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Chemical routes to GeS_2 and $GeSe_2$ nanowires†

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Nanowires of GeS_2 and $GeSe_2$ have been obtained by novel chemical routes involving the decomposition of organo-ammonium precursors containing super-tetrahedral Ge_4S_{10} and the dimeric Ge_2Se_6 units.

Nanowires of several inorganic materials including those of oxides, chalcogenides, nitrides and carbides have been synthesized and characterized by employing a variety of methods.[1,2] Besides the well-known vapor–liquid–solid, vapor–solid (VS) and hydrothermal processes, ingenious chemical routes have been employed to generate these nanowires. Thus, nanowires of Fe_7S_8 have been produced recently by first preparing nanowires of its hybrid composite with ethylenediamine and decomposing the hybrid at low temperatures.[3] An important aspect of nanoscience research today is to investigate mild chemical routes for the synthesis of one-dimensional nanostructures. We, therefore, considered it of interest to explore the synthesis of nanowires of GeS_2 and $GeSe_2$ both of which crystallize in layered structures. Knowing that the nanotubes of Mo and W dichalcogenides can be produced by the thermal decomposition of the ammonium chalcometallates containing tetrahedral MoS_4 and WS_4 units,[4] we sought to make use of precursors containing super-tetrahedral adamantanoid-type $Ge_4(S/Se)_{10}$ units along with dimeric $Ge_2(S/Se)_6$ units formed by joining GeS/Se_4 tetrahedra,[5,6] for the purpose. We have carried out the decomposition of the molecular precursors to obtain δ-GeS_2 and $GeSe_2$ nanowires. While δ-GeS_2 nanowires could be prepared from $[TMA]_4Ge_4S_{10}$ (TMA = tetramethylammonium), $GeSe_2$ nanowires were produced from a new organo-ammonium precursor, $[(C_3H_7)_2NH_2]_4[Ge_2Se_6]$.‡

Ozin and co-workers[7] first reported the structure of δ-GeS_2 formed by the acid hydrolysis of $[TMA]_4[Ge_4S_{10}]$. Controlled acid hydrolysis of $[TMA]_4Ge_4S_{10}$ in the presence of sodium dodecylsulfate (SDS), followed by refluxing in PEG-600 yielded δ-GeS_2 nanowires in high yield ($>80\%$).§ The SEM image in Fig. 1a shows nanowires with lengths exceeding several micrometers. EDX analysis showed the Ge : S ratio to be ∼1 : 2. The TEM image in Fig. 1b shows the nanowires to have diameters in the 20–80 nm range and lengths of several microns. When the reaction mixture was refluxed for longer duration (6 h), the nanowires developed distortions and undulations. The high-resolution electron microscope (HREM) image in Fig. 1c shows the lattice fringes with an inter-layer separation of ∼6 Å. The growth direction of the nanowires is along the $<112>$ direction and there are very few defects in the nanowires. The good electron diffraction (ED) pattern (see inset A in Fig. 1c) shows spots due to the (213) reflection of δ-GeS_2 [JCPDS file, card no. 27-0239]. The Fourier transform (FFT) generated ED pattern given in inset B of Fig. 1c is comparable to the experimental pattern. The X-ray powder diffraction pattern of the nanowires agreed with that reported in the literature[7] showing the first line at ∼6 Å followed by an intense line at 3.88 Å and weaker reflections at 3.26 Å and 3.01 Å.

Acid hydrolysis of $[TMA]_4Ge_4Se_{10}$ gave selenium. Thermal decomposition of $[TMA]_4Ge_4Se_{10}$ yielded Se nanowires.[8] We therefore prepared a new organo-ammonium compound $[(C_3H_7)_2NH_2]_4[Ge_2Se_6]$¶ which on thermal decomposition yielded $GeSe_2$ nanowires. EDX analysis of the individual nanowires revealed a composition of 1 : 2 for Ge : Se and the XRD pattern was comparable to that of monoclinic $GeSe_2$. In Fig. 2a, we show a TEM image of $GeSe_2$ nanowires. The nanowires have a diameter of ∼30 nm with lengths of a few microns. The nanowires were electron beam-sensitive and decomposed on prolonged exposure forming an amorphous covering. Fig. 2b shows a HREM image of a $GeSe_2$ nanowire. The image shows lattice fringes of ∼5.8 Å corresponding to the separation between the (002) planes of monoclinic $GeSe_2$ which has a layered structure. The ED pattern (shown in the inset of Fig. 2b) shows the single crystalline nature of

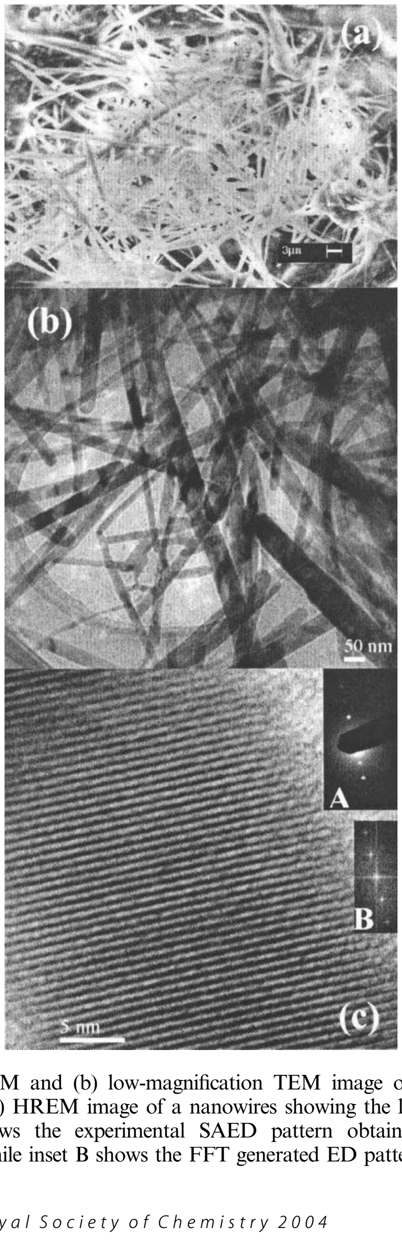

Fig. 1 (a) SEM and (b) low-magnification TEM image of the δ-GeS_2 nanowires; (c) HREM image of a nanowires showing the lattice fringes. Inset A shows the experimental SAED pattern obtained from the nanowires while inset B shows the FFT generated ED pattern.

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† Electronic supplementary information (ESI) available: synthesis and characterisation details and Fig. S1 showing the structure of the molecular precursor $[C_6H_{14}NH_2]_4[Ge_2Se_6]$ showing the $[Ge_2Se_6]$ dimer and the amine. See http://www.rsc.org/suppdata/cc/b4/b412056f/

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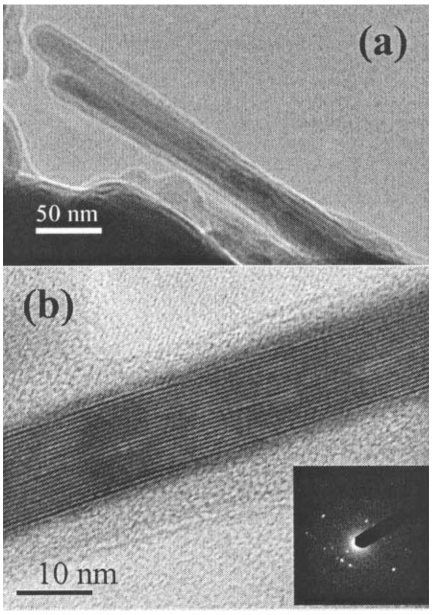

Fig. 2 (a) Low-magnification TEM image of the $GeSe_2$ nanowires; (b) HREM image of a $GeSe_2$ nanowire. The inset shows the typical ED pattern.

the wire and the spots could be indexed as (002), (200) and (142) planes of monoclinic $GeSe_2$ with a layered structure [a = 7.016, b = 16.796, c = 11.831 Å, JCPDS file card no. 30-0595].

The mechanism of formation of the δ-GeS_2 and $GeSe_2$ nanowires can be understood as follows. δ-GeS_2 is formed by the condensation polymerization of the $Ge_4S_{10}^{4-}$ adamantanoid units which are present in the precursor, $[TMA]_4Ge_4S_{10}$ (see Fig. 3a). The adamantanoid moiety is an attractive precursor which can give rise to various architectures under appropriate reaction conditions. For example, in the presence of long-chain amines/surfactants the adamantanoid-type building blocks form lamellar structures,[9] and microporous[5] or mesoporous[9] networks in the presence of transition metal ions. Furthermore, controlled hydrolysis of an organized assembly of $Ge_4S_{10}^{4-}$ is known to form micro-crystals δ-GeS_2 with an expanded framework structure.[7] In the present case, the presence of a surfactant in the reaction mixture may trigger the condensation polymerization reaction in the micellar cavity formed by the surfactant molecules, leading to a confined reaction. The morphology of the final product would depend on the shape of the micellar cavity, a cylindrical cavity giving rise to one-dimensional nanostructures.[10] $[(C_3H_7)_2NH_2]_4[Ge_2Se_6]$, when heated under the gas flow, decomposes forming small clusters of $GeSe_2$. These clusters may aggregate under the gas flow to reduce the surface energy.[11] Oriented attachment of the aggregates can give rise to one-dimensional growth similar to that found in the case of ZnO nanorods grown in a colloid system under solvothermal conditions.[12] Accordingly, the decomposition of the organo-ammonium compound at lower temperatures or at a lower gas flow gave nanoparticles. The existence of Ge_2Se_6 dimers in the molecular precursor¶ may facilitate the formation of $GeSe_2$ which contains dimeric Ge_2Se_6 units joining corner-shared chains of $GeSe_4$ tetrahedra (Fig. 3b).

Nanowires of δ-GeS_2 and $GeSe_2$ have been synthesized by novel chemical routes starting from different molecular precursors containing the adamantanoid $Ge_4S_{10}^{4-}$ and $Ge_2Se_6^{4-}$ units respectively which are also present in the nanostructured product.

Notes and references

‡ Synthesis of precursors: The $[TMA]_4Ge_4S_{10}$ salt was prepared by the known hydrothermal procedure.[13] $[(C_3H_7)_2NH_2]_4[Ge_2Se_6]$ was prepared solvothermally from metallic Ge and Se powders heated in the presence of dipropylamine.¶ IR spectra, CHN and EDX analyses were used to confirm the chemical composition.

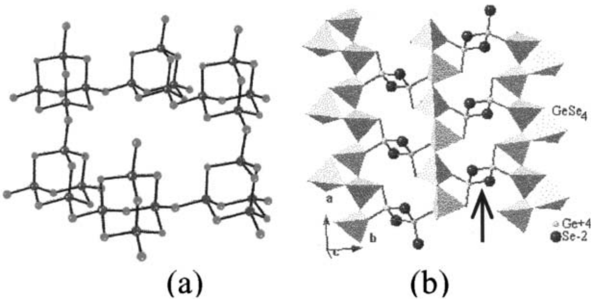

Fig. 3 (a) A part of the δ-GeS_2 structure showing the linking of six Ge_4S_{10} units; (b) a perspective view of the layer in $GeSe_2$, the Ge_2Se_6 dimer joining the two chains is marked by an arrow.

§ Synthesis of nanowires: In a typical reaction, 35 mg of SDS was dissolved in 1 ml of distilled water. 45 mg of $[TMA]_4Ge_4S_{10}$ was separately dissolved in 1.4 ml distilled water and added to the surfactant solution. 1.1 ml of freshly prepared 0.22 M HCl was then added to the reaction mixture with constant stirring. The reaction mixture turned turbid and the smell of H_2S liberated confirmed the onset of hydrolysis. Stirring was continued for about 1 h and the turbid solution was left standing overnight. The reaction mixture was then added to 12 ml PEG-600 solution and refluxed for 3 h. A dirty white fine precipitate adhering to the walls of the refluxing vessel, was separated by decanting the supernatant solution, washed with methanol and dried in air. Nanowires of $GeSe_2$ were obtained by the thermal decomposition of $[(C_3H_7)_2NH_2]_4[Ge_2Se_6]$ in a horizontal tube-furnace heated to 450 °C under a flow of Ar (180 sccm) + H_2 (20 sccm). After the completion of the reaction, the furnace was cooled to room temperature and the blackish product containing $GeSe_2$ nanowires was collected from the sample boat (yield ~50%).

¶ The structure of the compound was determined with the help of single-crystal X-ray diffraction data. Crystal data for $[(C_3H_7)_2NH_2]_4[Ge_2Se_6]$: Empirical formula = $C_{12}H_{32}GeN_2Se_3$, M_r = 513.87, monoclinic, $P2_1/c$, a = 10.8528(8), b = 18.3953(14), c = 10.9941(8) Å, β = 103.42°, V = 2134.9(3) Å^3, Z = 4, μ = 6.540 mm^{-1}. 8642 reflections measured and 3051 independent reflections, R_{int} = 0.0671, R_1 = 0.0709 and wR_2 = 0.1128 (observed data), R_1 = 0.1124 and wR_2 = 0.1237 (all data). The structure of this compound consists of the edge-shared dimer ($Ge_2Se_6^{2-}$) formed by $GeSe_4$ tetrahedra which are assembled in the presence of dipropylammonium cation (see Fig. S1†), the latter balancing the charge of the anionic cluster. The synthesis and characterization including detailed X-ray crystallographic data are supplied as supplementary material. CCDC 247347. See http://www.rsc.org/suppdata/cc/b4/b412056f/ for crystallographic data in .cif or other electronic format.

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