Top-down Preparation of Dispersions of C_{60} Nanoparticles in Organic Solvents

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Nanoparticles of C_{60}, prepared by hand-grinding bulk solids in an agate mortar, were found to disperse stably in various organic solvents, in which molecular solubility of C_{60} is negligibly small. The resulting dispersions contained the C_{60} nanoparticles, whose average size varies between 200 and 300 nm depending on the solvent. The C_{60} concentrations in the dispersions were an order of magnitude higher than those prepared by the conventional methods.

Solubility in various solvents distinguishes fullerenes from other allotropes of carbon. The property makes it possible to develop rich chemistry and new applications of fullerenes, including optical and electronics materials, superconductors, sensors, and building blocks for new chemicals and materials.[1] More interestingly, when turned into nanoparticles, fullerenes disperse stably in solvents, in which molecular solubility is negligibly small. Particularly, interesting example is a stable dispersion of the C_{60} nanoparticles in water. Although fullerenes are hydrophobic carbon allotropes and not at all soluble in water,[2] the nanoparticles of them remain dispersed in water even without the aid of dispersing agents such as surfactants.[3] This is in marked contrast to carbon nanotubes, which requires surfactants or polymers to form stable dispersions in water.[4] The C_{60} nanoparticles also disperse in organic solvents, in which C_{60} is only sparingly soluble.[5,6]

Dispersibility as the nanoparticles may lead to new applications of C_{60} without performing chemical modifications to improve solubility in various solvents. For example, biological activities, including cytotoxicity, of the C_{60} nanoparticles have attracted interests in the recent years.[7,8] Optical properties of the C_{60} nanoparticles have attracted some interests.[6] Such aggregation was also found important in unique nonlinear optical properties of C_{60} derivatives.[9]

The dispersions of the C_{60} nanoparticles can be obtained by recrystallization or redox reactions in solutions.[3,5] For the dispersions in organic solvents, a saturated solution of C_{60} or C_{70} in toluene is injected into an excess amount of nonsolvent such as methanol, ethanol, acetone, or acetonitrile to give a dispersion of the C_{60} nanoparticles, whose size is between 150 and 490 nm.[5] However, low fullerene content in the resulting dispersions ($\approx 10\,\mu g\,mL^{-1}$) prevents further investigations or applications. Very recently, we found that hand-grinding bulk solids of C_{60} in an agate mortar efficiently generates the nanoparticles including those as small as 20 nm, and that the hand-ground C_{60} nanoparticles disperse in pure water.[8] In this paper, dispersibility of the hand-ground C_{60} nanoparticles in various organic solvents is reported.

The nanoparticles of C_{60} was prepared by hand-grinding.[8] Hand-ground C_{60} (2 mg) was mixed with a solvent (2 mL), and the mixture was subjected to ultrasonic treatment for 30 min, after which large particles were filtered off by a membrane filter (pore size, 5 μm). For concentration determination, 0.1 mL of the dispersion was evaporated to dryness under vacuum, the residue was redissolved in 1 mL of toluene, and absorption spectra were measured. For the dispersions in silicone oil and fluorinated oil, 0.1 mL of the dispersion was mixed with 0.9 mL of toluene, and absorption spectra were measured. Concentration of C_{60} was calculated using absorbance at 334 nm ($\log \varepsilon = 4.71$).[10] Dispersion efficiency is reported as a weight fraction of C_{60} in the dispersion to that used for sample preparation. Longer sonication did not change the size and the dispersion efficiency noticeably.

Dispersions of the C_{60} nanoparticles were obtained in a variety of nonsolvents for C_{60} (Figure 1). Examination of the particles dispersed in methanol by transmission electron microscopy (TEM) revealed particles in an aggregated state (Figure 2).

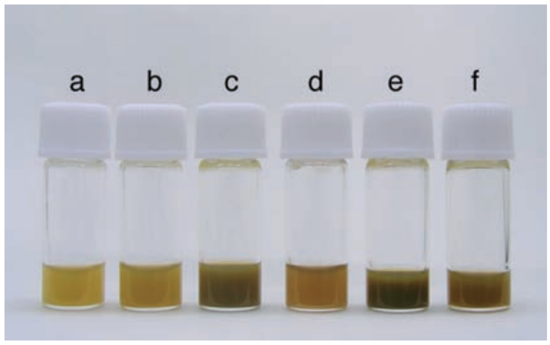

Figure 1. Photograph of dispersions of the C_{60} nanoparticles in various solvents. a) Methanol, b) ethanol, c) 2-propanol, d) 1-octanol, e) acetone, and f) silicone oil.

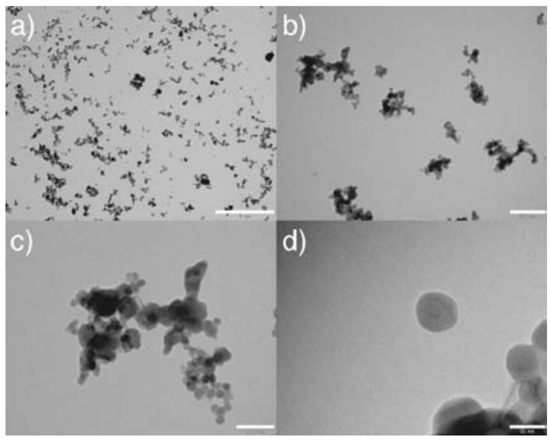

Figure 2. TEM images of the C_{60} nanoparticles dispersed in methanol at different magnifications. a) Scale bar, 5 μm. b) Scale bar, 500 nm. c) Scale bar, 200 nm. d) Scale bar, 50 nm.

Table 1. Characteristics of dispersions of C_{60} nanoparticles in various organic solvents

Solvent	Solubility /μg mL^{-1}	Size/nm	C_{60} dispersed /μg mL^{-1}	Efficiency /%
Methanol	0.035[c]	281	65	6
Ethanol	0.8[c]	253	98	9
1-Propanol	4.1[c]	247	330	28
2-Propanol	ND	227 ± 18[e]	221 ± 89[e]	21 ± 7[e]
2-Propanol	ND	356[f]	9[f]	1[f]
1-Octanol	47[c]	288	265	21
Acetone	1[d]	307	341	31
Acetonitrile	0[d]	229	221	19
Silicone oil[a]	ND	ND[g]	274	27
Fluorinated oil[b]	ND	ND[g]	59	4

[a]WF-30, Toray Dow Corning Silicone, Co., Ltd., Tokyo, Japan. [b]Demnum S200, Daikin Industries, Ltd., Osaka, Japan. [c]Ref. 2. [d]Ref. 11. [e]Average value of five independent runs. Error represents standard deviation. [f]Prepared by shaking the mixture by hands for 100 strokes. [g]Attempts to measure the size by DLS failed due to continuously fluctuating scattering from these solvents.

The aggregates were consisted of particles smaller than 200 nm, and some particles were even smaller than 50 nm (Figure 2d). It should be stressed that sonication simply helps to disintegrate and disperse the agglomerated C_{60} nanoparticles formed by hand-grinding, and does not have a significant effect of reducing the size of the C_{60} nanoparticles.[8] Rather large average size (281 nm) obtained by dynamic light scattering (DLS) (Table 1) may indicate that there remain aggregates in the dispersion even after sonication.

Characteristics of the dispersions in various solvents are summarized in Table 1. It is clearly seen that average size of the C_{60} nanoparticles, which was measured by DLS, and dispersion efficiency depend on the solvent used. Among the solvents tested, 1-propanol, 2-propanol, 1-octanol, acetone, and silicone oil gave high dispersion efficiency between 20 and 30 wt %. Concentrations of C_{60} in these dispersions are order of magnitude higher than those prepared by the conventional methods. More concentrated dispersions may be obtained by using a larger amount of hand-ground C_{60}.[8] The nanoparticles could be dispersed even by shaking the mixture by hand, although the dispersion efficiency is significantly lower. Dispersions were not obtained for solvents that dissolve a finite amount of C_{60}. In the case of decane (solubility of C_{60}: 71 μg mL^{-1}[11]), a turbid dispersion was obtained after sonication, but filtration gave a clear solution exhibiting magenta color, which is characteristic to molecular solutions of C_{60}. An attempt to prepare a dispersion in acetic acid also failed.

Visible sediment was formed upon storage in the dark for 1 day. However, it seems that the sedimentation took place not because larger particles were formed by flocculation, but simply because of the density difference between the C_{60} nanoparticles and the solvents, as the sediment could be redispersed easily by agitating the dispersion by hand. The supernatant remained colored even after storage for months.

The stabilizing mechanism is not clear at present. For the dispersions in acetonitrile prepared by recrystallization, the C_{60} nanoparticles were stabilized by electrostatic repulsion due to negative surface charges of the C_{60} nanoparticles (ζ-potential, -32.5 mV).[5] The hand-ground C_{60} nanoparticles were also found to bear negative surface charges in pure water, and showed ζ-potential of a similar extent (-39.0 mV).[8] It seems likely that the dispersion stability of the hand-ground C_{60} nanoparticles in organic solvents also stems from similar surface charging, although further work is necessary to clarify the issue.

In summary, we found that the hand-ground C_{60} nanoparticles disperse in a variety of organic solvents, in which C_{60} is only sparingly soluble. The top-down approach gives dispersions containing a significantly higher amount of the C_{60} nanoparticles compared with the previous methods. Considering the facility and efficiency, we anticipate that the top-down approach presented here has a potential of becoming the basis for studying the dispersions of the C_{60} nanoparticles.

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