Buckyball sandwiches

Rasim Mirzayev,* Kimmo Mustonen,*† Mohammad R. A. Monazam, Andreas Mittelberger, Timothy J. Pennycook, Clemens Mangler, Toma Susi, Jani Kotakoski, Jannik C. Meyer†

Two-dimensional (2D) materials have considerably expanded the field of materials science in the past decade. Even more recently, various 2D materials have been assembled into vertical van der Waals heterostacks, and it has been proposed to combine them with other low-dimensional structures to create new materials with hybridized properties. We demonstrate the first direct images of a suspended 0D/2D heterostructure that incorporates C_{60} molecules between two graphene layers in a buckyball sandwich structure. We find clean and ordered C_{60} islands with thicknesses down to one molecule, shielded by the graphene layers from the microscope vacuum and partially protected from radiation damage during scanning transmission electron microscopy imaging. The sandwich structure serves as a 2D nanoscale reaction chamber, allowing the analysis of the structure of the molecules and their dynamics at atomic resolution.

INTRODUCTION
Graphene (1), a single layer of carbon in a hexagonal lattice, is the thinnest imaginable membrane, with unique intrinsic properties. It has no bulk, and it interfaces with other materials through van der Waals (vdW) forces. This has made graphene appealing as one of the main components for so-called vdW heterostructures consisting of either only two-dimensional (2D) materials (2) or mixtures of 2D materials with structures of other dimensionalities (2, 3). One of the earliest examples of mixed-dimensional hybrid structures was the carbon peapod (4), in which a linear array of (quasi-)1D fullerences (5) is confined inside a (quasi-)1D carbon nanotube. Recently, collapsed double-walled carbon nanotubes have been intercalated with C_{60} to form a nanoribbon-type peapod (6, 7).

Fullerenes have many interesting properties: They have a band gap under ambient conditions (8), can become metallic when doped, and even exhibit superconductivity under certain conditions (9). Fullerences belong to the rare group of saturable absorbers and can exhibit peculiar ferromagnetic behavior at low temperatures and when polymerized (10–12). They are commonly synthesized by ablating graphite, a process in which defects are thought to cause the carbon lattice to curve into minimum-energy spheroids (13). In the carbon peapods, fullerenes can be studied in a confined and well-defined space without the need of a suspension. This has made it possible to directly image their dynamics and bonding under atomic-resolution electron microscopy (14, 15). However, fullerenes have also been reported to self-assemble into hexagonally close-packed islands on surfaces and exhibit epitaxial ordering on graphene and even on some transition metals (16, 17).

Here, we present the first example of suspended buckyball sandwiches, where C_{60} molecules are confined between two graphene monolayers. The resulting structures contain large atomically clean areas, allowing the direct study of C_{60} islands through scanning transmission electron microscopy (STEM). Similar to carbon peapods, the buckyball sandwiches are expected to have hybridized properties that could be suited for applications ranging from nanoscale lasers to spin cubit arrays and the electron beam, similar to fullerences encapsulated in carbon nanotubes (14). On the basis of high-resolution images, it is easy to distinguish between monolayer and multilayer regions, with an example shown in Fig. 1A. Figure 1B shows an atomically resolved close-up, and Fig. 1C shows its Fourier transform, from which the two graphene layers (with a misorientation angle $\theta_{Gr} \approx 11^\circ$) and the fullerene lattice can be identified. Unlike on a single layer of graphene, the sandwiches also contain fullerene monolayers, whose edges exhibit nonlinear image contrast of the moiré pattern of the suspended graphene layers (fig. S3).

RESULTS AND DISCUSSION
The buckyball sandwiches were fabricated by thermally evaporating C_{60} onto commercially available graphene-coated TEM grids, followed by the placement of a second graphene-coated grid on top and bringing the two films into contact by evaporating a droplet of solvent (see Materials and Methods; figs. S1 and S2 show the general sample morphology, Raman spectrum of the sandwich, and the structure of the multilayers). The sandwich C_{60} show remarkable stability under the electron beam, similar to fullerences encapsulated in carbon nanotubes (14). On the basis of high-resolution images, it is easy to distinguish between monolayer and multilayer regions, with an example shown in Fig. 1A. Figure 1B shows an atomically resolved close-up, and Fig. 1C shows its Fourier transform, from which the two graphene layers (with a misorientation angle $\theta_{Gr} \approx 11^\circ$) and the fullerene lattice can be identified. Unlike on a single layer of graphene, the sandwiches also contain fullerene monolayers, whose edges exhibit nonlinear image contrast of the moiré pattern of the suspended graphene layers (fig. S3).
Using the graphene lattice as a calibration standard, we measured the C₆₀ lattice spacing (the distance between the centers of the neighboring molecules) for crystalline monolayer regions. Surprisingly, this spacing (9.6 ± 0.1 Å) is 4 to 5% smaller than that of 3D crystallites (29). This distance is also smaller than in 1D carbon peapods, whose reported values vary from 9.7 to 10.0 Å (possibly influenced by the endohedral metal atoms present in some studies) (14, 30, 31).

To understand this change in spacing, we used atomistic simulations to calculate the equilibrium lattice constants of the molecules in bulk 3D and 2D C₆₀ crystals and in a 2D sandwich (see Materials and Methods). The simulated sandwich consisted of two graphene nanoribbons with an orientation mismatch of θGR ≈ 11°, with a 7 × 20 array of C₆₀ in between (Fig. 1D). For 3D C₆₀, we found an equilibrium distance of 9.65 Å, whereas for an infinite 2D sheet, this distance was 9.62 Å. Hence, the mere dimensionality of the crystallites is unable to explain the observed monolayer spacing. However, in the simulated sandwich, the average equilibrium distance was 9.22 Å (with an SD of 0.15 Å due to directional anisotropy), which represents a contraction of 4.7% compared with the bulk value. Thus, despite the difference in the absolute distances, the interaction with the graphene sheets in the simulated sandwich compresses the C₆₀ lattice, in agreement with the experiment.

Individual fullerenes are found to be highly mobile at the unconstrained edges of the C₆₀ monolayers: Some C₆₀ in the partially filled outermost row of Fig. 2A have occupied and vacated edge sites multiple times during the acquisition of subsequent lines of the scanned image, resulting in the “interlaced” appearance of the fullerenes. For example, the fullerene marked by an arrow has disappeared and reappeared at least 17 times during the acquisition of 100 scan lines (~1 s) in this region of the image. However, it typically remained stationary during the ~1 ms the probe took to traverse the molecule in each line of the scan. Evidently, it is possible to quantify even single-molecule diffusion in the sandwich structure using direct STEM imaging. Regardless of their mobility inside this area, it appears that the molecules remain confined in the graphene wrap and cannot completely escape.

To understand these dynamics, we also calculated the relevant diffusion barriers using the nudged elastic band method (Fig. 2B; see Materials and Methods and movies S1 and S2): one for a C₆₀ diffusing along the edge of the monolayer (234 meV) and another for a C₆₀ diffusing from one edge to another across the gap (371 meV). These values are in reasonable agreement with those reported for fullerene diffusion on C₆₀ crystallites (32, 33). These energies are easily available from the electron beam, but these transitions might also be thermally activated at room temperature. From the second path, we could also estimate the barrier for moving the C₆₀ inside the gap in the sandwich to be less than 5 meV. This explains why isolated fullerenes are never observed in the experimental images.

Different dynamics are observed in disordered C₆₀ regions, as shown in Fig. 2 (C and D): In this case, voids in the C₆₀ arrangement can propagate inside the lattice. For example, between the two shown frames, a void propagated from location 1 to 2, and a single molecule escaped outside the field of view from position 3. However, overall, this edge appears to be more tightly constrained by the two graphene layers, displaying no oscillations like those seen in Fig. 2A.

Next, we consider the rotation and bonding of sandwiched C₆₀ molecules during imaging with 60-keV electrons. At least three types of modifications are possible: knock-on damage of the C₆₀ [initially resulting in the formation of C₅₉ (34), with a reactive dangling bond next to the vacancy], bonding between fullerenes, or the bonding of C₆₀ to graphene; graphene knock-on damage is completely suppressed at this energy (35). Although the graphene lattice is clearly resolved in the original images of the time/electron dose sequence in Fig. 3 (A to C) (see the
bond with a neighbor without fusing together (especially the blue and yellow color). The dimers (purple) and molecules with a one-directional bond (red) still appear to be moving, obscuring their internal structure. (E to G) STEM image of a pair of C_{50} dimers in (D) and a simulation of a rotating (left) and a stationary (right) C_{60} in (E). (F) A loosely bound pair of fullerenes and a simulated C_{59}−C_{59} dimer with one bond in (G) and a tightly bound pair and a simulated C_{59}−C_{59} with three bonds in (H) and (I). A typical peanut dimer in (J) and an image simulation of C_{120} in (K). The red dashes in (D) indicate the integration width of the line profiles plotted in (D) to (K).

Supplementary Materials), no structure beyond spherical symmetry can be discerned for isolated fullerenes at the beginning of the sequence. Because the absorption energy of C_{60} on graphene is around 0.9 eV (36) and different absorption geometries are separated by <0.1 eV (16), even the graphene sandwich should not prevent C_{60} rotation under our experimental conditions. We therefore attribute the lack of internal structure of the C_{60} in our images to rotation, either thermally activated or driven by the electron irradiation. Throughout the sequence in Fig. 3 (A to C), all isolated fullerenes (unmarked objects) display only spherical symmetry, in contrast to clustered objects (marked by the yellow dashed lines) where internal structure is evident. Upon increasing the electron dose, some C_{60} clearly form bonds with their neighbors, becoming “locked” into a certain position and allowing their structure to be revealed.

Even more remarkable are the few fullerenes that appear to form a bond with a neighbor without fusing together (especially the blue and red dashed lines in Fig. 3, A and B). Consider, for example, the trimer marked with I, II, and III in Fig. 3A: Here, the fullerene I that is bound to two neighbors is presumably locked in its rotation and shows clear internal structure; however, those having been bonded only on one side (II and III) apparently still rotate (or oscillate around a ground state) because their structure is smeared out. The appearances of rotating and locked molecules are quite distinct, as revealed by the STEM image simulation shown in Fig. 3E; the molecule on the left is an average of 100 random orientations, and the one on the right is locked. On the basis of their appearance, we also conclude that the fullerene dimers or “peanuts” (37), highlighted by purple dashed lines in Fig. 3 (A to C), exhibit rotation around their longitudinal axis that smears out any internal structure (note the clear difference between the purple marked dimers and polymers with additional cross-linking marked with yellow).
Already one bond between two fullerenes should make the structure rotationally stiff because of the overlap of the $p$ orbitals on the connecting C atoms. However, the energy input from the electron beam can overcome this barrier. Movie S3 shows a density functional theory (DFT) molecular dynamics simulation (see Materials and Methods) of a dimer where one molecule is prevented from rotating by fixing atoms on its back wall, and one atom on the side of the other molecule is given a high kinetic energy, emulating an electron impact. This mimics the situation where a fullerene is bonded by a single C–C bond to an already rotationally locked neighbor. As can be seen from the video, the simulated impact results in a noticeable rotation of the second molecule even while the bond is preserved.

We further analyzed the dimer bonding by measuring the apparent center-to-center distances ($d$) of paired molecules from Fig. 3A. For comparison, Fig. 3D shows a pair of free molecules (IV and V), whose center-to-center distance $d'$ is set to 9.6 Å based on the average monolayer spacing. To extract the bound $d$ of bound molecules, we fitted Gaussian line shapes to the outer edges of the intensity profile and used the peak-to-peak separation ($D$) to calculate $d = d' + D - D'$, where $D'$ is the reference distance measured for nonbonded molecules. Figure 3F shows what is possibly a singly bonded C59–C59 dimer with $d = 9.6$ Å (molecules I and III), closely resembling the simulated equivalent in Fig. 3G. (We also simulated the spacing of a singly bonded C60–C59 and a C40–C60 dimer with two bonds, yielding slightly larger values of 9.9 and 10.0 Å, respectively; see fig. S7.) An apparently more tightly bound pair (molecules I and II) is compared in Fig. 3 (H and I): This might be a pair of C59 molecules connected by three bonds, based on the measured $d = 8.6$ Å, matching well to a simulated value of 8.7 Å. The peanut structures are compared in Fig. 3 (J and K), where we see that the experimental structure (molecule VI) is slightly smaller than the simulated one, 8.5 versus 8.9 Å. However, stable fullerene peanuts will likely have fewer than 120 atoms and thus many possible structures.

CONCLUSIONS
In conclusion, we have created and characterized a mixed-dimensional sandwich heterostructure of C60 fullerenes encapsulated by two layers of graphene. The fullerene monolayers inside the sandwich exhibit a lattice spacing of 9.6 Å, ≈5% smaller than the bulk spacing. Dynamics of entire molecules can be observed, with weakly bound fullerenes oscillating between different positions at the edges of 2D C60 molecular crystals where the graphene layers are suspended over nanometer areas, along with mobile vacancies in disordered 2D fullerene layers. Last, we observed the transition from rotating individual fullerenes through dimers with suppressed rotation to molecular clusters locked into position, allowing their internal structure to be revealed. The graphene sandwich thus provides a nanoscale reaction chamber, a clean interface to the microscope vacuum, some suppression of radiation damage, and a low-contrast background that can be subtracted from the image.

MATERIALS AND METHODS
Sandwich fabrication
C60 was thermally evaporated at a pressure of $\sim10^{-5}$ mbar onto commercial graphene-coated TEM grids from Graphenea Inc. Before deposition, the grids were annealed for 30 min at 400°C in air, and the C60 powder was annealed for 120 min at 200°C under vacuum. The evaporation took place in a vacuum chamber (Mantis HEX deposition system) with the target at 100°C at a rate of $\sim1$ Å/s, measured with a quartz-crystal monitor. A second TEM grid used for stacking was placed on top and adhered via the tensile forces resulting from evaporating a droplet of isopropyl alcohol (semiconductor-grade PURANAL, Sigma-Aldrich), followed by drying and then separating the grids with tweezers.

Scanning transmission electron microscopy
Atomic-resolution imaging was conducted using an aberration-corrected Nion UltraSTEM 100 STEM operated with a 60-kV primary beam energy, with a near-ultrahigh vacuum of $2 \times 10^{-7}$ Pa at the sample. The angular range for the medium-angle annular dark-field (MAADF) detector was 60 to 200 mrad.

Raman spectroscopy
Raman spectra (fig. S1E) were acquired using an ND-MDT NTEGRA Spectra AFM/Raman instrument with a 473-nm excitation wavelength (2.62 eV) under ambient conditions. The output laser power was 4 mW over a focused spot with a diameter of $\sim0.5$ μm.

STEM simulations
STEM simulations used QSTEM version 2.31 with a chromatic aberration coefficient of 1 mm, a spherical aberration coefficient of 1 μm, energy spread of 0.48 eV, and MAADF detector angle range set to the experimental range of 60 to 200 mrad. The illumination semiangle was 35 mrad. In Fig. 3E, to mimic the experimental contrast of the rotating fullerene, graphene was included in the simulations and, later, Fourier-filtered.

Atomistic simulations
Most simulations were carried out with the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) code (38), using an AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) potential augmented by a Morse potential for the intermolecular interaction (A–M) to describe the covalent and vdW interactions, respectively (39, 40). To study the intermolecular spacing and diffusion barriers in sandwiched C60 layers, we used a model supercell consisting of seven rows of C60 with periodic boundary conditions along the overlying and underlying graphene sheet edges. The misorientation angle between the graphene lattices was set to 11.6°, resulting in a moiré pattern periodicity of $\sim12$ Å, which matched that in the experiments. This unit cell was repeated 5 and 20 times, resulting in a supercell consisting of 33,820 carbon atoms, including the C60 molecules. The total energy was minimized by relaxing the layers without constraints until the forces were $<10^{-4}$ eV Å$^{-1}$.

For bulk C60 crystals, we additionally compared these results with DFT, calculated using two different vdW functionals (C09 and DF2) (41, 42). We relaxed the minimal single-molecule unit cells of both 3D face-centered cubic and 2D crystallites using the plane wave mode in the GPAW simulation package (43) (600-eV cutoff energy, and 5 × 5 × 1 and 5 × 5 × 5 Monkhorst-Pack $k$-point meshes for the 2D and 3D cases, respectively). The results agreed with the A–M calculation in that there is no significant difference between the 2D and 3D spacing of the fullerenes in the absence of the graphene sandwich. For 3D bulk C60, we found 0-K equilibrium distances of 9.65 Å (A–M), 9.86 Å (C09), and 10.03 Å (DF2), whereas for an infinite 2D sheet, the distances were 9.62 Å [A–M; consistent with that from the study of Reddy et al. (44)], 9.91 Å (C09), and 10.02 Å (DF2).
For the diffusion barrier simulations, we cut out part of the fullerene-containing area of the model, created a gap inside the fullerene monolayer, and fixed the outermost rows of fullerenes and the edges of the graphene layers. The barriers were calculated using the nudged elastic band method (45) with a spring constant of 10 eV/Å.

To study the bonding of the fullerenes, we placed two C_{60} in the center of a 32 × 20 × 20 Å unit cell and relaxed their atomic structure using the CO9 functional in the GPAW finite difference mode (0.19 Å grid spacing, Gamma point only) (46). To study the effect of irradiation on apparent bond length, we first removed one C atom from the second C_{60} and then relaxed the structure and then further removed another C atom from the first C_{60} and relaxed that structure, resulting in dimers with either one or three bonds. For the C_{60}·C_{59} system, we further ran molecular dynamics simulations in the linear combination of atomic orbitals DFT mode (15-eV kinetic energy; movie S3) to simulate the rotation of the C_{60} caused by electron impact on one of the carbon atoms.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/6/e1700176/DC1

Sample morphology

C_{60} Multilayers

Stem contrast of the sandwich

Fourier filtering

Unfiltered STEM images of the C_{60} sandwich

Additional filtered views of the C_{60} sandwich

Stem simulations of a C_{60}·C_{60} with two bonds and singly bonded C_{60}·C_{59}

fig. S1. Overview STEM micrographs, electron diffraction patterns, and Raman spectra.

fig. S2. Structure of C_{60} multilayers.

fig. S3. Moiré contrast at the edges of the C_{60} monolayer.

fig. S4. Fourier filtering.

fig. S5. Unfiltered version of the STEM micrographs of fig. 3 (A to C).

fig. S6. Fourier-filtered views of the rotating and fusing fullerenes.

fig. S7. STEM simulations of merged fullerenes.

movie S1. C_{60} diffusing away from a row of molecules enveloped by graphene.

movie S2. C_{60} diffusing along a row of molecules enveloped by graphene.

movie S3. Bond rotation in fullerene dimer after a 15-eV electron impact.

REFERENCES AND NOTES


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Sci Adv 3 (6), e1700176.
DOI: 10.1126/sciadv.1700176

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