Nanoparticles Produced by Laser Ablation of HfS_3 in Liquid Medium: Inorganic Fullerene-Like Structures of Hf_2S

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Inorganic fullerene-like structures (IF) of the layered hafnium sulfide, Hf_2S, have been synthesized by the laser ablation of HfS_3 in *tert*-butyl disulfide medium. Apart from the Hf_2S IFs exhibiting quasi-spherical as well as faceted nested-shell geometries, quasi-spherical nanoparticles of HfS were observed by this means. Whereas Hf_2S has anti-NbS_2 structure with S layers sandwiched between two Hf layers, HfS has the nonlayered WC-type structure. The nanoparticles of HfS show excess sulfur in the core, and they do not possess closed-shell geometry. The mechanism of formation of these nanoparticles has also been discussed.

Introduction

There has been a surge of interest in recent years in the understanding and applications of the unique optical, electronic, mechanical, and catalytic properties of nanoscale materials. Advancement in this regard rests largely on the preparation of well-defined nanoscale materials in terms of both size and shape. Consequently, an important part of research in this field is devoted to the development of simple and versatile methods to prepare size- and shape-selected nanosized materials. Several wet chemical methods have been reported to prepare nanoparticles in solution, and alternatively, lasers have also been employed for the purpose.

Graphite nanoparticles were shown to undergo spontaneous transformation to multi-shell fullerenes and carbon onions upon prolonged electron beam irradiation.[1] Hexagonal boron nitride with layered structures analogous to graphite was among the first non-carbon systems to be predicted and found to exhibit fullerenic and nanotubular structures.[2] The smallest stable fullerene-like boron-nitride particle was calculated to be $B_{12}N_{12}$,[3] and experimental verification was later obtained through the synthesis of BN octahedra.[4] Nanoparticles of other layered inorganic compounds (with layered structure analogous to graphite) such as the chalcogenides, (MoS_2, WS_2, NbS_2), halides, ($NiCl_2$, $CdCl_2$),[5] and oxides (Tl_2O)[6] have been shown to form closed-cage nested structures generically called *inorganic fullerene-like materials* designated as IF nanostructures. The abundance of dangling bonds at the periphery of the quasi two-dimensional planar structure makes the nanoparticles of the planar form of these materials unstable with respect to bending and folding, thus forming hollow cage structures. Among the inorganic fullerene-like materials, nano-octahedra of MoS_2,[7] and inorganic fullerene-like materials of $NiCl_2$,[8] MoS_2, and WS_2,[9] were produced by the laser ablation technique.

Laser ablation is a powerful technique for producing nanoparticles such as C_{60}.[10] In comparison to high-temperature gas-phase or solid−gas-phase reactions, the laser ablation was found to be suitable for the growth of nanocrystals of a specific shape and size (number of atoms). Closed-cage nanoclusters of metal−carbohedrene (MET-CARS) clusters such as $C_{12}M_8$ (M = Ti, V, Cr) were among the first species to be produced by this technique.[11] In the basic setup, a pulsed laser beam is directed toward a target material which undergoes local ablation forming a hot plume that recoils into the hot gas, followed by cooling and condensation of the nanocrystals. Recently, laser ablation was also

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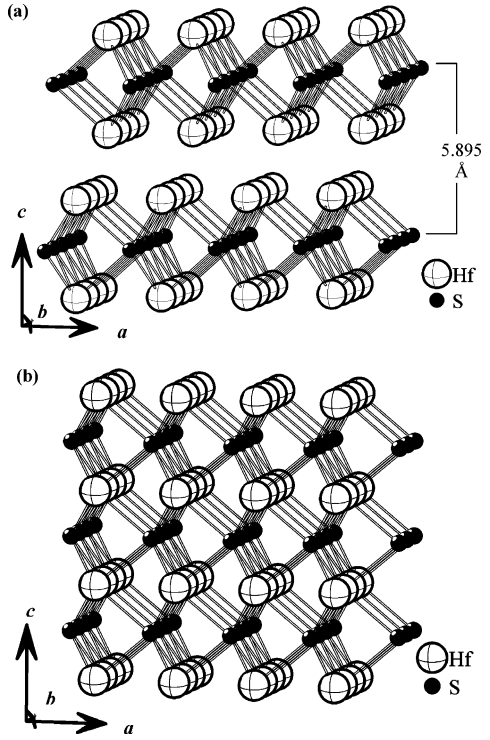

Figure 1. Schematic depction of Hf_2S (a) and HfS (b) structures.

done in solution or solid−solution interfaces. Gold and silver nanoparticles have been prepared by direct laser ablation of metal plates in solution containing suitable surfactant.[12] Diamond particles, diamond-like films, and diamond films were prepared by pulsed laser ablation at solid−liquid interface.[13] Recently, nanocrystals of *c*-BN and *c*-carbon nitride were prepared by pulsed laser induced solid−liquid interfacial reaction.[14] Colloidal solutions of gold, nickel, and carbon nanoparticles were obtained by laser ablation of the respective films in mixed water and aprotic solutions.[15] However, to the best of the authors' knowledge, there are no reports on laser-ablation-assisted synthesis of inorganic fullerene-like materials from solutions.

Apart from the di- and trisulfides of the group 4 metals, some lower sulfides such as M_2S (M = Ti, Zr, and Hf) and HfS are also known to be stable at high temperatures.[16,17] Among the sulfides of Hf, the disulfide HfS_2 and a lower sulfide, Hf_2S, possess layered structures (Figure 1a). Hf_2S possesses an anti-NbS_2 structure ($P6_3/mmc$) with the sulfur atoms sandwiched between two layers of Hf arranged in a trigonal prismatic structure. The lattice constants for this compound are $a = 3.3736$ Å and $c = 11.7882$ Å. The HfS, on the other hand, possesses a WC (hexagonal) structure (Figure 1b) with the lattice constants $a = 3.3748$ Å and $c = 3.4351$ Å. These sulfur-deficient phases of Hf-sulfide are formed at high temperatures.[16] In the present work, laser ablation of HfS_3 in solution was employed in an attempt to prepare IF nanostructures based on hafnium sulfide. Instead of the expected HfS_2 nanoparticles, quasi-spherical nanoparticles with sulfur-deficient compositions were obtained. In addition to amorphous *a*-HfS_x nanoparticles, fullerene-like structures of Hf_2S as well as spherical, poly-crystalline HfS nanoparticles have been obtained.

Experimental Section

In the laser ablation reactions, a pulsed, frequency-doubled, Nd:YAG laser ($\lambda = 532$ nm, 10 Hz, 10 ns, ~30−50 mJ/pulse) was used. Approximately 2 mg of HfS_3 powder was sonicated in 3 mL of an organic solvent, *tert*-butyl disulfide [$((CH_3)_3C)_2S_2$, TBS], taken in a 5-mL-capacity quartz beaker which was placed in the laser-beam path. The ablation was typically done for a duration of 20−30 min. During the course of ablation, the reaction mixture was continuously stirred by a magnetic stirrer. The laser spot was moved on the beaker surface, such that it always remained within the solvent meniscus. A drop from the reaction mixture after laser ablation was placed on a holey carbon-coated Cu grid, and analyzed by transmission electron microscopy (TEM). The following microscopes were used: TEM-Philips CM120 (120 kV) with EDS system (EDAX Phoenix) and a field-emission gun high-resolution TEM (HRTEM) model FEI Tecnai F-30 (300 kV). Gatan imaging filter (GIF) for electron energy loss spectroscopy (EELS) was used for elemental mapping. Energy filtering by the GIF provided zero loss (provides a clear image of the nanoparticles after filtering of the inelastically scattered electrons) carbon (K-line) and sulfur ($L_{2,3}$-line) mapping of the samples. Fast Fourier transform (FFT) of the high-resolution images was obtained by Digital Micrograph software (Gatan).

Results and Discussion

After the laser ablation of HfS_3 in *tert*-butyl disulfide, the color of the resulting solution became yellow or orange, depending on the amount of HfS_3 (1−4 mg). Some insoluble material was seen to settle at the bottom of the reaction vessel. The SEM image in Figure 2 shows the morphology of the product obtained, which consists of spherical nanoparticles. A drop of the supernatant yellow solution contains a very good yield of the spherical nanoparticles as seen in the low-magnification TEM images shown as zero loss image in Figure 3. In general, the size of these nanoparticles is in the 20−80 nm range. Some of these nanoparticles are hollow, and they tend to self-assemble and form beadlike aggregates (or nanoparticle chains). The oriented attachment and aggregation of the nanoparticles have been observed earlier and are attributed to the reduction of surface energy and the van der Waals attractive force between the particles.[18] Sulfur mapping of the sample, shown also in Figure 3, demonstrates that the nanoparticles have an even distribution of sulfur. However, some differences in the sulfur contrast among the different particles suggest that they are not necessarily of the same stoichiometry. Carbon mapping shows that the nanoparticles are claded in a carbon-rich coating. This layer could originate from the capping of the nanoparticles

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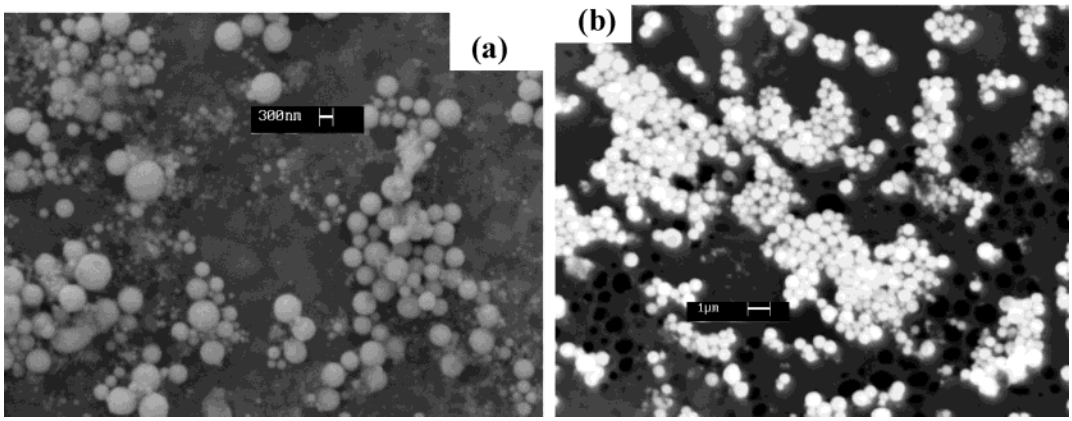

Figure 2. SEM image of spherical hafnium sulfide nanoparticles obtained by laser ablation of HfS_3 suspended in *tert*-butyl disulfide solution.

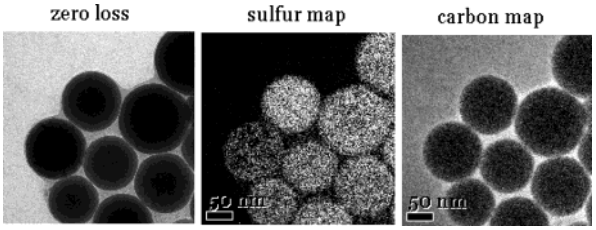

Figure 3. TEM (zero-loss) image, sulfur map, and carbon map of self-aggregated hafnium sulfide nanoparticles obtained by laser ablation of solution.

by the TBS solvent molecules, or form an amorphous carbon−sulfur film produced by decomposition of the TBS molecules during the ablation.

High-resolution microscopic (HRTEM) images show that the nanoparticles obtained by laser ablation of HfS_3 can be conveniently divided into three distinct groups: amorphous *a*-HfS_x, and crystalline HfS and Hf_2S nanoparticles. The image in Figure 3 shows randomly distributed HfS and *a*-HfS_x nanoparticles, which cannot be easily distinguished by the sulfur map. However, in contrast to the *a*-HfS_x, the HfS nanoparticles produce a clear electron diffraction pattern.

The Hf_2S nanoparticles exhibit a closed-shell, nested geometry analogous to multi-shell fullerene-like structures and generically referred to as IF. A TEM image of such nanoparticles presented in Figure 4 clearly exhibits the IF geometry. The layered structure of the walls forming these IF nanoparticles is quite clear from the images; the number of layers in the walls is usually greater than 10. A high-resolution image of such a nanoparticle is shown in Figure 5, together with the line profile. The interlayer separation estimated from the line profile of the lattice fringes in the HRTEM image is 5.85 Å. The literature value for the interlayer separation in both HfS_2 and Hf_2S is 5.8 Å. Note also that within the core of the IF nanoparticles a few Hf_2S nanocrystallites are present in the form of platelets. It is difficult to judge from the image whether the nanoparticles are indeed encapsulated in the core of the IF nanoparticles or they are present above (below) the IF nanoparticles. Fast Fourier transform (FFT) of individual nanoparticles (see inset of Figure 5) further confirms the crystallinity and the structure of these nanoparticles.

To determine the composition of the nanoparticles, and in particular the Hf/S ratio, EDS analysis was undertaken. The analysis confirmed the presence of both S and Hf in the IF nanoparticles. The Hf/S ratio obtained from the analysis is ∼2−2.5:1, suggesting that the inorganic fullerene-like nanoparticles belong to the Hf_2S phase.

Some of the fullerene-like structures are perfectly spherical or quasi-spherical. Indeed, a tilt of ±10° does not cause much change in the shape of the particle as revealed by the TEM images. Apart from the quasi-spherical and perfectly spherical fullerene-like structures, some faceted IFs were also observed. Some of the structures are faceted at several corners giving polygonal cages (Figure 6a). A rectangle-like polyhedral fullerenic particle shown in Figure 6b exhibits an almost 90° bending of the layers at the corners. Such types of faceted edges are indicative of the presence of rhombohedral point defects in the sandwich layers. It was suggested earlier that the symmetric occurrence of rhombohedral point defects leads to formation of nanooctahedra of MoS_2.[7] It was also predicted that the arrangement of four triangular point defects at the corners produces fullerene-like structures with triangular projections.[5,7a]

On the basis of continuum theoretical considerations, a first-order phase-transition from evenly curved (quasi-spherical) fullerene-like structures to polygonal particles was predicted for MoS_2 and WS_2 nested fullerene-like structures with a shell thickness larger than about $^1/_{10}$ of the IF Nanoparticle radius.[19] It was also shown that increasing the number of layers in the IF wall (or decreasing the diameter) leads to formation of highly faceted polyhedra. In accordance with these observations, fullerene-like structures of Hf_2S with thicker walls were found to form faceted polyhedra (see Figure 6a and b), whereas those with thinner walls are more spherical (see Figure 4). The number of layers in the faceted polyhedra in Figure 6a is 35, whereas in the spherical nanoparticles (Figures 4 and 5a) it is 10−14. The presence of faceted edges is believed to be a mechanism for strain relief in the closed cage structures. Note, however, that the earlier prediction[18] was made on purely energetic (thermodynamic) grounds, which are not necessarily attained in the laser ablation process, where high cooling rates produce nonrelaxed structures

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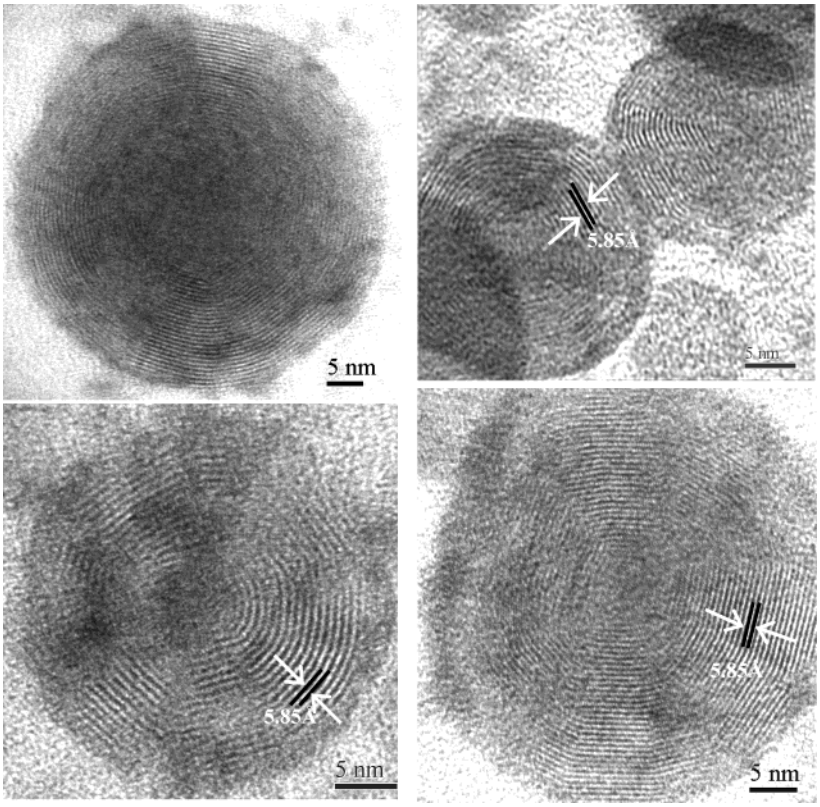

Figure 4. TEM images of an assortment of Hf_2S nanoparticles.

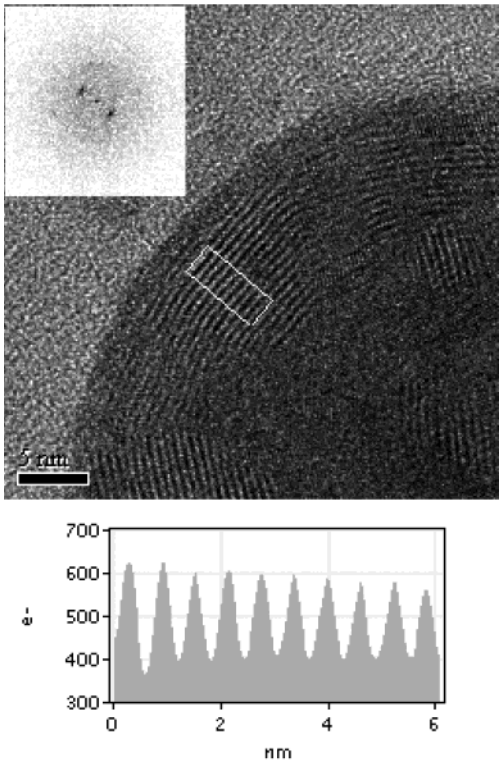

Figure 5. Magnified HRTEM image of a portion of fullerene-like Hf_2S, with the line profile of the marked region shown at the bottom. The inset shows the FFT of the image.

with numerous point or line defects. These point defects can be easily recognized in the IF nanostructures.

Some of the spherical nanoparticles examined, while containing only Hf and S, exhibited a stoichiometry and structure totally different from that of the Hf_2S IFs (Figure 7). While being also quasi-spherical in shape,

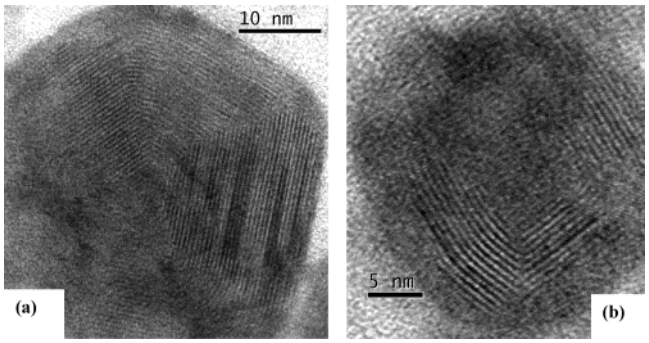

Figure 6. TEM micrographs of two IF−Hf_2S nanoparticles with highly faceted structure.

the distance between neighboring fringes was found to be 3.4 Å, i.e., appreciably smaller than the layer to layer separation in Hf_2S (5.8 Å). This lattice spacing agrees with the structure of HfS having a WC packing mode. The FFT pattern shown in the inset is consistent with the suggested structure. Recently, Wang and Li[20] observed closed and hollow spherical nanostructures of the LaF_3 series, which resemble the morphology of the HfS nanoparticles. These compounds crystallize in a hexagonal lattice and can be considered as intermediate between genuine 2-D layered compounds and isotropic 3-D compounds. Because HfS does not have slip planes typical of a layered compound, the strain energy involved in the folding of the nanoparticles is appreciably higher. It is, therefore, difficult to visualize the formation of a perfectly crystalline closed structure of this compound. Unfortunately, the size of the nanoparticles is too large to afford a high-quality TEM analysis. Therefore, clear-cut demarcation between pure IF struc-

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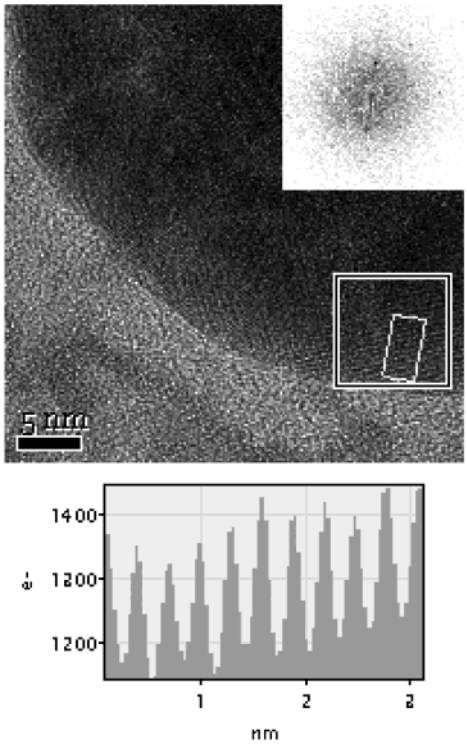

Figure 7. HRTEM of a portion of a quasi-spherical HfS nanoparticle, with the line profile of the marked area shown at the bottom. The inset shows the FFT of the marked square.

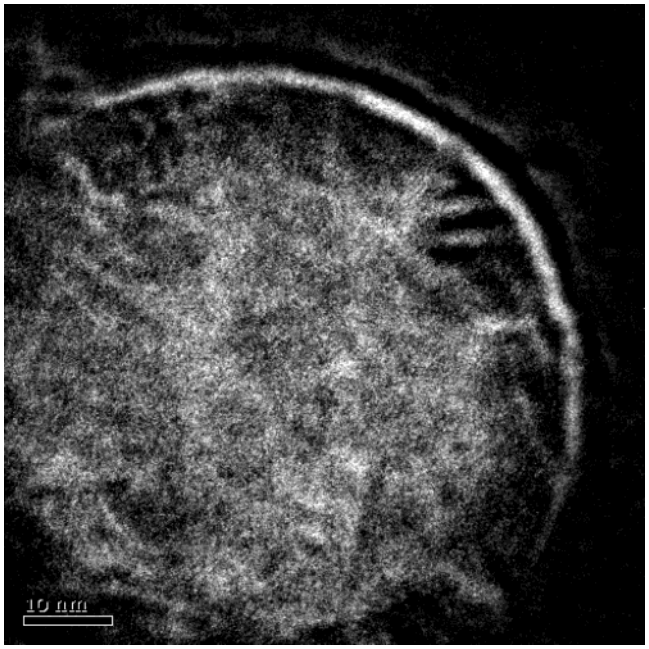

Figure 8. Sulfur map of a HfS nanoparticle.

tures of Hf_2S and the hollow quasi-spherical images of the HfS is not possible. First principle theoretical calculations would shed more light on the accurate structures of these hollow and closed nanoparticles.

Sulfur mapping of HfS nanoparticles by the GIF (Figure 8) revealed a core−shell-type structure. Excess sulfur is obsereved in the core. The shell layer is characterized by a domain structure, whereby sulfur deficient regions are separated by sulfur-rich "walls". A narrow layer of sulfur is observed also on the nanoparticles' surface, which can be linked to the amorphous carbon shell (see Figure 3). A totally different sulfur map was found in the case of Hf_2S IF nanoparticles. The sulfur distribution was quite homogeneous throughout the nanoparticles, but the lattice fringes are nevertheless delineated. This information indicates that the two kinds of particles are grown along two different growth mechanisms.

The sharp border between the sulfur-poor shell and the sulfur-rich core in the HfS nanoparticles suggests that a redistribution of sulfur occurred during crystallization of the nanoparticle's shell. The presence of a thin layer of C (Figure 3) and S on the periphery of the nanoparticles could be due to the presence of undecomposed TBS on the surface. Accordingly, the nanoparticles of HfS are probably capped by TBS.

The sonicated HfS_3 is dispersed into rather small droplets in the *tert*-butyl disulfide solvent. Once heated by the laser beam, the droplet may vaporize into monomolecular sulfur-deficient hafnium sulfide clusters, HfS_{3-x}, or into molten nanodroplets encapsulated by the solvent, the vapors of which are present in the gas phase. These spherical nanodroplets crystallize upon the fast cooling, preserving their spherical shape. The surface of these nanodroplets loses sulfur and crystallizes into the sulfur-deficient phases. In the case of the HfS nanoparticles, the excess sulfur is secreted to the core, whereas in the case of the Hf_2S IF the excess sulfur is likely to evaporate out from the nanoparticle's surface. A more common mechanism for laser ablation processes is the vaporization of the solid into molecular clusters, which condense to larger clusters, and eventually into nanocrystallites, during the rapid cooling. It is not unlikely that the IF nanoparticles are obtained from the condensation of ablated molecular Hf_2S clusters. The temperature profile of the laser-heated spot on the liquid surface is not uniform and can be the detrimental factor for the growth of either species. More work is needed to elucidate the growth mechanism for both phases.

The solvent has an important role in determining the Hf/S ratio in the ablated products. It was observed that the use of water or ethanol as solvent yielded spherical nanoparticles which were rich in Hf, but contained little sulfur (<5%). A judicious choice of a sulfur-containing solvent as the medium is justified by the increased amount of S in the ablated product. After ablation of HfS_3 in TBS, the solution turns yellow. On the other hand, laser irradiation of TBS itself (in absence of HfS_3) does not show any color, thus indicating that the yellow color imparted to the solution is due to the nanoparticles and inorganic fullerene-like materials present in the medium or to the released sulfur. The yellow color of the solution is stable without causing precipitation even upon long storage, and this yellow solution also shows fullerenes and nanoparticles in TEM. Thus, the organic solvent may act as a capping agent stabilizing the nanoparticles in the solution. It is, therefore, important that the liquid is regarded as not only a confinement for laser ablation growth, but also as a possible capping agent for stabilizing the resultant nanosized materials.

Conclusion

Inorganic fullerene-like structures (IF) of layered hafnium sulfide, Hf_2S, have been successfully synthesized employing laser ablation of HfS_3 in a liquid medium. The solvent used for the purpose was *tert*-butyl

disulfide. The TEM images of the Hf_2S nanoparticles shows a layer separation of 5.8 Å in the walls corresponding to the (001) planes. The IF of Hf_2S exhibited both quasi-spherical and faceted morphologies. Whereas the spherical fullerenes have a thinner wall, the faceted particles are characterized by thicker walls with more layers in the walls. The IF-nanostructures also show some point defects, produced as a result of the high cooling rates of the laser ablation process. Apart from the spherical and faceted Hf_2S IF, spherical nanoparticles of HfS are also obtained by this method. Whereas Hf_2S has an anti-NbS_2 type structure, HfS crystallizes in a WC-type structure having no van der Waals gaps. Some theoretical calculations are expected to shed more light on these hollow and closed nanoparticles of hafnium sulfide.

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