs was recognized by the stereogenic centers at the peripheries of the porphyrins (X in **Scheme 2**), giving optically active CNTs [21-22]. The author and coworkers extended this methodology to the separation of various CNTs by tuning the distance and angle of the two porphyrins in the host molecules [23-25]. The porphyrins at the nanotweezers (**Fig. 3a** and **Scheme 2**) were replaced by pyrenes to simplify the synthesis [26]. Since the nanocalipers have larger cavity in depth and width, they accommodated CNTs with larger diameters deeply [27-28]. Metallic CNTs were found to be selectively extracted by nanocalipers **3** to recognize metallicity of the CNTs in addition to the handedness and diameter [29]. The porphyrins in the nanocalipers (**Fig. 3b** and **Scheme 2**) can also be replaced by pyrene, which also recognized metallic CNTs [30].

The separation of CNTs has been attracting enormous interest in view of the CNT applications. Therefore, more practical methods than our ones mentioned above have been reported, which are summarized in the reviews [31-34].
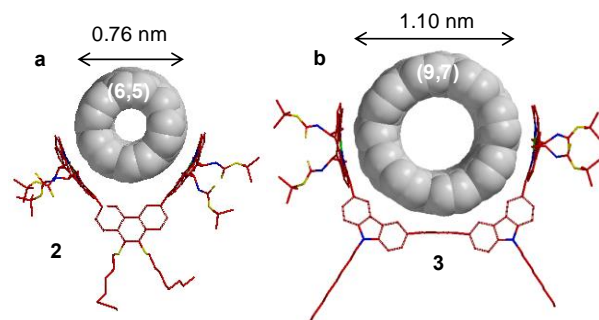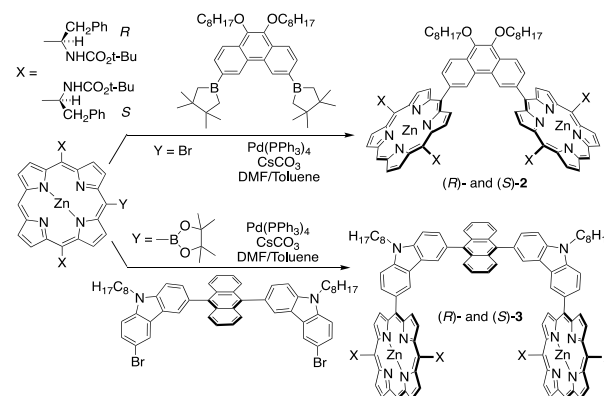

Fig. 3. Selective extraction of (6, 5)- and (9, 7)-SWNTs (single-walled carbon nanotubes) with nanotweezers **2** and nanocalipers **3**, respectively.

Scheme 2. Synthesis of chiral diporphyrin-based nanotweezers ((*R*)- and (*S*)-**2**) and nanocalipers ((*R*)- and (*S*)-**3**) via Suzuki coupling reaction.
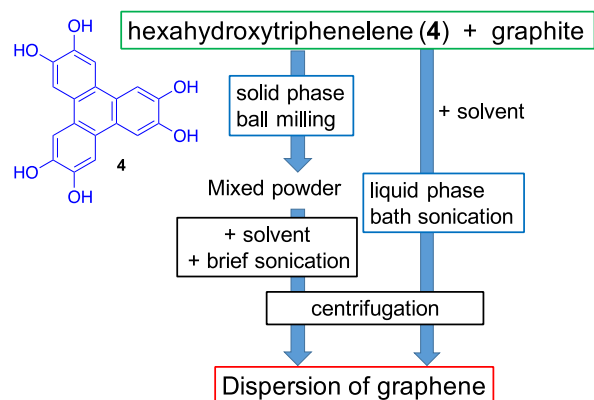
Fig. 4. Exfoliation of graphene with 2,3,6,7,10,11-hexahydroxy-triphenylene (**4**).

Hexahydroxytriphenylene for exfoliation of graphene

In view of large scale synthesis of graphene, liquid phase exfoliation of graphite is attracting great interest [**35-36**]. Since only limited kinds of solvents such as NMP (*N*-methylpyrrolidone) allow exfoliation of graphite without exfoliant [**37**], appropriate exfoliant should be used in various solvents such as water and tetrahydrofuran (THF) for exfoliation of graphite with the aid of sonication.

Flat surfactant, 2, 3, 6, 7, 10, 11 -hexahydroxy-triphenylene (**4**), was employed to exfoliate graphite to give thin layer graphene. The surfactant we found is versatile because it works as exfoliant and dispersant through ball milling in solid phase and sonication in liquid phase to give stable dispersions in aqueous solution and low-boiling point organic solvent (**Fig. 4**) [**38**]. The triphenylene (**4**) was found to be applied to other 2D materials such as h-BN and MoS_2 in both dry and wet processes. The author and coworkers extended this methodology to graphene exfoliation by chlorin e6 [**39**]. Since chlorin e6 has similar structural characteristics to those of triphenylene such as extended flat π-system and polar functional groups, it works similarly as exfoliant and dispersant in addition to photosensitized property. The composite consisting of chlorin e6 and graphene showed good aqueous dispersibility and phototherapeutic property in the in vitro cell experiments [**39**].

Polyglycerol for solubilization of nanodiamond

Polyglycerol have been used as hydrophilic polymer for functionalization of nanoparticle [**40**]. There are two ways, "grafting from" and "grafting to", for the functionalization [**41-44**].

Nanodiamond was covalently bound to hydrophilic polymer, polyglycerol (PG), through ring opening polymerization of glycidol as shown in **Scheme 3**. The surfactant gave large dispersibility to nanodiamond, which is not less than 20, 16, and 6 mg / mL in pure water, phosphate buffered saline, and methanol, respectively [**45**]. The PG functionalization was found to be applicable to various nanoparticles such as iron

oxide [**46**], titanium oxide [**47**], and zinc oxide [**48**] to impart good aqueous dispersibility. In addition, further derivatization of the PG layer enables nanodiamond and iron oxide nanoparticle to be employed as a drug carrier and an imaging probe [**49-53**].
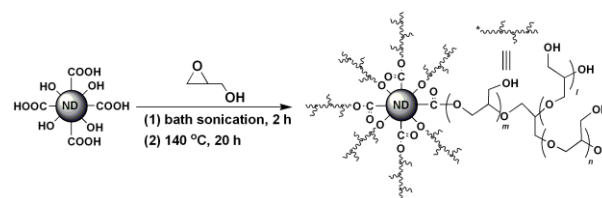
Scheme 3. Polyglycerol-functionalization of nanodiamond to disperse it in an aqueous solution.

Conclusion and perspective

Surfactant plays a role to add solubility or dispersibility to the entity. If the surfactant has another function such as discrimination of the structure, shape, and property, surfactant can separate the entity. Such multi-functional surfactant should attract growing interest in the scientific community and the target entity should also expand from the molecules to nanomaterials.

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