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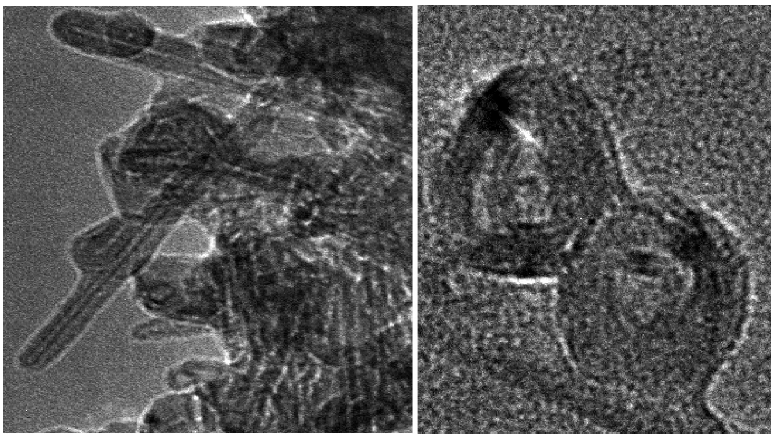
J. Am. Chem. Soc., **2005**, 127 (11), 3658-3659• DOI: 10.1021/ja042294k • Publication Date (Web): 24 February 2005



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Published on Web 02/24/2005

Generation of Onions and Nanotubes of GaS and GaSe through Laser and Thermally Induced Exfoliation

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Graphite nanoparticles are known to spontaneously transform to onion and related nanostructures on electron-beam irradiation.[1] Onion structures are hyperfullerenes arising from concentric fullerenes. Formation of nanotube structures from graphite by the rolling of graphene sheets is well-documented.[2] Layered inorganic compounds such as MoS_2, WS_2, and $NiCl_2$ also form fullerene and nanotube structures.[3] On the basis of theoretical calculations, Cote et al.[4] predicted that GaSe with a layered structure should form nanotubes similar to carbon nanotubes. Kohler et al.[5] have recently proposed that GaS with a layered structure should also form nanotubes. It may be recalled that both GaS and GaSe crystallize in the $P6_3/mmc$ space group and exhibit mica-like morphology. To our knowledge, however, there is no report on the formation of fullerene structures and nanotube structures by GaS and GaSe. We have, therefore, investigated the formation of such structures by laser irradiation and thermal treatment of GaS and GaSe.

Polycrystalline powders of GaS or GaSe were dispersed in a liquid medium such as di-*tert*-butyl disulfide, toluene, or *n*-octylamine and irradiated for 2 min by using a Q-switched Nd:YAG laser (λ = 532 nm, 10 Hz, 6−7 ns). The color of the dispersion turned orange after irradiation. The sample as such was used for further characterization. Di-*tert*-butyl disulfide is found to be a good medium for laser irradiation experiments with metal sulfides.[6] Powders of GaS and GaSe were also heated in a sealed quartz tube to 900 °C. One end of the sealed tube was kept at a relatively lower temperature of 400 °C. Heating the samples in this manner gave rise to solid deposits in the cooler region. Powder X-ray diffraction patterns of the solid products corresponded to those of hexagonal GaS and GaSe (see Figure S1). Energy-dispersive X-ray analysis of the samples showed Ga-to-S and Ga-to-Se ratios to be 1:1. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out on the products of irradiation and heat treatment.

Direct laser irradiation of solid GaS yields nanoparticles, but laser irradiation of GaS powder dispersed in di-*tert*-butyl disulfide leads to the exfoliation of the GaS layers. The exfoliated sheets roll over to form tubular or fullerene structures. In Figure 1a, we show a TEM image revealing the rolling of an exfoliated GaS sheet. The sheet is single-crystalline as seen from the selected area electron diffraction pattern shown as the inset in Figure 1a. We could isolate nanotubes and onionlike structures as products of laser irradiation, as revealed by the TEM image of these in Figure 1b. The proportion of the nanotubes was correspondingly higher (≥75%) than that of the onions.

The nanotubes are somewhat sensitive to the high-energy electron beam, making it difficult to obtain good high-resolution electron microscope (HREM) images. Figure 1c shows an HREM image of a wall of a nanotube, showing an interlayer spacing of 3.15 Å corresponding to the separation between (100) planes of GaS. There is a small lattice expansion of 1.5% commonly seen in such nanostructures.[7] When toluene was used as the liquid medium for laser irradiation, instead of di-*tert*-butyl disulfide, a few tubular structures were obtained (Figure 1d). Laser irradiation of GaSe powder in *n*-octylamine also gave nanotubes and onionlike structures as shown in Figure 1e,f.

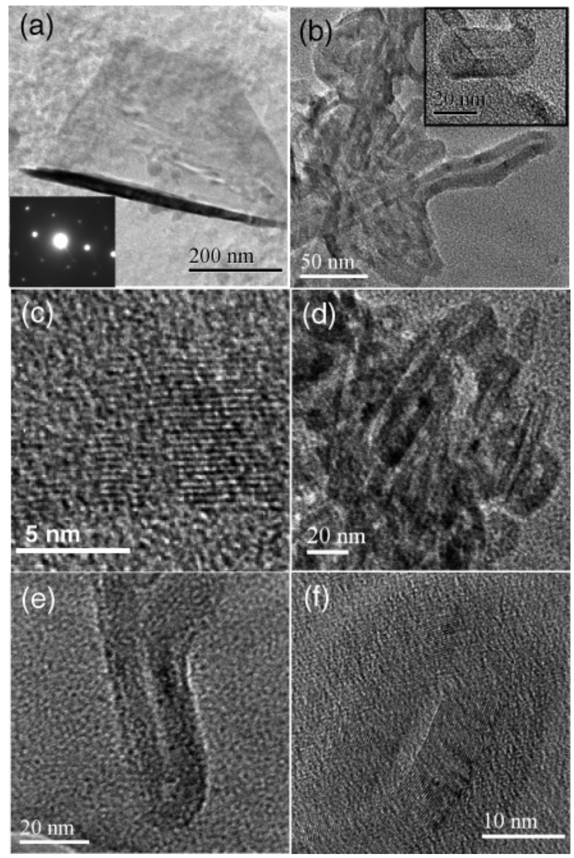

Figure 1. TEM image of (a) an exfoliated GaS sheet rolling to form a nanotube. Inset shows the SAED pattern of the sheet. (b) TEM image of GaS nanotubes obtained by laser irradiation in a di-*tert*-butyl disulfide medium. Inset shows an onionlike structure. (c) HREM image of a wall of a nanotube. (d) TEM image of GaS nanotubes obtained by laser irradiation in toluene medium. TEM images of a GaSe (e) nanotube and (f) onionlike structure obtained by laser irradiation in *n*-octylamine medium.

Heating GaSe powder to 900 °C in a sealed tube led to exfoliation, giving rise to nanoflowers and nanotubes. Figure 2a shows the SEM images of the product of heat treatment collected

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10.1021/ja042294k CCC: $30.25

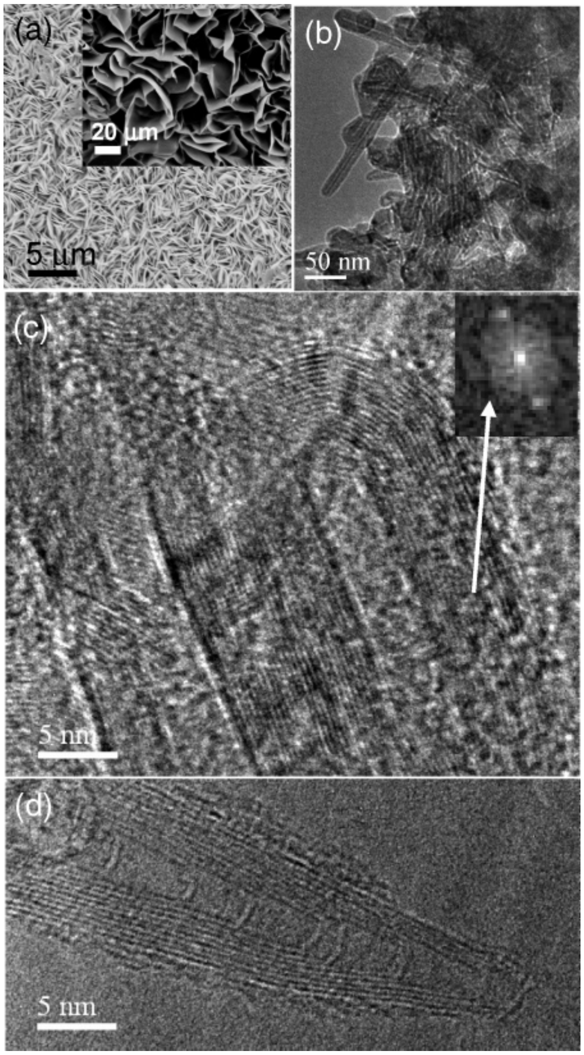

Figure 2. (a) SEM image of GaSe scrolls. Inset shows nanoflowers. (b) TEM image of GaSe nanotubes obtained by thermal treatment. (c), (d) HREM images of GaSe nanotubes.

in two different regions of the sealed tube. The images reveal scrolls and nanoflowers. TEM images show the presence of nanotubes as well (Figure 2b). The electron diffraction pattern gave *d* values characteristic of hexagonal GaSe. The nanotubes are uniform and straight with an inner diameter of 5 nm and an outer diameter of ∼20 nm. The HREM images of the nanotubes in Figure 2c,d give a lattice spacing of ∼3.46 Å corresponding to the spacing between the (100) planes of hexagonal GaSe, showing a small expansion. The fast Fourier transform (FFT) pattern of the flat region of the tube (inset in Figure 2c) is consistent with the *d* values observed experimentally. The nanotubes have closed spherical or conical tips. The FFT pattern of the cap region yields broad smeared spots with similar *d* values, suggesting concentrated defects caused by the bending of the tube. Figure 3, parts a and b, shows the TEM images of the onionlike structures. Thermal exfoliation of GaS also yields scrolls, nanotubes, and nanoflowers, similar to those of GaSe.

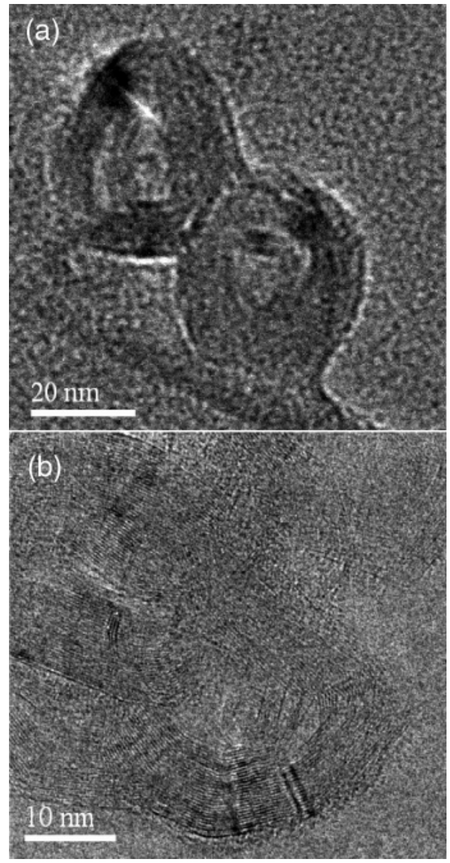

Figure 3. (a) TEM image of GaSe onionlike structures. (b) HREM image of the onionlike structures.

In conclusion, we have demonstrated that layered GaS and GaSe, possessing mica-type morphologies, form nanotubes and onionlike structures on exfoliation by laser irradiation or thermal treatment, thereby verifying earlier theoretical predictions.

Acknowledgment. We thank DRDO and DST (India) for supporting this research.

Supporting Information Available: Powder XRD patterns of the GaS and GaSe nanostructures. This material is available free of charge via the Internet at http://pubs.acs.org.

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