Room temperature synthesis of water-soluble spherical particles of a uniform diameter composed of carbon nanobelts and C60 molecules

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Abstract

A carbon nanobelt (CNB) is a loop of fused benzene rings and in a sense a cutout of a single-walled carbon nanotube. Various types of CNBs have been successfully synthesized in recent years and CNBs have been utilized for the development of practical devices. A C60 molecule is a football shaped fullerene composed of 60 carbon atoms. Patterns and structures formed by atoms, molecules and particles via bottom-up self-assembly are of great interest and importance not only from a scientific point of view but for the design and production of functional materials and devices, the size of which ranges from nano to macroscopic scales. Colloidal particles are commonly used/utilized in mechanical, chemical and biophysical/biochemical/biomedical engineering, where size uniformity and mono dispersibility of the particles in the solvent, particularly in water, become crucial factors. In this study, we investigate secondary structures formed by (6,6)CNBs and C60 molecules, which are dissolved in 1,2-dichlorobenzene. We find that uniform spherical particles are formed by (6,6)CNBs and C60 molecules in 1,2-dichlorobenzene at room temperature via bottom-up self-assembly, setting the molar concentrations of (6,6)CNBs and C60 molecules at appropriate values, and furthermore those particles are monodisperse even in water. The present facile room temperature synthetic methodology may well be applied to the creation of nano/micro structures/materials using basic carbon nano units such as cycloparaphenylene (CPP, carbon nanorings) and fullerenes; e.g., C60, C70 and C59N.

Full Text

A carbon nanobelt (CNB) is a loop of fused benzene rings and in a sense a cutout of a single-walled carbon nanotube. Various types of CNBs have been successfully synthesized in recent years[1–7] and CNBs have been utilized for the development of practical devices[8–10]. A C_{60} molecule is a football shaped fullerene composed of 60 carbon atoms[11]. Patterns and structures formed by atoms, molecules and particles via bottom-up self-assembly are of great interest and importance not only from a scientific point of view but for the design and production of functional materials and devices, the size of which ranges from nano to macroscopic scales[12–14]. Colloidal particles are commonly used/utilized in mechanical, chemical and biophysical/biochemical/biomedical engineering, where size uniformity and mono dispersibility of the particles in the solvent, particularly in water, become crucial factors[15–23]. In this study, we investigate secondary structures formed by (6,6)CNBs[1,2] and C_{60} molecules, which are dissolved in 1,2-dichlorobenzene (see Fig. 1 in the Supplementary Information for the molecular structure of a (6,6)CNB). We find that uniform spherical particles are formed by (6,6)CNBs and C_{60} molecules in 1,2-dichlorobenzene at room temperature via bottom-up self-assembly, setting the molar concentrations of (6,6)CNBs and C_{60} molecules at appropriate values, and furthermore those particles are monodisperse even in water. The present facile room temperature synthetic methodology may well be applied to the creation of nano/micro structures/materials using basic carbon nano units such as cycloparaphenylene (CPP, carbon nanorings) and fullerenes; e.g., C_{60}, C_{70} and $C_{59}N$.

The solutions of (6,6)CNBs, C_{60} molecules and a mixture of (6,6)CNBs and C_{60} molecules dissolved in 1,2-dichlorobenzene are shown in Fig. 2 in the Supplementary Information. The colour of the solution of (6,6)CNBs dissolved in 1,2-dichlorobenzene was yellowish, whereas that of C_{60} molecules dissolved in 1,2-dichlorobenzene was deep purple as well known. The colour of the solution changed to brown after the solutions of (6,6)CNBs and C_{60} molecules had been mixed together.

We found that particles were produced in 1,2-dichlorobenzene after the mixture of the two solutions in all of the cases of different ratios of the molar concentration of (6,6)CNBs to that of C_{60} molecules (see Table 1 in the Methods for the actual concentrations of (6,6)CNBs and C_{60} molecules dissolved in 1,2-dichlorobenzene). However, smooth spherical particles of a uniform diameter were formed when the ratio of the molar concentration of (6,6)CNBs to that of C_{60} was set at 1 : 2 (the concentrations of (6,6)CNBs and C_{60} molecules were, respectively, 0.35 and 0.70 μmol ml^{-1}). SEM images of particles formed by (6,6)CNBs and C_{60} molecules are shown in Fig. 1, where the ratio of the molar concentration of (6,6)CNBs to that of C_{60} was 1 : 2. The size of the particles increased with time (see also Fig. 3 in the Supplementary Information for the size distributions of the particles as a function of the time and Fig. 2 for the time variation of the diameter of a particle). Note that no particles were formed in the solution of (6,6)CNBs dissolved in 1,2-dichlorobenzene and in the solution of C_{60} molecules dissolved in 1,2-dichlorobenzene. The surface of the spherical particles was smooth and the diameter of a particle was uniform when the particles were synthesized setting the ratio of the molar concentration of (6,6)CNBs to that of C_{60} at 1 : 2 as mentioned, whereas the surface of the particles was uneven and the size of a particle varied when the ratio was different from 1 : 2 (see Fig. 4 in the supplementary Information for the size distributions and SEM images of particles produced when the ratio of the molar concentration of (6,6)CNBs to that of C_{60} was 1 : 1, 1 : 2 and 1 : 3).

The absorption spectra by the supernatant of the solution, in which a mixture of (6,6)CNBs and C_{60} molecules were dissolved in 1,2-dichlorobenzene, are shown in Fig. 5 in the Supplementary Information, where the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules was changed (see Fig. 5(a) in the Supplementary Information) and the time variation of the absorption spectra when the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules was 1 : 2 is shown in Fig. 5(b) in the Supplementary Information. Note that the wavelengths of photons absorbed by (6,6)CNBs and C_{60} dissolved in 1,2-dichlorobenzene had been measured and those by (6,6)CNBs were 296, 318, 355, 373 and 396 nm, while those by C_{60} were 297, 329 and 407 nm (see Fig. 6 in the Supplementary Information for the absorption spectra by the individual solution of C_{60} and (6,6)CNBs dissolved in 1,2-dichlorobenzene). It is supposed that $m \times$ (6,6)CNBs and $n \times C_{60}$ molecules ((m, n) = (2, 1) and (1, 1 ~ 3) in the present study. See Methods Table 1) were physically combined to form a compound of $((6,6)CNB)_m$-$(C_{60})_n$ in the solution since the absorption peaks corresponding to (6,6)CNBs and C_{60} decreased when the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules was m : n, noting that smooth spherical particles of a uniform diameter were formed when the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules was 1 : 2 as mentioned. The intensity of the

absorption spectra corresponding to (6,6)CNBs and C_{60} molecules decreased with time (see Fig. 5(b) in the Supplementary Information, where the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules was set at 1 : 2). In other words, the number of compounds; (6,6)CNB-$(C_{60})_2$, increased with time and those compounds formed spherical particles.

The time variation of the diameter of a particle and the peaks of the absorption spectra corresponding to (6,6)CNBs and C_{60} molecules in 1,2-dichlorobenzene are shown in Fig. 2, where the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules was set at 1 : 2. The diameter of a particle increased with time, whereas the amount of (6,6)CNBs and C_{60} molecules in the solution decreased with time, which means that the number of (6,6)CNB-$(C_{60})_2$ produced in the solution and the diameter of a particles formed by (6,6)CNB-$(C_{60})_2$ increased with time as mentioned.

The mean diameter of a particle formed 168 h after the mixture of the two solutions and the hydrodynamic diameter and zeta potential of a particle dispersed in distilled water are shown in Table 1, where the particles were synthesized setting the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules at 1 : 2. The diameter and hydrodynamic diameter of a particle synthesized 168 h after the mixture of the two solutions were quite uniform. Importantly, the absolute value of the zeta potential of a particle dispersed in water was so high as 38.8 mV that the particles were monodisperse even in water (see Fig. 7 and Video-1 in the Supplementary Information for the precipitation process of the solution and Fig. 8 in the Supplementary Information for the time variation of the turbidity of the suspension). Note that the particles eventually precipitated in water due to their own weight, but once the suspension had been shaken, the particles evenly dispersed again thanks to the high absolute value of the zeta potential in water (see Video-2 in the Supplementary Information).

The mass spectra of particles formed 168 h after the mixture of the two solutions are shown in Fig. 9 in the Supplementary Information, where (6,6)CNBs are positively charged, while C_{60} molecules are negatively charged. It is clear that the particles were composed of compounds formed by (6,6)CNBs and C_{60}.

We carried out some preliminary simulations concerning the structures formed by compounds [(6,6)CNB-$(C_{60})_m]_n$, where (m, n) = (1, 1), (2, 1), (2, 2) and (2, 3), based on a semi-empirical method; PM6[24], according to which a compound; (6,6)CNB-$(C_{60})_2$, can be stably formed, but the configuration of triple compounds is not aligned in a regular form (see Fig. 10 in the Supplementary Information). A TEM image of a particle formed when the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules was 1 : 2 is shown in Fig. 11 in the Supplementary Information. It is clearly shown that the particle is not formed by regularly oriented compounds.

In summary, particles composed of (6,6)carbon nanobelts and C_{60} molecules were synthesized via self-assembly at room temperature by mixing two solutions of (6,6)carbon nanobelts and C_{60} molecules dissolved in 1,2-dichlorobenzene. Smooth spherical particles of a uniform diameter were formed

particularly when the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules was set at 1 : 2 (the concentrations of (6,6)CNBs and C_{60} molecules were 0.35 and 0.70 μmol ml^{-1}). The absolute value of the zeta potential of the particles dispersed in distilled water was so high that the particles were monodisperse in water, which means that the particles may well be used as stable colloidal particles in water. The present synthetic methodology is so simple that it may also be applied to the creation of nano/micro structures/materials using basic carbon nano units such as [*n*]cycloparaphenylene (CPP, carbon nanorings) and fullerenes; e.g., C_{60}, C_{70} and $C_{59}N$.

Table

Table 1: Diameter of a particle produced 168 h after the mixture of the two solutions, and the hydrodynamic diameter and zeta potential of a particle dispersed in distilled water.

Diameter†1 [nm]	Hydrodynamic diameter†2 [μm]	Zeta potential†3 [mV]
$(7.12 \pm 0.63) \times 10^2$	1.30 ± 0.09	$- 38.8 \pm 0.7$

The particles were synthesized setting the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules at 1 : 2 (the concentrations of (6,6)CNBs and C_{60} molecules were, respectively, 0.35 and 0.70 μmol ml^{-1}).

†1The diameter of the particles was measured, targeting at 100 particles from SEM images.

†2The hydrodynamic diameter of a particle dispersed in distilled water was measured by Zetasizer.

†3The zeta potential of a particle dispersed in distilled water was measured by Zetasizer.

Methods

Synthetic procedure of particles

We developed a facile room temperature methodology for producing particles composed of (6,6)CNBs and C_{60} molecules. The synthetic procedure is summarized below.

(a) (6,6)CNBs (Tokyo Chemical Industry Co. Ltd.) and C_{60} molecules (Kanto Chemical Co. Inc.) were individually dissolved in 1,2-dichlorobenzene. The molar concentrations of (6,6)CNBs and C_{60} molecules dissolved in 1,2-dichlorobenzene are listed in Methods Table 1.

(b) Those two solutions were mixed, adding 2 ml of the solution of C_{60} molecules dissolved in 1,2-dichlorobenzene to 2 ml of the solution of (6,6)CNBs dissolved in 1,2-dichlorobenzene. The ratio of the

molar concentration of (6,6)CNBs to that of C_{60} was set at 1 : 1, 1 : 1.25, 1 : 1.5, 1 : 1.75, 1 : 2, 1 : 2.25, 1 : 2.5, 1 : 2.75, 1 : 3 and 2 : 1 (see Methods Table 1).

(c) The mixed solutions were left still for 1, 2, 3, 4, 24 and 168 h at room temperature.
(d) The solvent; i.e., 1,2-dichlorobenzene, was replaced by ethanol 1, 2, 3, 4, 24 and 168 h after the mixture of the two solutions, followed by sonication and centrifugation twice.
(e) The particles separated by centrifugation were dispersed in distilled water, followed by sonication.

Characterization and observation procedure

The following is the characterization and observation procedure.

(a) The absorption spectra by the supernatant of the solution were measured by ultraviolet-visible (UV-Vis) spectroscopy (DU730, Beckman Coulter Inc.).

(b) The structures of the particles were observed by scanning electron microscopy (SEM) (SU8030, Hitachi Ltd.) and transmission electron microscopy (TEM) (2200FS, JEOL Ltd.). The size of the particles was measured, targeting at 100 particles from the SEM images.
(c) The hydrodynamic diameter and zeta potential of the particles dispersed in distilled water were measured by Zetasizer (Nano-ZS, Malvern Panalytical Ltd.).
(d) The precipitation procedure of the particles dispersed in distilled water was observed, and photographed and recorded on videotape. The intensity of the transmitted light of 500 and 600 nm wavelengths through the whole solution confined in a glass container was measured with a spectral photometer (U-3500 Spectrophotometer, Hitachi High-Tech Co.) and the turbidity was defined as $\left(1 - I_{trans} / I_{in}\right) \times 100\%$, where I_{in} and I_{trans} ae, respectively, the intensities of the incident and transmitted light.
(f) The molecular weight of the compounds forming the particles was measured with time-of-flight mass spectrometry (TOF-MS) (autoflex2, Bruker Co.), where (6,6)CNBs are positively charged, whereas C_{60} molecules are negatively charged.

Methods table

Table 1 Molar concentrations of the solution of CNBs and C_{60} dissolved in 1,2-dichlorobenzene.

Ratio of the molar concentrations of (6,6)CNBs and C_{60}	Molar concentration of (6,6)CNBs [μmol ml^{-1}]	Molar concentration of C_{60} [μmol ml^{-1}]
1 : 1	0.70	0.70
1 : 1.25	0.70	0.875
1 : 1.5	0.70	1.05
1 : 1.75	0.70	1.225
1 : 2	0.70	1.40
1 : 2.25	0.70	1.575
1 : 2.5	0.70	1.75
1 : 2.75	0.70	1.925
1 : 3	0.70	2.10
2 : 1	1.40	0.70

The molar concentrations of (6,6)CNBs and C_{60} molecules became half after the mixture of the two solutions.

Declarations

Data availability

All of the data supporting this work are available from the corresponding author upon reasonable request.

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Author contributions

SC performed experiments, characterizations and data analyses, and drew graphs; SK performed experiments, characterizations, data analyses and computer simulations, and drew graphs; YM performed experiments, characterizations and data analyses; TMi performed experiments; and TMa organized the present research project, raised the fund, carried out data analyses and wrote the manuscript. All the authors checked the manuscript, images and graphs and agreed with the contents of the paper.

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Competing interests

The authors declare no competing interests.

Additional information

Supplementary information. The online version contains supplementary material available at https://doi.org/10.???????????.

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Figures

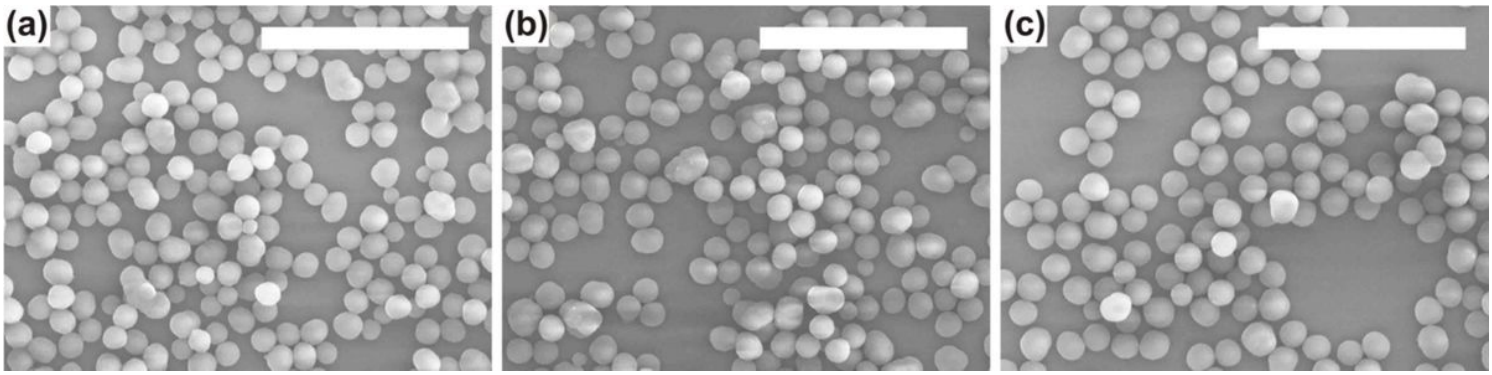

Figure 1

SEM images of particles formed by (6,6)CNBs and C_{60} molecules. The particles were synthesized setting the ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules dissolved in 1,2-dichlorobenzene at 1 : 2 (the concentrations of (6,6)CNBs and C_{60} molecules were 0.35 and 0.70 μmol ml^{-1}). The scale bars represent 5 μm. (a) 3 h after the mixture of the two solutions; (b) 4 h; (c) 24 h.

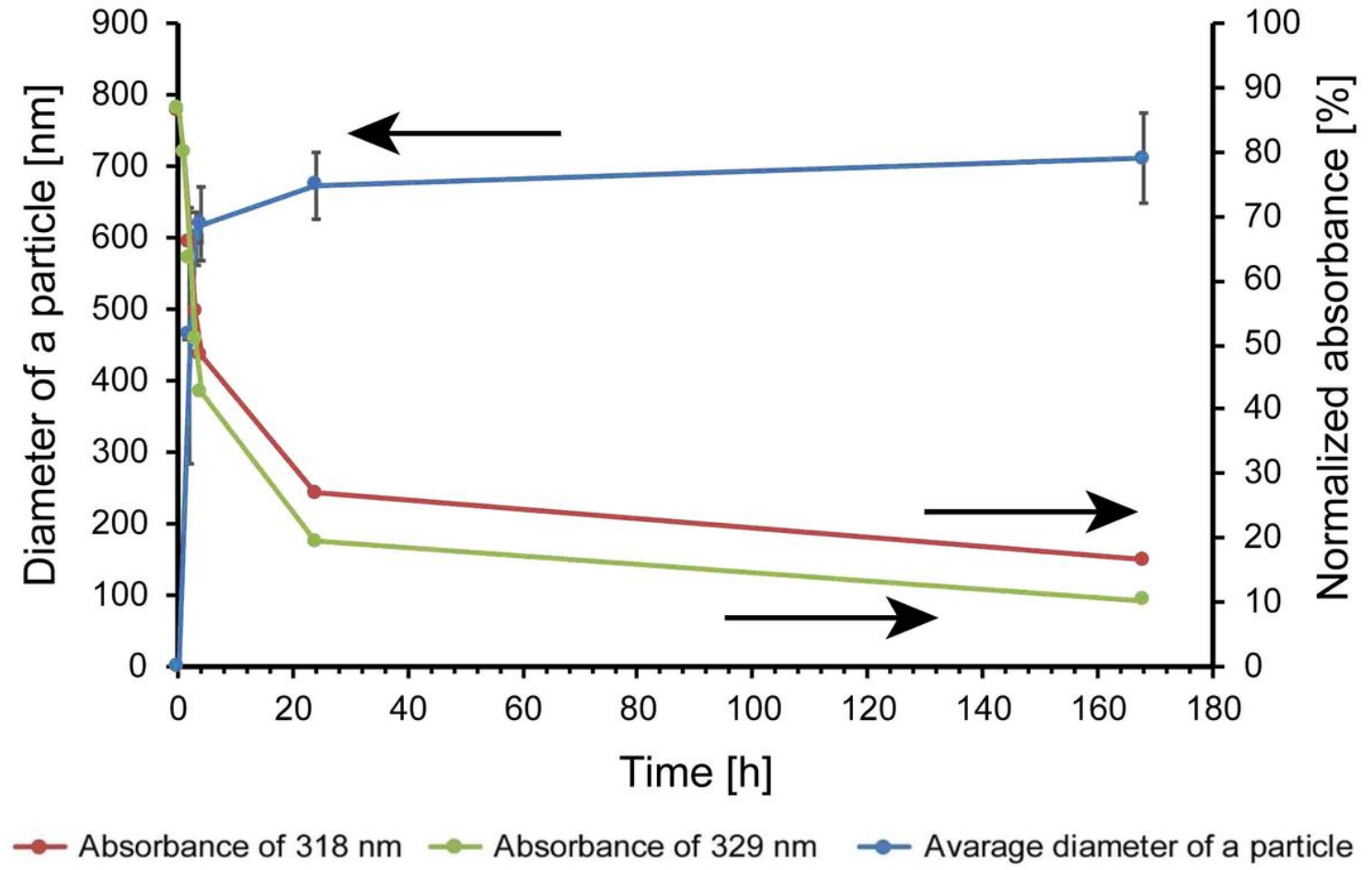

Figure 2

Time variation of the diameter of a particle and the peaks' intensities of the absorption spectra corresponding to (6,6)CNBs and C_{60} molecules dissolved in 1,2-dichlorobenzene. The ratio of the molar concentration of (6,6)CNBs to that of C_{60} molecules is 1 : 2.

Supplementary Files

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