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Non-Engineered Nanoparticles of C_{60}

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We discovered that rubbing bulk solids of C_{60} between fingertips generates nanoparticles including the ones smaller than 20 nm. Considering the difficulties usually associated with nanoparticle production by pulverisation, formation of nanoparticles by such a mundane method is unprecedented and noteworthy. We also found that nanoparticles of C_{60} could be generated from bulk solids incidentally without deliberate engineering of any sort. Our findings imply that there exist highly unusual human exposure routes to nanoparticles of C_{60}, and elucidating formation mechanisms of nanoparticles is crucial in assessing their environmental impacts.

Nanoparticles, fine particles having length ranging from 1 to 100 nanometres in two or three dimensions[1], exhibit properties that are not observed for molecules or bulk counterparts[2]. They are widely used as building blocks for nanotechnology-derived applications such as single-electron devices, ultra dense recording media, bioelectronic devices and sensors, bioimaging, optoelectronic devices, catalysis and chemical sensors, and energy conversion and storage[2,3]. Such ultrafine particles are usually prepared in a bottom-up manner by allowing molecules or atoms to assemble and build up into nanoparticles through chemical reactions in solutions or gas[2,3].

Fine particles can also be obtained in a top-down manner by pulverising bulk solids[4]. When physical forces are applied to a solid, it undergoes plastic deformation to a breaking point, above which fracture results. The size of the solid is reduced as fracturing is repeated during pulverisation. However, as the size becomes smaller, the applied energy is rather dissipated as heat and the size reduction becomes increasingly difficult. Consequently, conventional milling devices typically produces particles with an average size no smaller than several ten micrometres[5], and nanoparticles are not obtained unless very high energy is applied using a special device such as a high-energy ball mill[6,7]. We discovered entirely different size-reduction characteristics for bulk solids of fullerene C_{60}.

Results

Solid C_{60} (1.5 mg) was placed between two glass microscope slides (76 mm × 26 mm, thickness 0.8 – 1.0 mm) and rubbed repeatedly between fingertips for a few minutes (Fig. 1a). Frictional resistance of C_{60} increased progressively as it was rubbed, and coarse black particles (Fig. 1b, median diameter 129 μm)[8] eventually turned to fine brownish powder and adhered to the glass surface.

Examination by scanning electron microscopy (SEM) revealed that rubbed C_{60} had a bimodal size distribution, consisting of particles no larger than a few tens of micrometres and significantly smaller ones (Fig. 1c). Remarkably, detailed examination of the smaller particles showed that nanoparticles, some of which were even smaller than 100 nm, were generated by this mundane treatment. Such nanoparticles were mostly found associated on the surface of large particles (Figs. 1d and 1e), but agglomerates of nanoparticles were also observed around large particles (Fig. 1f).

Use of the glass slides was not critical. When solid C_{60} (ca. 2 mg) was rubbed between fingertips without using the glass slides for 1 minute (a polyethylene glove was used to avoid direct contact of C_{60} with skin), nanoparticles smaller than 100 nm (Fig. 2b) were also observed in rubbed C_{60} on the surface of the glove (Fig. 2a), although chances of finding such nanoparticles was much less compared with C_{60} rubbed with the glass slides.

To quantify the size reduction by rubbing, C_{60} on the glass slides was dispersed in 2 mL of water containing 1 wt% of an anionic surfactant, sodium dodecyl sulphate (SDS). When the aqueous solution of SDS was poured onto rubbed C_{60} on the slides with a pipette, a brown and turbid dispersion was immediately formed. The dispersion was subjected to ultrasonic treatment for 5 min (Model 5510, 42 kHz output frequency, Branson

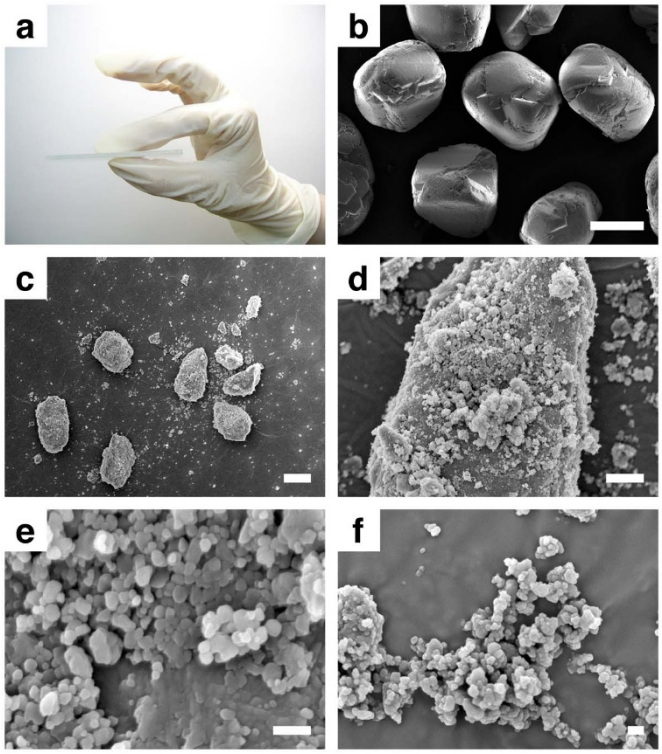

Figure 1 | Formation of nanoparticles by rubbing solid C_{60} between glass slides. (a) Experimental procedure. (b) SEM image of particles of as-received solid C_{60}. Scale bar represents 100 μm. (c, d, e and f) SEM images of nanoparticles of C_{60} formed by rubbing bulks solids between glass slides. Scale bars represent 10 μm (c), 2 μm (d), and 200 nm (e and f).

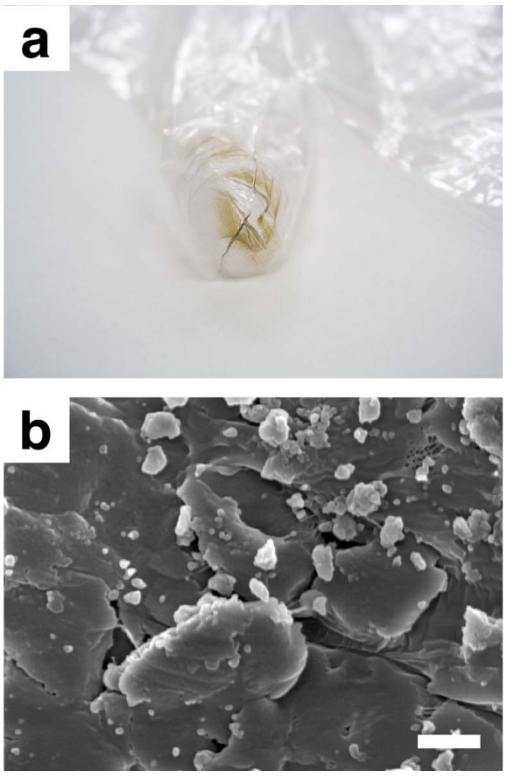

Figure 2 | Formation of nanoparticles by rubbing solid C_{60} between fingertips. (a) A photograph showing C_{60} on the surface of the glove after rubbing. (b) SEM images of rubbed C_{60} on the glove surface. Particles that are smaller than 100 nm are seen. Scale bar represents 500 nm.

Ultrasonic Corporation, Danbury, USA), and filtered with a membrane filter (nominal pore size, 5 μm). It should be noted here that ultrasonic treatment only helped disintegrating agglomerated nanoparticles and did not induce further size-reduction[9].

The highly turbid and brown filtrate (Fig. 3a) was found to contain nanoparticles of C_{60}, whose average diameter was 256.8 ± 1.1 nm by dynamic light scattering (Fig. 3b). The concentration of C_{60} in the dispersion (Fig. 3a), which was measured spectrophotometrically[10], was $2.46 \pm 0.17 \times 10^{-4}$ M (177 ± 12 μg/mL), meaning that approximately 24 wt% of C_{60} solids was turned to particles smaller than 5 μm simply by rubbing them between fingertips. Examination by high-resolution transmission electron microscopy (HRTEM) revealed the presence of particles smaller than 20 nm in the dispersion (Figs. 3c and 3d). The particle in Fig. 3c had a dimension 9 nm × 12 nm, and the nearly spherical particle in Fig. 3d was 14 nm in diameter. Mean fringe spacing of both particles was 0.50 nm, and agreed well with the value for C_{60} crystal of (220) plane (0.50074 nm)[11], showing that these particles are nano-sized crystals of C_{60} having an face-centred cubic (fcc) structure. Calculation using crystallographic data indicates that the spherical particle in Fig. 3d consists of approximately 2500 C_{60} molecules and 46% of them are exposed to the particle surface[8]. Rubbed C_{60} on the surface of the glove (Fig. 2a), on the other hand, could not be analysed in this way. C_{60} strongly adhered to the glove surface, and could not be removed and dispersed in water containing SDS.

Several unconventional engineering can produce nanoparticles of C_{60} from bulk solids. These include sonication of solid C_{60} in water[12], prolonged stirring of solid C_{60} in water for several weeks[13], or hand-grinding of solid C_{60} with an agate mortar and pestle[8,9,14,15]. Nevertheless, formation of nanoparticles by such a mundane treatment as rubbing between fingertips is unprecedented and noteworthy. Moreover, efficiency of size-reduction by rubbing between fingertips appears to be comparable to that of hand-grinding with an agate motor and pestle, by which approximately 34 wt% of C_{60} was turned to particles smaller than 5 μm[8,9].

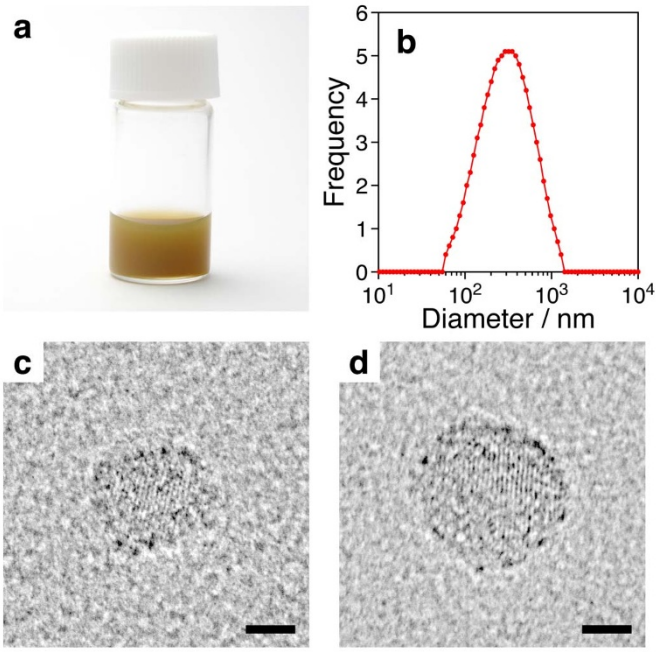

Figure 3 | Size distribution of nanoparticles produced by rubbing solid C_{60} between glass slides. (a) An optical photograph of a dispersion of nanoparticles of C_{60} in water containing 1 wt% SDS. (b) Size distribution of the nanoparticles of C_{60} in the dispersion. (c and d) HRTEM images of nanoparticles of C_{60} found in the dispersion. Scale bars represent 5 nm.

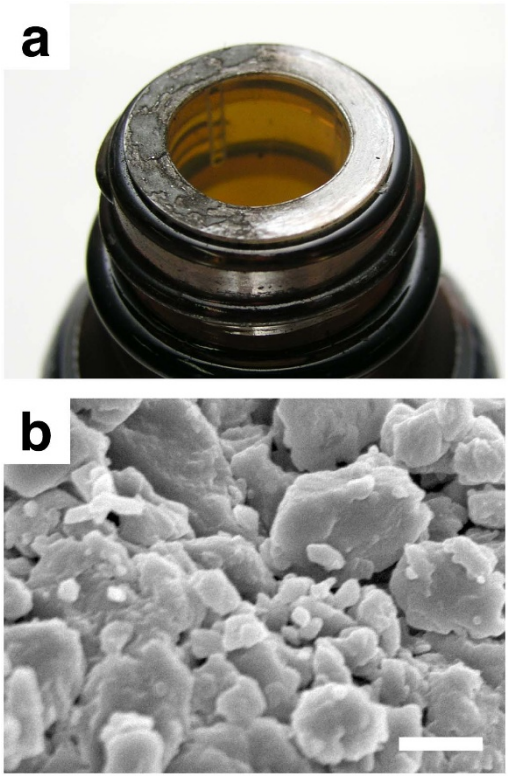

Figure 4 | Non-engineered nanoparticles of C_{60}. (a) A photograph showing a white bushing of the month of a reagent bottle of C_{60}. Right-hand side of the bushing was cleaned before taking the picture to reveal the original white colour. (b) SEM image of C_{60} that was collected from the bushing. Nanoparticles that are smaller than 100 nm are clearly seen. Scale bar represents 500 nm.

Comparable size-reduction characteristics observed for both hand-ground and finger-rubbed C_{60} strongly suggests that top-down fabrication of nanoparticles of C_{60} by mechanical means require a surprisingly little effort. Far from it, we found that nanoparticles of C_{60} were generated even without deliberate engineering of any sort. Fig. 4a shows a mouth of a reagent bottle of C_{60}. A white plastic bushing at the mouth was covered with brown powder of spilt C_{60}, which had been compressed and sheared repeatedly by a screw cap whenever the bottle had been opened and closed. Examination by SEM revealed particles smaller than 100 nm in C_{60} that was collected from the bushing (Fig. 4b).

Discussion

Considering the efforts usually required to prepare the nanoparticle by pulverisation[6,7], the size-reduction characteristics of C_{60} are truely anomalous. The size-reduction process of solid C_{60} is purely physical, and is not associated with change in crystalline structure or chemical/mechanochemical reactions[8,9]. Formation of nanoparticles of C_{70} by pulverisation was also reported[16], suggesting that anomalous size-reduction is a common characteristics among fullerenes. Detailed mechanisms behind the anomaly are not clear at present, but it could be ascribed to inherent properties of crystalline C_{60} such as fast isotropic rotation of the molecule[17] or low cohesive energy (1.6 eV)[8,9,18]. Labille et al. used X-ray diffraction to study nanoparticles of C_{60} that were prepared by prolonged stirring of bulks solids in water, and proposed that nanoparticles of C_{60} are formed by an erosion of large C_{60} crystals, which occurs preferentially via (111) lattice plane exfoliation[19]. The adhesion energy between smooth C_{60} surfaces is an order of magnitude lower than that of typical van der Waals solids[20]. This is ascribed to structural features of the C_{60} molecule including a large size, rigidity and smooth surface, which makes the C_{60} molecule behave like a macroscopic spherical object rather than a conventional molecule[20]. Shear stress exerted by fingertips or a screw cap may be sufficient enough to overcome the low adhesion energy to induce exfoliation.

Concerns have emerged on possible adverse effects of engineered nanomaterials[21], and nanoparticles of C_{60} have attracted considerable scientific attention in this regard[22–24]. Pulverization has widely been used to prepare C_{60} nanoparticles for evaluating their possible environmental and health impacts[25]. Compared with conventional methods for producing C_{60} nanoparticles such as recrystallisation from organic solvents (toluene[26] or tetrahydrofuran[10]), pulverisation has distinct advantages that the product is free from residual solvents and the procedure is simple to perform. A major drawback of pulverisation is a broad size distribution of the nanoparticles produced, but this can be circumvented by size-fractionation using filtration or centrifugation[8,15]. The size of pulverised nanoparticles can also be controlled when an automated milling device (wet grinding using a bead mill) is employed[27].

Present study shows that anomalous size-reduction characteristics of solid C_{60} have immediate implications for assessing health risks of C_{60} nanoparticles. Assessing possible human exposure routes to nanoparticles is an important consideration[21,28], and is among five grand challenges necessary toward safe handling of nanotechnology[29]. As nanoparticles are usually engineered by chemical reactions in gas phase or solutions[2,3], possible exposure routes appear to be foreseeable. Inhalation of airborne nanoparticles is a major exposure scenario[30], and an interim report on risk assessment of C_{60} proposed the acceptable exposure concentration of 0.8 mg/m^3 as respirable dust in working environments[31].

The supposition is not always true, however. Glover et al. showed nanoparticles were spontaneously generated from macroscopic silver and copper objects when they were simply in contact with surfaces in a humid air[32]. Proposed chemical mechanism involves surface oxidation with ambient oxygen and adsorbed water, diffusion of metal ions from the parent particle in the adsorbed water layer, and nucleation via chemical and/or photochemical reduction of the ions. Their findings imply that macroscopic objects can be a potential source of incidental nanoparticles in the environment, and that humans have long been in direct contact with these nanomaterials without being noticed[32].

Our results show there exists a mechanical pathway for similar incidental generation of nanoparticles from bulk C_{60} solids, and suggest highly unconventional exposure routes to nanoparticles of C_{60}. For example, if one rubs a spillage of C_{60} solids on a lab bench with a bare fingertip, he/she may be exposed inadvertently to risk of dermal uptake and inhalation of C_{60} nanoparticles, even though he/she presumes handling bulk solids of C_{60} and does not foresee exposure to nanoparticles. Similar situations may be encountered commonly in research laboratories or manufacturing facilities that use C_{60}, or during disposal of products that are deemed to contain solid C_{60} of macroscopic size. A possibility was also suggested that commercial solid C_{60} contains nanoparticles that are generated by friction of solid particles during production, storage, or transportation[9].

Although formation of nanoparticles by simple pulverisation is not known for other materials to the best of our knowledge, it is worth mentioning that nanoparticles are produced by simple pulverisation when mechano-chemical reactions are involved. For example, Rao et al. demonstrated that nearly pure Ag_9 quantum clusters were prepared by hand-grinding $AgNO_3$ and mercaptosuccinic acid solids followed by reduction by $NaBH_4$ using a mortar and pestle[33]. Thus, detailed understandings of underlying mechanisms behind the mechanical and/or mechano-chemical generation of nanoparticles form bulk solids, which still remain largely unclear, are crucial in characterizing environmental and health impacts of nanoparticles.

Methods

Materials. C_{60} (> 99.9% pure) was obtained from Tokyo Kasei, Co., Ltd. (Tokyo, Japan), and used as received. Sodium dodecyl sulphate (SDS) was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Millipore water was used throughout the work.

Scanning electron microscopy. After rubbing C_{60} between glass microscope slides, one slide was held, with the side with C_{60} down, above a conductive double-sided tape that was mounted on a brass stub. The upper side of the slide was tapped with a lab spoon so that fine particles of rubbed C_{60} fell on the tape. Solid C_{60} at the mouth of a reagent bottle was collected in a same manner. The specimens were coated with osmium (estimated coating thickness, < 10 nm), and examined on a JSM-6700F (JEOL, Tokyo, Japan).

High-resolution transmission electron microscopy. A drop of the dispersion of nanoparticles of C_{60} in water containing 1 wt% SDS was deposited on a carbon TEM grid. The surface of the carbon supporting film was subjected to hydrophilic treatment before the sample deposition. Crystals of SDS that precipitated after drying the specimen was removed with methanol. The specimen was air-dried again, and was examined on a Hitachi HF-2000 operating at 200 kV incident beam energy. The observations were performed at Nissan-Arc, Ltd. (Yokosuka, Japan).

Dynamic light scattering. Average size of the C_{60} nanoparticle in the aqueous dispersion containing 1 wt% SDS was measured by dynamic light scattering on an FDLS-1200 (Otsuka Electronics Co., Ltd., Osaka, Japan) equipped with a solid-state laser (λ = 532 nm, 100 mW). The measurements were done at 25.0 ± 0.1°C and at a fixed scattering angle of 90°. Average hydrodynamic diameter was calculated by using a cumulant method[34], while CONTIN[35] was employed to obtain a size distribution. The dispersion was 100-fold diluted with water before the measurements.

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Author contributions

S.D. and S.M. conceived and designed the research. S.D., S.M., H.S. and Y.N. performed the experiments and analysed the data. S.D. wrote the paper, and all authors reviewed the manuscript.

Additional information

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