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Extraterrestrial, shock-formed, cage-like nanostructured carbonaceous materials

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ABSTRACT

Shock caused by impacts can convert carbonaceous material to diamond. During this transition, new materials can form that depend on the structure of the starting carbonaceous materials and the shock conditions. Here we report the discovery of cage-like nanostructured carbonaceous materials, including carbon nano-onions and bucky-diamonds, formed through extraterrestrial impacts in the Gujba (CB_a) meteorite. The nano-onions are fullerene-type materials and range from 5 to 20 nm; the majority shows a graphitic core-shell structure, and some are characterized by fully curved, onion-like graphitic shells. The core is either filled with carbonaceous material or empty. We show the first, natural, 4-nm-sized bucky-diamond, which is a type of carbon nano-onion consisting of multilayer graphitic shells surrounding a diamond core. We propose that the nano-onions formed during shock metamorphism, either the shock or the release wave, of the pre-existing primitive carbonaceous material that included nanodiamonds, poorly-ordered graphitic material, and amorphous carbonaceous nanospheres. Bucky-diamonds could have formed either through the high-pressure transformation of nano-onions, or as an intermediate material in the high-temperature transformation of nanodiamond to nano-onion. Impact processing of planetary materials was and is a common process in our Solar System, and by extension, throughout extrasolar planetary bodies. Together with our previous discovery of interstratified graphite-diamond in Gujba, our new findings extend the range of nano-structured carbonaceous materials formed in nature. Shock-formed nano-onions and bucky-diamonds are fullerene-type structures, and as such could contribute to the astronomical 217.5 nm absorption feature.

INTRODUCTION

Shock metamorphism resulting from hypervelocity impacts is a fundamental process in our Solar System (Sharp and DeCarli 2006). It plays a major role in planetary evolution and is evidenced by shock-induced modifications in minerals and formation of high-pressure and high-temperature phases (e.g., Chen et al. 1996; El Goresy et al. 2008). The nature of these modifications strongly depends on the material and the shock conditions (Sharp and DeCarli 2006). Since shock metamorphism is a rapid event, during which pressure equilibration can be completed within nano- or microseconds after impact, novel materials may form and be quenched (Chao et al. 1962; Chen et al. 1996; Sharp et al. 1997, 1999). There has been considerable interest in shock compression of carbonaceous material, of which the formation of diamond from graphitic material has been widely described (e.g., DeCarli and Jamieson 1961; Erskine and Nellis 1991; Yamada and Tanabe 2002; LeGuillou et al. 2010). In addition to diamond, a range of sp^2- and sp^3-bonded structures have been reported including defective and stacking disordered diamond (Németh et al. 2014; Németh et al. 2015; Ohfuji et al. 2015; Murri et al. 2019), interstratified graphite-diamond (Garvie et al. 2014), amorphous- (Kis et al. 2016), and onion-like carbons (Shumilova et al. 2014).

Carbonaceous chondrite meteorites contain a wide range of nano-structured materials encompassing sp^3-bonded structures, dominated by nanodiamonds, and sp^2-bonded materials. Nanodiamonds are present in the matrix of all unmetamorphosed carbonaceous chondrites, with matrix-normalized values of ca. 700 to 1500 ppm (Huss and Lewis, 1995). Their small sizes, typically ~2 nm, and high abundances, imply large numbers, on the order of 3×10^{17} nanodiamonds, per gram of matrix. The total C content of unmetamorphosed carbonaceous chondrites varies from ~ 5 wt% in the CIs (Orgueil 4.88 wt%) to ~2 wt% for the CM2 (e.g., Murchison, 2.25 wt%) chondrites (Pearson et al. 2006). Much of this C occurs as sp^2-bonded carbonaceous material, also called macromolecular carbon (Garvie and Buseck, 2006). In HRTEM images, this material presents itself as poorly-ordered “graphitic material” that typically has a crumpled tissue-like texture, with poorly ordered, small, irregularly-shaped regions having fringes with 0.34–0.38 nm spacings and locally 0.21 nm cross-fringes. Also present are solid or hollow carbon nanospheres: HRTEM images of these nanospheres are typically devoid of fringes revealing their amorphous character (Garvie and Buseck, 2004; 2006). Well-crystallized graphitic material is also present in the CC meteorites, but is less common.

Here we report the discovery of cage-like nanostructured carbonaceous materials, including carbon nano-onions and bucky-diamonds from the Gujba (CB_a) meteorite. Carbon nano-onions are fullerene-like structures consisting of spherical carbon shells (Ugarte 1992), whereas bucky-diamonds are nanoparticles containing a nanodiamond covered by fullerene-like shells (Raty et al. 2003). Carbon nano-onions are well-known from syntheses (Ugarte 1992; Kuznetsov et al. 1994a, b; Qin and Iijima 1996; Sano et al. 2001; Xiao et al. 2014), and although onion-like structures have previously been described from the Murchison (Bernatowitz et al. 1996) and the martian meteorite Allan Hills 84001 (Steele et al. 2012) as well as from Popigai impact materials (Shumilova et al. 2014), those resembling large multilayered fullerenes (Ugarte 1992; Xiao et al. 2014) have not been reported from natural materials. Although, Smith and Buseck (1981) showed a nano-onion from Allende meteorite, the authors argued that it might have been an artifact of the sample preparation. Our report is also the first description of natural bucky-diamonds. We studied these nanocarbons with a view of shedding light on their possible formation conditions and draw attention to their characteristic absorption feature at the wavelength of 217.5 nm, which matches that of interstellar dust (Stecher 1965; Wright 1988; Chhowalla et al. 2003; Bradley et al. 2005).

Gujba meteorite

Gujba belongs to a group of metal-rich meteorites called CB chondrites, and currently comprises 21 meteorites. Gujba belongs to the CB_a subgroup and is characterized by ~60 vol% metal and cm-sized chondrules separated by a sparse, often dark-colored, matrix (Weisberg and Kimura 2010). While the origin of the CB chondrules has generated significant debate, it is generally accepted that they (and similarly CH and CH/CB chondrites) are the end result of a combination of events that was initiated by the glancing blow impact of two planetesimals (Asphaug et al. 2011), condensation of materials including the metal spheres in the dense impact-formed metal-rich gas, followed by reaccretion on the impacted parent body (Morris et al., 2015). Such a scenario was explored in detail for the Isheyevo (CH/CB_b) meteorite (Morris et al. 2015; Garvie et al. 2017). Chondrules within the CB meteorites Gujba are dated at 4562 Myr (Krot et al. 2005), which is ~5.5 Myr after the formation of the calcium-aluminum-rich inclusions (CAIs) of 4568.2 Myr (Bouvier and Wadhwa 2010) and 4567.3 Myr (Connelly et al., 2017). However, the CB parent body also underwent a later major impact at ~4200 Myr (Marty et al. 2010); evidence for this impact is a suite of high-pressure minerals (Garvie et al. 2011; Garvie et al, 2014; Weisberg and Kimura 2010; Weisberg et al. 2006).

EXPERIMENTAL METHODS

Transmission electron microscopy (TEM) samples were prepared from the carbonaceous residue obtained from fragments of the Gujba meteorite interstitial to the metal following the protocol described by Garvie et al. (2014). High-resolution TEM (HRTEM) images were acquired with a Tecnai F20 (200 *kV*; Schottky field-emission gun, side-entry, double-tilt stage; point resolution = 0.24 nm), a Topcon 002B (200 keV, LaB_6 filament, side entry, C_s = 0.4 mm, point resolution = 0.19 nm), and a JEOL JEM 4000EX (400 *kV*; LaB_6 filament, top-entry, double-tilt stage; C_s = 1 mm; point resolution = 0.17 nm) electron microscope. Fast Fourier transforms (FFTs) obtained from the HRTEM images were calculated using Gatan Digital Micrograph 3.6.1 software. Background-filtered images were calculated by applying a mask filter on graphite and diamond reflections using the same software.

RESULTS AND DISCUSSION

HRTEM images of the Gujba acid residue reveal the structural diversity of carbonaceous particles including amorphous to poorly graphitized carbon, ordered graphitic material, interstratified graphite-diamond (Garvie et al. 2014), nanodiamonds, and cage-like nanostructured carbonaceous grains. The nanodiamonds are small (2-3-nm) and typically aggregated (Fig. 1a), consistent with those found in un-shocked carbonaceous chondrites (Garvie 2006; Daulton et al. 1996). Carbonaceous objects with rounded morphology occur in the residue. In particular, compact (Fig. 1b) and hollow nanospheres (Fig. 1c) occur, and they are similar in shape, size, and structure to those reported from a range of carbonaceous chondrites (Nakamura-Messenger et al. 2006; Garvie 2005; Garvie and Buseck 2006). Their size ranges between 20- and 200-nm, and according to Garvie (2006) their HRTEM and EELS data are consistent with an essentially amorphous material, although regions with poorly ordered graphite can also be detected (Figs. 1b and 1c). They are dominated by carbon and contain minor amounts of sulfur, nitrogen and oxygen (Garvie 2006) and possibly some hydrogen (Naraoka et al. 2004).

In addition to the afore-mentioned carbonaceous materials, we discovered nano-sized cage-like nanostructured carbonaceous materials in the residue. These cage-like materials are prominent in the HRTEM images, and are visible as individual particles composed of concentric graphitic shells. Approximately 40 nano-onions were imaged and their sizes ranged from 5 and 20 nm (Fig. 2). They have similar morphologies to synthetic nano-onions (Ugarte 1992; Xiao et al. 2014). Many of the nano-onions are attached to or spatially associated with grains of interstratified graphite-diamond.

The nano-onions are characterized by concentric graphitic shells with 0.34-0.35 nm spacing around a hollow or filled core. The continuity of these spacings around the core is consistent with a nested shell-like with structure of graphitic shells. Most nano-onions showed between 5 and 10 graphitic shells, and the largest contained 30 shells (Fig. 2a). The nano-onions are either hollow (Figs. 2a, 2b, 2c, and 2d) or filled (Figs. 2e and 2f). According to literature reports (Terrones and Terrones, 1997), the cores could be crystalline or amorphous, although in our sample we only identified crystalline core materials. Some HRTEM images show cores with 0.21-nm spacings, consistent with both graphite and diamond (Figs. 2e and 2f). The d-spacing of graphite {100} is 0.212 nm and that of diamond {111} is

0.206 nm. The experimental error of the d-value measurements from HRTEM images is ~ 2-5 %, therefore, distinguishing between graphite and diamond based on one set of 0.21-nm fringes alone is not possible. However, graphite and diamond can be identified by the 60° and 71° 0.21-nm cross-fringes, respectively.

One nano-onion was found fortuitously oriented so that its central part showed fringes consistent with graphite projected along <001> (Fig. 3). Since an HRTEM image is a 2D projection of a 3D object, this graphite could be in the core of a nano-onion or part of its shell occurring on the top or the bottom of the onion. If it occurred inside the onion, it would be a new type, the first graphite-filled nano-onion.

A single caged nano-onion was discovered that shows a distinct diamond core (Fig. 4) containing {111} diamond reflections in <110> projection. Visible are the 0.206-nm spacings of the {111} planes with 71° cross fringes. This caged-nanostructure is a special type of nano-onion referred as bucky-diamond (Barnard et al. 2003; Raty et al. 2003).

The carbonaceous materials in Gujba reflect the diversity of structures acquired and formed under a range of environments including, unmodified materials primarily from the impactor, formation and modification in the impact plume during cooling and condensation, reaccretion on the planetesimal, and finally modification by post-accretion shock events. The similarities in mineral and O isotopic compositions of the CB (Δ^{17}O ~− 2‰) and CR (Δ^{17}O=−4‰ to 0‰) chondrites suggest a common nebular reservoir (Krot et al. 2006). Hence the precursor carbonaceous materials were likely similar to those found in primitive, unmetamorphosed carbonaceous chondrites, such as CM2 and CR2 chondrites. We propose that both nanodiamonds (Fig. 1a) and the poorly-ordered, amorphous nanospheres (Figs. 1b and 1c) of the Gujba meteorite are the precursor materials for the cage-like nanostructured carbonaceous materials (Figs. 2, 3, and 4).

The close association of many of the nano-onions with grains of interstratified graphite-diamond is consistent with contemporaneous formation of both during the same shock event. The materials could have formed during the initial shock wave or during the release wave following the initial shock compression, when the local structures were placed under tension. The Gujba peak shock conditions are estimated to be 2273 K and 19 GPa based on a suite of minerals formed at high pressure and temperature including majorite garnet, wadsleyite, coesite, and stishovite (Weisberg and Kimura 2004; Weisberg et al. 2006, Garvie et al. 2014). However, the complex and heterogeneous structure of the Gujba meteorite would have produced significant mm-scale pressure and temperature variations. Structurally, the Gujba meteorite is characterized by millimeter-sized metal spheres separated by silicate clasts and dark interstitial matrix (Rubin et al. 2003). The metal has higher shock impedance than the surrounding silicate-rich material, which would have produced significant differences in the shock conditions of the metal globules and surrounding material. Different shock velocities between metal and silicates could result in irregular shock front propagating through Gujba. In addition, the shock fronts can be refracted at the metal/silicate boundary producing localized, millimeter- to micrometer-scale, pressure spikes of nanoseconds duration in the low-impedance material. The peak pressures and temperature associated can vary by over an order of magnitude over short spatial distances, with pressure equilibration within a microsecond and temperature equilibration within seconds (Sharp and DeCarli, 2006). These small spatial-scale shock heterogeneities explain the observed association of unshocked carbonaceous materials, such as poorly ordered graphite, amorphous nanospheres and nanodiamonds, together with the shock-formed cage-like nanostructured carbonaceous materials.

Carbon nano-onions were first produced by intense electron irradiation of carbon soot in a TEM (Ugarte 1992). They were later found in detonation soot (Kuznetsov et al. 1994b) and were synthesized via a variety of methods including arc discharge of graphite in liquids (Sano et al. 2001) and combustion of naphthalene (Choucair and Stride 2012). Nano-onions can be prepared from nanodiamonds through heat treatment (Kuznetsov et al. 1994a), electron irradiation (Qin, L-C. and Iijima 1996), and at high pressures (Blank et al. 2007, 2018). Nano-onions can also be formed directly from graphite in a diamond anvil (>20 GPa) under shear deformation at room temperature (Blank et al., 2007), with nano-onion size increasing with increase of pressure and shear values. At higher pressures, >55GPa, diamond also transforms to onion-like structure (Blank et al. 2018). According to Blank et al. (2009), the formation of onions appears to be a "dead-end branch of high-pressure graphite transformations". However, Xiao et al. (2014) showed that during energetic irradiation, it is possible to convert nanodiamonds to nano-onions, which upon further irradiation can convert back to nano-onions. The reversible transition occurs via the bucky-diamond intermediary phase.

The structural and textural complexity of the starting carbonaceous material in the Gujba meteorite, together with the wide range of P and T conditions present during the shock, suggests several mechanisms and starting materials in their formation. Firstly, the nano-onions and bucky-diamonds may have formed through the shock processing of the pre-existing nanodiamonds. The small sizes of some of the cage-like onions are consistent with their formation from a nanodiamonds precursor (e.g., Figs. 2d, 2e, 2f, 3, and 4). It is possible that some of the larger, i.e., 10 to 20 nm nano-onions (Figs. 2a, 2b, and 2c) formed directly from the high-pressure transformation of the compact nanospheres. Alternatively, the close association of some nano-onions with the interstratified diamond-graphite particles suggests a common precursor material for both. The interstratified diamond-graphite represents the incomplete formation of diamond from graphitic material and forms short stubby grains to a few tens of nanometer in length (Garvie et al. 2014). These stubby grains likely formed from the shock-transformation of the poorly ordered graphitic material that is common in carbonaceous chondrites of low petrologic grade. This poorly ordered carbon forms ribbons with short flat regions and curved morphologies. We suggest that the interstratified diamond-graphite formed within the flat areas of the ribbons and the nano-onions along the curved areas.

IMPLICATIONS

Nano-onions, bucky-diamonds and the interstellar 217.5 nm absorption feature

A prominent feature of the interstellar dust ultraviolet absorption spectrum is a broad bump at 217.5 nm (Stecher 1965, Wright 1988; Bradley et al. 2005). Understanding the origin of this feature is still a major issue in astronomy. The feature is peculiar as the central wavelength is spatially invariant, but its bandwidth varies from one line to another, suggesting multiple carriers or a single carrier with variable properties. Bradley et al. (2005) associated the astronomical feature with organic carbon and amorphous silicates found in interplanetary dust particles, based on the spectral similarities of these materials. According to literature reports, the feature could match that of carbon nano-onions (Wright 1988; Chhowalla et al. 2003) and presumably bucky-diamonds since they also contain fullerene-type structure. However, extraterrestrial onion-like objects have so far only been reported from the martian meteorite Allan Hills 84001 (Steele et al. 2012). This report shows the finding of nano-onions and bucky-diamonds from Gujba meteorite and proposes that fullerene-type materials could form from the primitive carbonaceous material during impact, a fundamental geological process in the universe. Thus, we suggest that carbonaceous onion-type objects could be common in the Solar System and a component of the 217.5 nm astronomical feature.

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Figures

Fig. 1

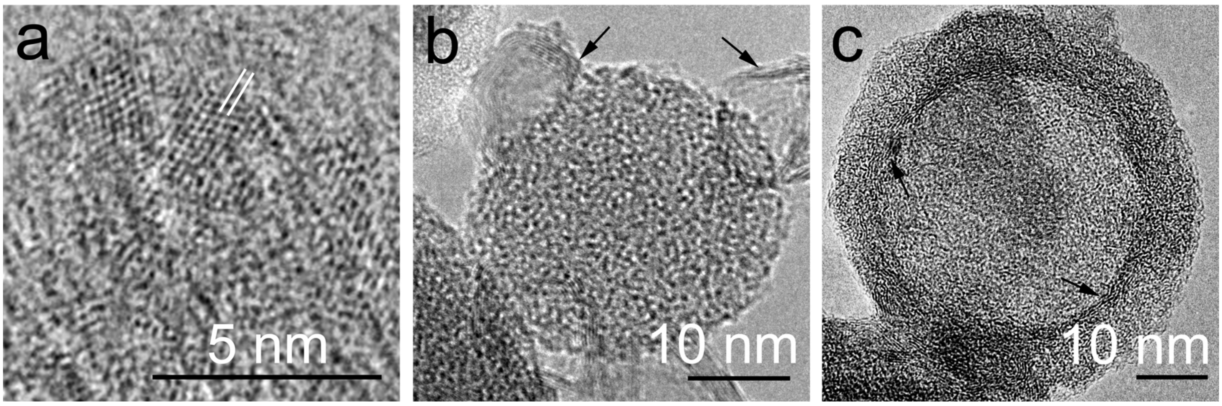

Figure 1. Un-shocked carbonaceous materials from the Gujba meteorite. **a**) A cluster of 2-3-nm-sized nanodiamonds. White lines mark diamond {111} spacings (0.206-nm). **b**) Compact amorphous carbonaceous nanosphere. **c**) Hollow carbonaceous nanosphere. Black arrows point to 0.34-nm spacings indicative for graphitic material.

Fig. 2

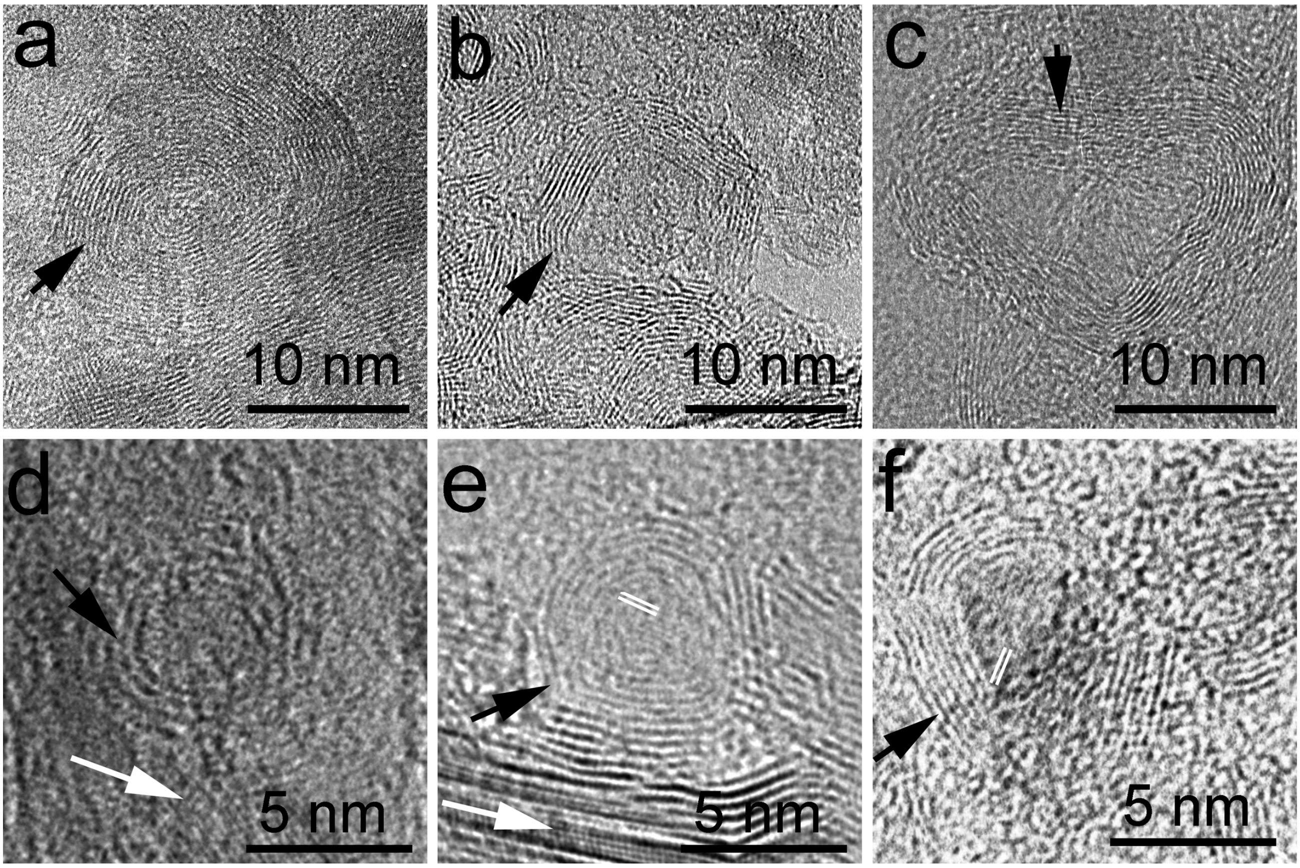

Figure 2. Representative HRTEM images of cage-like nanostructured carbonaceous materials. Black arrows point to 0.34-nm spacings of graphite. **a**) A hollow 20-nm-sized nano-onion. **b**) A hollow 14-nm-sized nano-onion. **c**) A deformed 20-nm-sized hollow nano-onion. **d**) A 7-nm-sized hollow nano-onion. White arrow points to nanodiamond outside the nano-onion. Visible are the 0.21-nm spacings of diamond {111}. **e)** An 8-nm-sized nano-onion with a core showing 0.21-nm spacings (white lines). The onion is attached to an incompletely transformed graphite-diamond particle (white arrow). **f)** An 8-nm-sized nano-onion with a core having 0.21-nm spacings (white lines).

Fig. 3

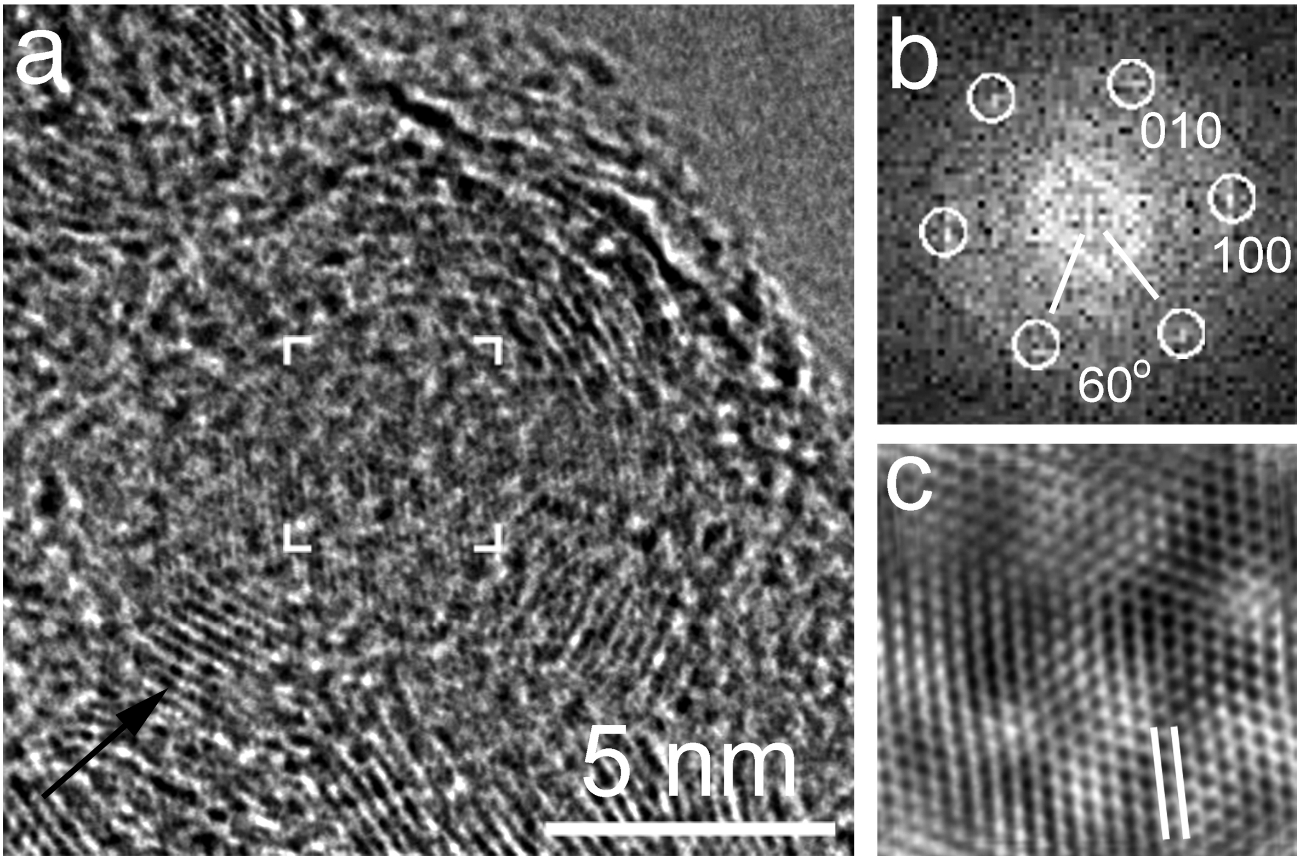

Figure 3. HRTEM lattice-fringe image of a nano-onion containing graphite. **a**) A 10-nm-sized nano-onion with graphite in its central part. Black arrows point to 0.34-nm spacings of graphite.

b) The FFT, calculated from the area marked by white corners of **a)**, shows hexagonally arranged reflections with 0.21-nm spacings consistent with graphite projected along <001>. **c**) Background filtered image, calculated from **a)** by selecting the reflections of **b)** enhances the visibility of graphite cross-fringes. White arrows mark {100} planes of graphite with 0.212-nm spacings.

Fig. 4

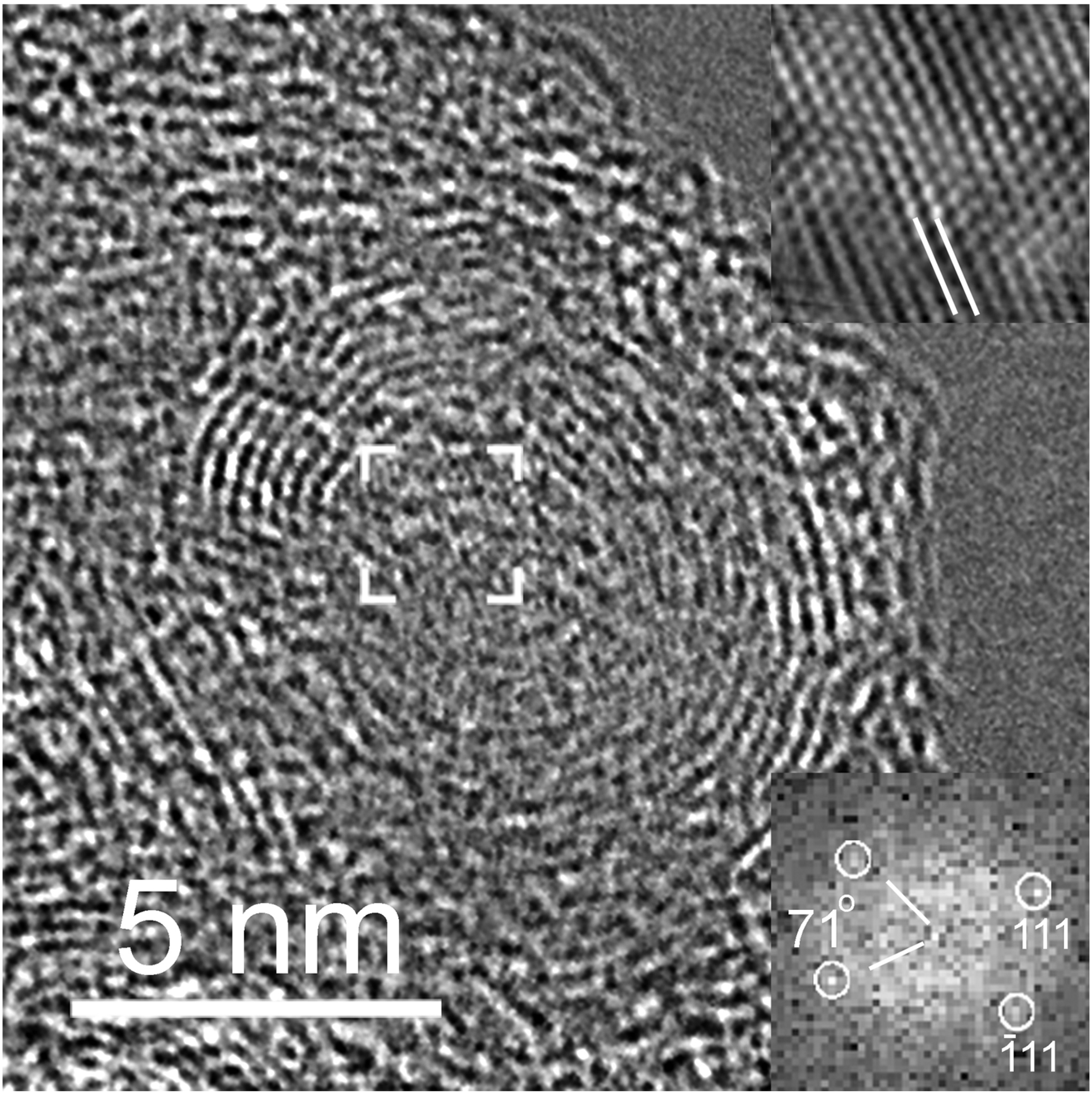

Figure 4. HRTEM lattice-fringe image of a 10-nm-sized bucky-diamond. The FFT (lower right corner) shows {111} diamond reflections in <110> projections. White arrows mark {111} planes of diamond with 0.206-nm spacings on the background filtered image (upper right corner).