Solar ablation creates the sharp radiative and temperature gradients, as well as the high-temperature annealing environment, that favor nanomaterial syntheses. Using highly concentrated sunlight, we generated fullerene-like MoS$_2$, ranging from single-walled nanotubes and closed-cage structures to their larger multi-walled counterparts. TEM, HRTEM and EDS unambiguously established the nanostructures, some achieving fundamentally minimum sizes predicted by molecular structural theory. Irradiation of MoS$_2$ and powdered mixtures of MoS$_2$ + SiO$_2$ in evacuated quartz ampoules also generated nanofibers and nanospheres of amorphous SiO$_2$: the first production of SiO$_2$ nanostructures purely from quartz. Also, solar ablation of MoS$_2$ + SiO mixtures produced nanowires and nanospheres of crystalline Si.

1. Introduction

Nanotubes and closed-cage inorganic fullerene-like structures (IFs, for short) have been realized for a wide variety of chemical compounds,\textsuperscript{1–3} many of which exhibit superior mechanical, electrical, optical, tribological and ablation characteristics.\textsuperscript{1–3} Compounds with a crystal structure of stacked planes with strong intraplanar chemical bonds and weak interplanar van der Waals forces are candidates for IF structures which stem from the competition between elastic strain and bonding defect forces vs. the closure favored by saturating dangling bonds.\textsuperscript{1–5} Necessarily, a 22-day catalyzed transport reaction in the presence of iodine with C$_{60}$ as an essential growth promoter.\textsuperscript{14,15} With observed nanotube diameters below 1 nm— and first-principles predictions\textsuperscript{8,16} of a corresponding lower bound of ~6–7 nm—there is also the question of precise nanotube chemical identity. \textit{Ab-initio} calculations clearly show that multi-walled MoS$_2$ nanotubes with 5–8 layers and a diameter larger than ca. 6 nm are more stable than the single-walled analogues.\textsuperscript{4}

1.2 SiO$_2$ and Si

SiO$_2$ nanofibers, Si nanowires and nanospheres of both have been produced by protracted high-temperature chemical methods. They offer a window to low-dimensional physics: for Si as quantum confinement wires and one-dimensional light-emitting devices, and for SiO$_2$ as nanoscale optical waveguides. Si nanospheres possess exceptional hardness (superior to diamond), and SiO$_2$ nanospheres serve as large surface area catalysts.\textsuperscript{17–21} SiO$_2$ and SI nanostructures derive from one-dimensional nucleation growth mechanisms and energetic tradeoffs different than those for IF-MoS$_2$.

1.3 Solar ablation

The generation of a wide variety of MoS$_2$ IFs, including those of fundamentally minimum size, plus the production of an assortment of SiO$_2$ and Si nanostructures, are reported here. Initially we aimed to generate closed-cage (IF) and nanotube MoS$_2$ structures in an uncomplicated photothermal procedure using concentrated sunlight, akin to the earlier success in synthesizing IF-CS$_2$.\textsuperscript{22} Although working with intense sunlight militated against straightforward reactor monitoring, reports\textsuperscript{12,13} from earlier oven-assisted pulsed-laser ablation generation of IF-MoS$_2$ can guide surmising reactor conditions. Also, based on thermal modeling and earlier experiments, the maximum temperature in black solid media such as MoS$_2$ at the solar power densities in our experiments\textsuperscript{23,24} can reach ~2000 K—exceeding the 1458 K melting/decomposition point of MoS$_2$ and adequate for melting SiO$_2$. 

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2. Experimental

2.1 The solar reactor

Precursor materials were irradiated continuously in sealed quartz ampoules. Solar radiation was concentrated outdoors and channeled to an indoor laboratory via optical fibers (Fig. 1(a)). Each concentrator is 20 cm in diameter, with different numerical aperture (NA), and couples concentrated sunlight into a high-transmissivity quartz-core optical fiber (of the same NA as its concentrator) the distal tip of which is placed flush with the quartz ampoule exterior (Fig. 1(b) and (c)). (NA is the sine of the acceptance half-angle of an optical system.)

The delivered solar power, measured pyrometrically, was 6 W from the 1.0 mm diameter fiber of NA 0.66 and 8 W from the 2.0 mm diameter fiber of NA 0.40. Continuous exposures of 300–900 s were performed, some with an individual fiber and others with both fibers. Large fiber NA and non-negligible ampoule thickness meant the target solar flux was about half that at the distal fiber tips (the latter being 7.64 and 2.55 \( \text{W mm}^{-2} \), respectively). The system is the same one reported earlier for solar-driven Cs\(_2\)O IF synthesis.\(^2\)

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and energy dispersive X-ray spectroscopy (EDS) of the irradiated samples were performed using a CM120 (120 kV Philips) microscope with an attached EDS detector (EDAX-Phoenix Microanalyzer) for determining chemical composition.

2.2 Materials and characterization

The commercially available 2H-MoS\(_2\) powder used in all experiments (Sigma-Aldrich, purity 99%, mp 1458 K) was sealed in evacuated quartz ampoules or under He. The commercially available SiO\(_2\) or SiO added to the MoS\(_2\) precursor were (1) SiO\(_2\) white amorphous powder (Alfa Aesar, Johnson Matthey GmbH, purity 99.8%, mp 1983 K, bp 2503 K), or (2) dark brown SiO amorphous powder (Alfa Aesar, Johnson Matthey GmbH, purity 99.8%, mp 1975 K, bp 2153 K, density 2.13 g cm\(^{-3}\)). Each was ground in an agate mortar with MoS\(_2\) powder in mass ratios of (a) 9 : 1 and 1 : 1 for SiO\(_2\) : MoS\(_2\), or (b) 9 : 1 for SiO : MoS\(_2\), and subsequently sealed in evacuated quartz ampoules under He.

The scattering patterns, HRTEM images and their Fourier transforms of all SiO\(_2\) and SiO samples revealed as-received amorphous materials devoid of fibers. No contrast due to SiO\(_2\) or SiO clustering, crystalline domains or the presence of nanofibers was observed.

To create different quenching conditions, some MoS\(_2\)-filled ampoules were prepared with He. Also, to test for metal-atom catalysis, powdered Ni was mixed with the precursor powder in several ampoules. There were no perceptible differences in the basic structure or quantity of the nanomaterials generated due to the addition of Ni, although the presence of He amplified yields.

3. IF-MoS\(_2\)

3.1 Closed-cage MoS\(_2\) nanostructures

Fig. 2–5 show representative closed-cage and tubular MoS\(_2\) nanostructures from the solar ablation of MoS\(_2\) in evacuated ampoules. The IF-MoS\(_2\) closed-cage, multi-walled nanoparticles (from \( \sim 10–15 \) up to \( 25–35 \) layers), 50–100 nm in diameter, appeared in groups of dense agglomerates. The larger multi-walled closed-cage formations (Fig. 2) (outer diameters \( \sim 20–100 \) nm) were elongated or quasi-spherical, whereas smaller configurations (Fig. 3) with only a few S–Mo–S planes exhibited facets similar to the nano-octahedral symmetry that derives from the triangular faces having the same symmetry as the trigonal Mo and S sub-lattices.\(^1\),\(^2\) The rounded corners and edges develop because MoS\(_2\) sheets cannot be sharply bent without strain. EDS revealed solely Mo and S in all

Fig. 1 (a) Schematic of one solar concentrator \( \sim 20 \) cm in diameter. A second concentrator of the same diameter but different NA is positioned on the same solar tracker, with its own fiber leading to the same ampoule. Photograph of both fibers aimed at the MoS\(_2\)-filled ampoule tip: (b) pre-irradiation, (c) during irradiation.

Fig. 2 (a) Low magnification TEM image of a representative agglomerate of large closed-cage nested IF-MoS\(_2\) nanoparticles. (b) HRTEM image of a closed-cage multi-walled IF-MoS\(_2\) visible at the lower right of (a).
nanostructures in Fig. 2–5. In all nested IFs, the Mo : S ratio was 1 : 2.

Small closed nearly octahedral nanoparticles, especially single-walled MoS$_2$ ~ 5 nm across (Fig. 3(a)), are striking evidence of the experimental realization of the theoretical lower limit of nanostructure stability: octahedra of edge length 3–7 nm, below which elastic strain does not allow nanoclusters to fold into smaller-diameter closed-cage structures. Closed 2–3 walled nano-polyhedra, though not perfectly symmetric, were more prevalent (Fig. 3(b)). Note that two-dimensional projections of three-dimensional nearly octahedral structures observed in TEM can appear as small rectangles, rhombi and hexagons, depending on their orientation in the microscope’s electron beam.

Fig. 2 and 3 accentuate that larger nanostructures evolve to multi-layered, elongated and quasi-spherical shapes, while smaller nanostructures comprise fewer-layered formations. Earlier reported MOCVD precursor synthesis and pulsed laser ablation of IF-MoS$_2$ indicated that colder annealing environments generate larger multi-layered IF nanostructures, whereas hotter annealing temperatures (~1300 K) proved essential in generating smaller, fewer-layered nanoparticles due to the large activation energies affiliated with the bending of otherwise flat 2D MoS$_2$ layers. Higher reactor temperatures leading to more faceted nanostructures has also been reported for different IF compounds.

The nanostructures reflect solar reactor conditions: larger nanoparticles with more layers signify colder conditions, whereas smaller polyhedral shapes with fewer layers imply hotter annealing that favors curling and closing due to MoS$_2$ nanolayer defects. The comparison between pulsed laser and solar ablation is not clear-cut: the solar reactor is suffused with graybody radiation from the irradiated precursor powder (in pulsed laser ablation the bulk undergoes less heating while the superficial ablated layer attains higher temperatures).

3.2 MoS$_2$ nanotubes

Nanotubes with outer and inner diameters of 10–25 and 6–15 nm, respectively, and nested tubes 60–80 nm in outer diameter, were also found (Fig. 4). EDS indicated a Mo : S ratio of 1 : 2. The most common nanotubes were hollow, straight, multi-walled with at least 20–25 layers, a 0.612 nm layer separation, layer defects and lengths ~50–2000 nm.

Fig. 4 illustrates layer defects along the walls and occasional nanotube tapering. Unlike carbon nanotubes, the number of layers on either side of the core can be different, and the growth of some layers terminates, resulting in an irregular-walled nanotube. Differently curved tip regions (Fig. 4(b)) arise primarily from lattice imperfections. These features are consistent with those in Mo$_{1-x}$W$_x$S$_2$ nanotubes. Although most MoS$_2$ nanotubes were open-ended, some exhibited closed tips with a variety of shapes that imply rhombohedral or triangular topological defects.

A startling observation was single-walled MoS$_2$ nanotubes of diameter ~7 nm and length ~60 nm (Fig. 5). Viewing the nanotubes at different angles evidenced a uniform circular cross-section. The dark basal plane lattice fringe along the tube corresponds to a single MoS$_2$ layer. EDS confirmed Mo and S in a 1 : 2 ratio.

The single-walled nanotubes confirm the stability limit$^4,16$ of a minimum 6–7 nm diameter predicted for MoS$_2$. This limit
also pertains to the inner diameter of multi-walled nanotubes—a theoretical bound eclipsed neither in previous multi-walled MoS₂ nanotubes nor here, e.g., Fig. 4(a). Unlike the repeatable production of MoS₂ multi-walled nanotubes and closed-cage structures, single-walled nanotubes and single-walled nearly octahedral nanoparticles emerged from a single experiment only, which precluded their systematic study. Reproducing the precise solar reactor conditions of that experiment has proved elusive.

4. SiO₂ nanostructures

Solar ablation of MoS₂ in vacuum produced amorphous SiO₂ nanofibers with diameters ~20–50 nm and lengths up to 5000 nm (solar heating of the ampoule’s MoS₂ region can melt quartz). Previous amorphous SiO₂ nanostructures included nanowires of diameter 5–50 nm and lengths up to hundreds of μm, as well as silica nanospheres tens of μm in diameter.¹⁸,¹⁹,²⁸

To augment SiO₂ nanoparticle yields, we irradiated powdered 1 : 1 mixtures of MoS₂ : SiO₂ in He, which produced amorphous nanofibers (Fig. 6(a)) and nanospheres (Fig. 6(b), diameters ~200–300 nm) of SiO₂, confirmed with EDS. In most cases one nanofiber end appears rooted in large dark particles (Fig. 6(a)) identified with EDS as MoSₓ (1.5 ≤ x ≤ 2). Fig. 6(b) exhibits monodisperse amorphous SiO₂ nanospheres, together with SiO₂ nanospheres agglomerated around or attached to a MoSₓ particle.

The presence of He and/or the MoS₂ + SiO₂ mixture may serve as nucleation points that improve both IF-MoS₂ and SiO₂ nanoparticle yields. However, none of the IF-MoS₂ nanoparticles examined contained Si or O, and SiO₂ nanoparticles were devoid of Mo and S.

To our knowledge, a purely photothermal production of SiO₂ nanoparticles had not been reported previously. Neither had SiO₂ nanostructures followed from pure quartz. Both points suggest alternative production pathways.

5. Si nanostructures

Earlier Si nanowires exhibited large aspect ratios (order 10²), were highly curved, with a crystalline Si core of diameter ~10–30 nm and an outer layer of amorphous SiO₂.²⁰,²¹ Reported Si nanospheres had diameters of 20–80 nm. Cognizant of the high-temperature (1) disproportionation of SiO into SiO₂ and Si, and (2) SiO₂-assisted growth of Si nanowires,²⁰ we applied solar ablation to powdered 1 : 9 mixtures of MoS₂ : SiO for synthesizing Si nanoparticles.

Low magnification TEM images in Fig. 7 illustrate representative morphologies: crystalline wire-like Si, oriented and distributed randomly, with uniform diameters of 10–25 nm over lengths from hundreds to thousands of nm. Crystalline Si nanospheres ~20–50 nm in diameter interconnect and/or cap the nanowires. The tangled aggregates appeared nucleate-like on the surfaces of large MoS₂ particles, which suggest a role for these surfaces in triggering nanowire growth.

From EDS, Si and O are present in a ratio of ~1 : 1, apparently comprised of a pure-Si core and amorphous SiO₂ coating formed during air exposure after deposition. Nanowire diameter, length and growth direction were similar to those

![Fig. 6 Amorphous SiO₂ nanostructures. (a) Low magnification TEM image of nanofibers several μm long. The framed inset is an HRTEM image of the nanofiber’s tip. (b) Low magnification TEM image of agglomerated and monodisperse nanospheres.](image)

![Fig. 7 Low magnification TEM image of representative Si nanowires and nanosphere morphologies produced by solar ablation. Inset: A higher magnification image taken from the framed nanowire segment reveals the structurally uniform Si crystalline core and thin amorphous SiO₂ shell. The Si lattice fringes are visible with 0.30 nm spacing, consistent with the characteristic 0.31 nm {111} interplanar spacing in Si.](image)
achieved in previous multi-hour pulsed laser ablation of SiC + SiO$_2$ mixtures in 1400 °C ovens.\textsuperscript{20}

6. Discussion

Solar ablation constitutes a relatively simple, economical and purely photothermal procedure for the synthesis of assorted nanostructures. It generated a variety of IF-MoS$_2$, as well as SiO$_2$ nanofibers, Si nanowires and nanospheres of both SiO$_2$ and Si. The MoS$_2$ nanostructures included single-walled nanotubes and single-walled closed-cage formations with dimensions constituting experimental confirmation of the minimum sizes predicted from theory. For SiO$_2$, the novelty is apparently the first synthesis of SiO$_2$ nanostructures per se. The exploitation of highly concentrated sunlight and hot annealing conditions amenable to nanostructure formation. The synthesis of single-walled MoS$_2$ is noteworthy for two reasons. First, there has been only one report of single-walled WS$_2$ and MoS$_2$ nanotubes,\textsuperscript{14,30} the latter being essentially reasons. First, there has been only one report of single-walled nanotubes with a distorted structure compared to the bulk. Second, detailed density functional tight-binding calculations indicate\textsuperscript{4} that the multi-walled nanotubes are appreciably more stable than their single-walled analogues. It is therefore expected that single-walled MoS$_2$ nanotubes could have been produced by kinetic control, via a far-from-equilibrium synthetic strategy. Solar ablation provides such a strategy. This observation also explains the considerable difficulties in reproducing the conditions for this kinetically controlled reaction.

In addition, the elevated temperatures required for melting and/or decomposition of the compounds involved can only be achieved with a strongly absorbing refractory medium (here MoS$_2$). It remains unclear whether MoS$_2$ catalyzes SiO$_2$ and Si nanoparticle formation and vice versa—issues to be probed in future studies.

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