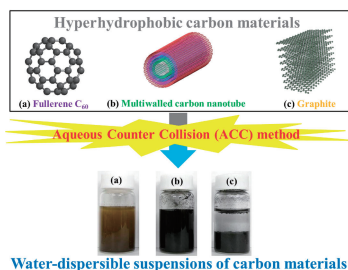


Preparation of Aqueous Carbon Material Suspensions by Aqueous Counter Collision

Yohei Kawano and Tetsuo Kondo*
Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

(E-mail: tekondo@agr.kyushu-u.ac.jp)



Aqueous dispersions of hyperhydrophobic carbon materials were successfully prepared using the aqueous counter collision method without any dispersant.

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Aqueous dispersions of hyperhydrophobic fullerene C₆₀, multiwalled carbon nanotubes, and graphite were prepared. This was achieved by the aqueous counter collision method, designed to fabricate nanofibers and nanoparticles. Dispersions of carbon materials could be prepared by collision from two high-speed water jets. The dispersed states of the materials differed significantly, presumably because of the different nanoscale configurations of the materials.

Fullerene C₆₀,¹ carbon nanotubes (CNTs),² and graphite are carbon allotropes, which have attracted much attention because of their potential applications in electroconductive, thermally conductive, and optically active materials.³ They form different aggregation states, depending on their three-dimensional structures, and contribute to their unique configurations. Graphene has a sheet structure, in which C atoms are covalently connected in a network through sp² hybrid orbitals.⁴ Fullerene C₆₀ has a hollow spherical structure, which is effectively a wrapped graphene sheet. It is chemically reactive, and it has been modified variously to introduce hydrophilic molecules into the cavity. Atoms can be trapped inside fullerenes to form inclusion compounds known as endohedral fullerenes.⁵ CNTs are tube-shaped structures of rolled graphene sheets and have excellent mechanical and electrical properties. Their use in numerous devices varying from electron devices to electrically conductive fillers is currently being investigated.⁶ Graphite has a lamellar structure of graphene sheets⁷ and is used in many products such as ink and batteries. Fullerene C₆₀, CNTs, and graphite exhibit poor solubility in most solvents because of their aggregation by van der Waals and π - π stacking interactions. This limits their widespread use, and a method allowing these materials to be dispersed in solution is required.

Techniques for dispersing C materials (fullerene C₆₀, multiwalled carbon nanotubes (MWCNTs), and graphite) can be classified as chemical or mechanical treatments. Chemical processes are limited to employing specific surfactants or surface modifications.⁸⁻¹⁰ There are numerous mechanical processes available for dispersing nanoparticles. For example, milling methods using fine grinding metal media (beads or balls) have been used to disperse nanoparticles in liquids.¹¹ MWCNTs have been dispersed in ethanol by wet bead milling.¹² Hand-grinding¹³ and laser ablation¹⁴ without surfactants have also been used to disperse fullerene C₆₀. However, no general method for dispersing various C materials has been proposed.

We recently reduced biomaterials into nanoscale objects using the collision energy of dual water jets. This strategy is capable of overcoming van der Waals forces and hydrogen bonds, without any chemical modification.^{15,16} This system is termed aqueous counter collision (ACC)¹⁷ and involves an aqueous suspension of the micrometer-sized sample divided

between two facing nozzles. The suspension rapidly collides with itself, resulting in the nanopulverization of the dispersed sample. The obtained material can be homogeneously reduced in size by repeating the collision or increasing the ejection pressure. In the current study, ACC is applied to hydrophobic fullerene C₆₀, MWCNTs, and graphite to prepare aqueous suspensions.

Fullerene C₆₀ was purchased from Kanto Kagaku (Tokyo, Japan). MWCNTs (VGCF-X, Showa Denko K. K., Tokyo, Japan) had an average diameter and length of 15 nm and 3 μ m, respectively. Graphite (>99.9995%) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Carbon material samples (1.25 mg mL⁻¹) in deionized water were ultrasonically agitated for several seconds and then subjected to ACC treatment (Sugino Machine, Ltd., Toyama, Japan) at an ejection pressure of 170 MPa for 60-cycle repetitions (denoted the pass number). Materials were completely phase-separated prior to ACC treatment. Increasing the ACC pass number overcame the phase separation. Samples became dispersed in water after 60 passes, as shown in Figure 1. The fullerene C₆₀ suspension shown in Figure 1a exhibited a relatively stable state that was partially precipitated compared with the graphite suspension shown in Figure 1c, which gradually precipitated. The MWCNT suspension in Figure 1b was more dispersed than the other samples.

To examine the different dispersion behaviors of the three samples, aqueous suspensions before and after ACC treatment were observed using optical microscopy (Figure 2). A drop of suspension on a glass slide was observed using an optical microscope (BHA, Olympus, Co., Ltd., Tokyo, Japan). Before ACC treatment, all samples contained aggregates with diameters >100 μ m. After ACC treatment, the fullerene C₆₀ sample contained dispersed aggregates of several μ m in diameter, as shown by the arrows in Figure 2d. The MWCNT sample was pulverized into aggregates of ca. 50 μ m in diameter, as shown in Figure 2e. The graphite sample contained aggregates a few tens of μ m in diameter, as shown in Figure 2f, which were not likely to disperse in water.

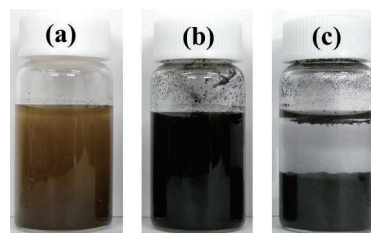


Figure 1. Aqueous dispersions of (a) fullerene C₆₀, (b) MWCNTs, and (c) graphite, after ACC treatment for 30 min.

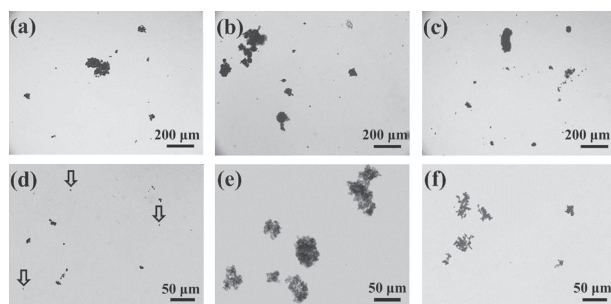


Figure 2. Optical micrographs of (a) fullerene C_{60} , (b) MWCNTs, and (c) graphite in water, and (d), (e), and (f) the same samples after ACC treatment. Arrows in (d) indicate dispersed particles.

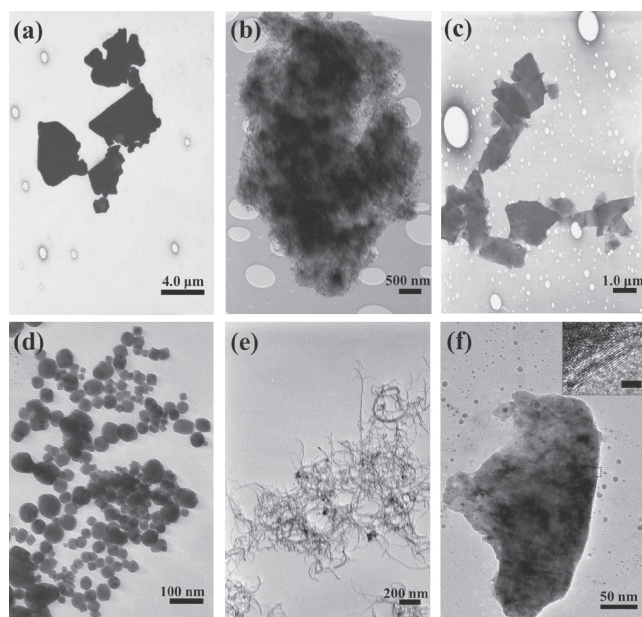


Figure 3. TEM images (a), (b), and (c) before, and (d), (e), and (f) after ACC treatment, respectively. (a) and (d) fullerene C_{60} , (b) and (e) MWCNTs, (c) and (f) graphite. The inset in (f) shows a HR-TEM image of the lattice (scale bar: 1.0 nm).

The different sample morphologies were investigated by transmission electron microscopy (TEM) using diluted sample dispersions. Specifically, the obtained suspensions of fullerene C_{60} and graphite were diluted to 1/30th of their concentration with deionized water, and the MWCNT suspension was diluted to 1/200th. Fullerene C_{60} and MWCNT diluents were mounted on Cu grids coated with formvar films, and the graphite diluent was mounted on a C-coated Cu grid. Grids were rapidly frozen with liquid N_2 and immediately freeze-dried. The samples were observed using TEM (JEM-1010, JEOL, Ltd., Tokyo, Japan) operated at 80 kV and/or high-resolution TEM (HR-TEM) (JEM-3200FSK, JEOL, Ltd.) at 300 kV. Figures 3a and 3c show those before ACC treatment, aggregates of several μm in diameter were observed for fullerene C_{60} and graphite, respectively. The TEM image of the MWCNT sample in Figure 3b shows fibers of ca. 15 nm in diameter, which formed networked

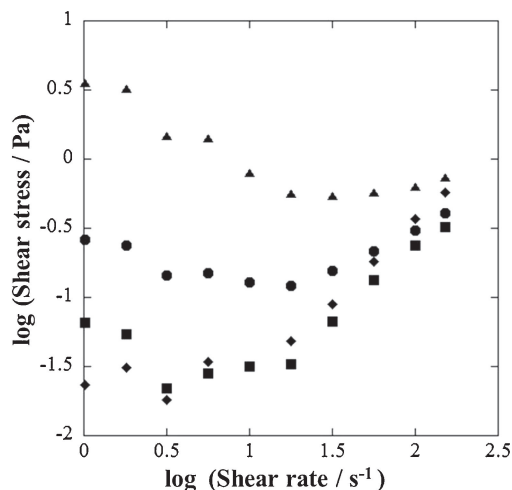


Figure 4. Log-log plots of shear stress as a function of shear rate, for ACC-treated water (◆), fullerene C_{60} (●), MWCNTs (▲), and graphite (■).

fiber aggregates. ACC treatment of the fullerene C_{60} sample provided spherical aggregates 10–100 nm in diameter. The empty “nanopockets” in the MWCNT fiber network widened upon ACC treatment, as shown in Figure 3e. Aggregates of a few hundreds of nm in diameter were observed in the graphite sample, as shown in Figure 3f. The HR-TEM lattice image inset in Figure 3f showed that the layered structure was maintained in the graphite particles after ACC treatment.

The aqueous dispersibility of the C materials was evaluated by steady flow measurements using a Rheosol-G2000 instrument (UBM, Ltd., Kyoto, Japan) with a shear rate of 1–300 s^{-1} . Figure 4 shows that the shear stress of the MWCNT sample responded more sensitively to the increase in the suspension shear rate than that of the C_{60} and graphite samples. This differed from the behavior generally observed for nanoparticles in water. At low shear rate, the aqueous MWCNT suspension exhibited a higher shear stress than the other C samples. This was presumably because of the dispersion responding as an aggregated network structure, as seen in the TEM image in Figure 3e. At high shear rate, the shear stress of the MWCNT sample was similar to those of the other C samples, which exhibited a similar response to water. The results indicated that all three samples existed in a phase-separated state at high shear rate.

Ultraviolet–visible (UV–vis) absorption spectra of ACC-treated suspensions were obtained at room temperature using an UV-3000 spectrophotometer (Hitachi, Ltd., Tokyo, Japan). Fullerene C_{60} particles of diameter >100 nm (shown in Figure 3d) were removed by centrifugation, prior to measurement. The gravitational sedimentation equation suggests that colloidal spheres of radius a will precipitate according to¹⁸

$$\frac{L}{T} = \frac{2a^2(\rho_p - \rho_m)g}{9\eta} \quad (1)$$

where L is the centrifuge tube length (10.7 cm), T the sedimentation time, ρ_p the colloidal sphere density, ρ_m the density of water (1 g cm^{-3}), g the acceleration owing to gravity, and η the viscosity of water (1 mPa s).

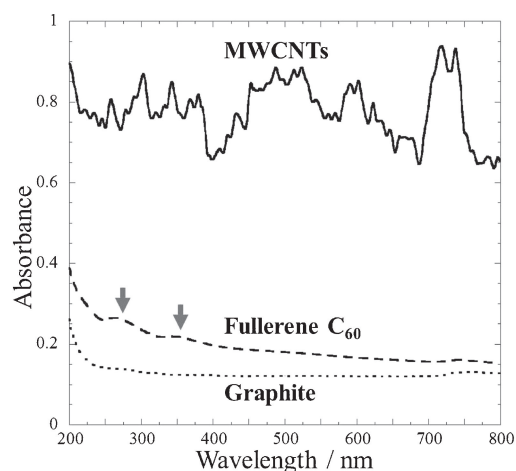


Figure 5. Absorption spectra of aqueous fullerene C_{60} (dashed), MWCNTs (solid), and graphite (dotted) suspensions.

The density of the fullerene C_{60} sample was assumed to be 1.73 g cm^{-3} . When the ACC-treated fullerene C_{60} suspension was centrifuged for $1.38 \times 10^3 \text{ s}$ at a force of $20 \times 10^3 g$, the smallest diameter of the precipitated spheres was calculated to be 100 nm. Similarly, the density of graphite was assumed to be 2.26 g cm^{-3} , and centrifuging an ACC-treated graphite suspension for 300 s at 500g yielded particles of diameter $<1000 \text{ nm}$. Figure 5 shows that the UV-vis absorption spectrum of fullerene C_{60} had two broad peaks at 350 and 270 nm (marked by arrows). These corresponded to those reported for other water-dispersed fullerene C_{60} samples.^{14,19} Numerous overlapped absorption peaks were observed in the spectrum of the MWCNT sample. This indicated that MWCNTs were homogeneously dispersed as an aqueous suspension, as shown in Figure 1b. The spectrum of the graphite sample exhibited no absorption features, because graphite and water were phase-separated.

The ζ potentials of the ACC-treated suspensions were measured at 298.5 K using a Zetasizer Nano instrument (Malvern Instruments, Ltd., Worcestershire, U.K.). The fullerene C_{60} and graphite suspensions were ultrasonically homogenized for 1 min prior to measurement, and that of MWCNTs was homogenized for 1 min after dilution to 1/100th. The fullerene C_{60} suspension exhibited a mean ζ potential of -35.4 mV , which corresponded to that reported for other water-dispersed fullerene C_{60} samples.¹⁹ The mean ζ potential for graphite was estimated to be -45.6 mV , and that of MWCNTs to be -36.3 mV . Graphite exhibited the largest ζ potential. This indicated that its coagulation force was larger than the dispersion force from the electrostatic interaction between the particles. This resulted in its precipitation, as shown in Figure 1c. Why do such C materials without dissociative functional groups exhibit negative surface potentials is not well understood, though H_2O molecules near the sample surfaces may be responsible.

Fullerene C_{60} was reduced from micrometer- to nanometer-sized aggregates by ACC treatment, resulting in a homogeneous aqueous dispersion. Its nanometer-sized particle diameter may have contributed to its water dispersibility. Nanopockets in the engaged MWCNT network shown in Figure 3e may have expanded during ACC treatment. Newly generated and expanded nanopockets were supposed to contain more bound water,

resulting in better dispersibility. Details of this phenomenon will be the focus of our future paper. Graphite was reduced from micrometer- to nanometer-sized particles by ACC treatment, while retaining its layered structure. This layered structure may have interrupted its water dispersibility to a higher degree than the other samples.

In summary, aqueous dispersed suspensions of hyperhydrophobic fullerene C_{60} , MWCNTs, and graphite were prepared by ACC treatment, without the use of dispersants or surfactants. The obtained dispersions exhibited different states of dispersibility, regardless of their similar negative surface potentials. This was attributed to changes in their nanometer-scale configuration during ACC treatment. This concept can be extended to using ACC treatment to generate an intrinsic hyperhydrophobicity in aqueous C materials.

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