Synthesis, structure, and gelling power of γ -In₂S₃ nanoribbons with large aspect ratio.

Lilian Guillemeney¹, Laurent Lermusiaux¹, Patrick Davidson², Bruno Canut³, Benoît Mahler⁴, and Benjamin Abécassis¹✉

¹Univ. Lyon, ENS de Lyon, CNRS, Laboratoire de Chimie, F-69342, Lyon, France

²Laboratoire de Physique des Solides, Université Paris-Saclay, CNRS, 91405 Orsay

³Univ. Lyon, CNRS, ECL, UCBL, INSA Lyon, CPE, INL UMR5270, F-69621 Villeurbanne, France.

⁴Univ. Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière (iLM), F-69622 Villeurbanne, France

We report the synthesis of ultrathin indium sulfide In₂S₃ nanoribbons (NR) which display a giant aspect ratio using a simple and fast solvothermal method. We show that these NR have a thickness controlled at the atomic level below the nanometer, a width of 8.7 ± 0.1 nm and a length which can reach several micrometers. We determined the atomic composition of the inorganic core by Rutherford backscattering spectrometry (RBS) and measured by X-ray photoelectron spectrometry (XPS) an oleylamine surface coverage of 2.3 ligands per nm². X-ray diffraction experiments and simulations as well as high-resolution dark-field STEM point towards a $P\bar{3}m1$ trigonal crystallographic structure (γ phase). Their lateral dimensions can be tuned by the amount of water present in the reaction medium: anhydrous synthesis conditions lead to hexagonal nanoplates whereas controlled addition of water induces a symmetry break yielding long NR with a rectangular shape. Depending on the dispersion solvent, these long ribbon-like nanoparticles can form either well-dispersed colloids or bundles in which they stack face to face. Their large aspect ratio induces the formation of gels at volume fractions as low as 1.3×10^{-4} .

indium sulfide | nanoribbons | nanoplatelets | gels |

Correspondence:

benjamin.abecassis@ens-lyon.fr

Introduction

Indium sulfide is a wide band gap semi-conductor material which has potentially useful properties such as long term stability and low toxicity when compared to its cadmium or lead containing counterparts. With band-gaps ranging from 1.65 eV to 3.7 eV depending on the crystal phase reported in the literature for In₂S₃ (1, 2), it could be used in a variety of optoelectronic applications such as buffer layers in photovoltaics (3), in display devices and photodetectors (4–8), or for water splitting (9). Although research on indium sulfide colloidal nanoparticles has been quite active in the past years, notably in the exploration of different synthetic pathways, only partial shape control could be achieved to date. For example, several reports describe the synthesis of 1D nanomaterials such as long nanotubes (10) using InCl₃ and sulfur in oleylamine while di-tert-butyl disulfide and indium acetylacetonate in oleylamine yield β -In₂S₃ nanorods with a mean length of 170 nm (11). As far as 2D nanomaterials are concerned, Park *et al.* have first reported the colloidal synthesis of In₂S₃ hexagonal nanoplates (4) while the Pradhan group obtained large ($> 1\mu\text{m}$) indium sulfide nanosheets through the thermal decomposition of

indium tris-diethyldithiocarbamate in hexadecylamine (12). Similar wrinkled nanosheets have been observed as transient intermediates towards smaller (≈ 60 nm) hexagonal In₂S₃ nanoplates when InCl₃ and thiourea are used as precursors in oleylamine (13). Shape control can also be achieved using other strategies than varying the precursor sources: Ni *et al.* obtained nanotubes from the self-assembly of ultrathin nanocoils synthesized from indium acetate and sulfur in octylamine (14, 15), whereas Tian *et al.* showed that nanoflakes, spherical nanoparticles or nanobelts could be obtained with the introduction of an appropriate metallic ion in the initial mixture (16). Finally, starting from the same type of precursors, other materials with a different indium oxidation state can be obtained. For instance, InS materials may appear in four different allotropic varieties (orthorhombic, monoclinic, cubic and tetragonal) where orthorhombic $Pnmm$ structure is predicted to be the most stable (17). 1D-InS nanomaterials have already been reported in the form of wire or rod (18) whereas 2D-InS nanomaterials were obtained from a solvothermal synthesis between thioacetamide and indium metal in the resulting form of thin NR (19). Overall, the control of particle shape and atomic composition in indium sulfide nanoparticles is strongly dependent on the synthesis parameters but remains incomplete. More specifically, the aspect ratios for 2D materials cannot be controlled with current synthetic strategies and either relatively small (below 100 nm) or very large ($> 1\mu\text{m}$) square shaped platelets can be synthesized.

Phase identification for indium sulfide has been so far ambiguous. Most of the reported syntheses are thought to yield In₂S₃ but definitive attribution of the crystal structure is often difficult because the X-ray diffraction patterns do not exactly match the entries of crystallographic databases. These discrepancies were attributed to the anisotropy of the nanoparticles since reflections corresponding to small crystalline domains are expected to be broadened, as reflected in Scherrer's equation (20). In the case of subnanometer dimensions, this broadening can be so important that these peaks may be experimentally difficult to observe. In the Powder Diffraction Files of the International Centre for Diffraction Data (ICDD), four different In₂S₃ phases are reported. The cubic phase corresponding to the space group $Fd\bar{3}m$ ($n^\circ 227$) is often coined the α phase while the most common is the tetragonal β phase bearing the $I4_1/amd$

($n^\circ 141$) space group. Two other phases with a trigonal crystal system have also been reported, one with a rhombohedral space group ($R\bar{3}c$, ϵ phase) and the other with a hexagonal one ($P\bar{3}m1$, γ phase). Pistor *et al.* describe three different structures of In_2S_3 (21): a low temperature tetragonal phase β , an intermediate-temperature cubic phase α and a high-temperature trigonal phase γ , also reported in Diehl *et al.* (22). In any case, the experimental distinction between tetragonal β and cubic α phases is difficult to make without high-quality X-ray diffraction data. We have to point out that an ambiguity exists on the designation of the different In_2S_3 phases (21). Indeed, the low-temperature cubic phase was initially coined α while the higher-temperature tetragonal phase was called β (21). Later, it was shown that the initial report misidentified the low-temperature phase as being cubic. In fact, this low-temperature phase is tetragonal and a transition towards the cubic structure is observed as temperature increases. Hence, some authors have renamed the cubic phase β for the names of the different phases to be consistent and follow the right alphabetical order as temperature increases. However, this is very confusing. For instance, the cubic phase is named α in some files of the international crystallographic database and this notation is also present in publications. In this contribution, we will stick with the notations of Pistor *et al.* (21) and designate the different phases as described above.

Here, we present the solvothermal synthesis of ultrathin γ - In_2S_3 nanoribbons (NR) with a high aspect ratio. Using multiple techniques, we unambiguously ascribe the NR composition and crystallographic structure to trigonal $P\bar{3}m1$ γ - In_2S_3 . We found that a small amount of water added during the synthesis induces anisotropic growth, yielding long NR which reach more than one micrometer in length. We study the organization of these long NR in solution depending on the solvent using small angle X-ray scattering. We show that the NR tend to form bundles and to precipitate in toluene, whereas unbundled NR are obtained on short time frames when using tetrahydrofuran. In some instances, we discovered that gels form due to the high anisotropy of the NR. Gels are defined as low volume fraction dispersions (typically between 0.1 and 10 % in volume) with solid-like rheological properties arising from the self-assembled percolating network made by their components. They can be made of small organic molecules which form threaded structures, polymers or colloidal particles with attractive interactions. In this case, a network of particles without long-range order percolates through the whole solution and induces the gelation. Gels are classically observed at high volume fractions in dispersions of large micron-sized particles but the formation of gels from nanoparticles has also raised significant interest. In this case, nanoparticle gels can be subsequently dried to form aerogels whose porosity and large surface area are highly beneficial for various applications such as photocatalysis or sensing. (23) Current strategies to make gels from nanoparticles usually involve tuning the interaction potential between small isotropic building blocks. (24, 25) As the interaction

shift from repulsive to attractive depending on various factors such as solvent, temperature or concentration in depletant, the colloidal dispersion is destabilized and eventually forms a gels. Both thermodynamic and kinetic effects have to be taken into account to rationalize the gelling behaviour of colloidal nano dispersion. (26) A too fast destabilization triggered by a large interaction strength leads to irreversible aggregation and precipitation while with softer interaction slower aggregation kinetics enables the particle network to span the whole solution. Another parameter to take into account is the aspect ratio of the particles since highly anisotropic particles will more easily form percolating structures than spherical ones.

Experimental Section

Chemicals. Indium (III) chloride (anhydrous, 99+%) and THF (HPLC grade, 99.7 %) were purchased from Fisher-Alfa Aesar. Indium (III) chloride was stored and manipulated in an inert atmosphere glovebox. Sulfur (powder, 99.998%) was purchased from Sigma-Aldrich. Oleylamine (approximate C18-content 80-90%) was purchased from Fisher-Acros Organics. Absolute ethanol and toluene ($\geq 99.5\%$) were purchased from VWR.

Solvothermal synthesis of In_2S_3 NR. The long ultrathin nanoribbons presented in the main text are obtained as follows. 0.2654 g of anhydrous indium (III) chloride (1.2 mmol, 1 eq.), 0.0577 g of sulfur powder (1.8 mmol, 1.5 eq.), 11.8 mL of oleylamine, 170 μL of water (9.6 mmol, 8 eq) are introduced in a 20 mL Teflon-lined autoclave. The reaction mixture is sonicated for 10 minutes with an ultrasonic probe to obtain a homogeneous solution. The autoclave is then sealed and heated in an oven at 215°C for 2 h and under agitation. Once cooled down to room temperature, the yellow viscous resulting mixture is centrifuged for 5 minutes at 6153g; the product is then redispersed in 5 mL of ethanol before being centrifuged for 5 minutes at 6153g. The product is then redispersed in 5 mL of toluene and 3 mL of absolute ethanol are added. The solution is then centrifuged again for 5 minutes at 6153g, and this last step is repeated at least once with a redispersion in 5 mL of toluene. The final yellow product is redispersed in 10 mL of toluene. The typical mass concentration in NR obtained at the end of the purification process is 31 g/L.

RBS. The sample, initially in powder form, was deposited on a carbon adhesive tape. The analysis was performed with $^4\text{He}^+$ ions of 2 MeV energy delivered by the 4 MV Van de Graaff accelerator of the "ANAFIRE" platform (Institut de Physique des 2 Infinis, Lyon). The backscattered particles were detected with a 15 keV resolution implanted junction set at an angle of 169° with respect to the beam axis. The experimental data were fitted with the help of the SIMNRA simulation code (<http://www2.if.usp.br/lamfi/guia-simnra.pdf>).

XPS. XPS spectra were recorded on a THERMO K-alpha+ spectrometer with the Al K α line used as the excitation source at the Laboratoire Science et Surface of Ecully (Serma Technologies).

Transmission electron microscopy and High-resolution Electron Microscopy. TEM images were acquired on a JEOL JEM-1400 (accelerating voltage of 120kV). The samples are prepared by drop-casting In₂S₃ NR suspensions in toluene onto 200 carbon-coated copper grids. To avoid agglomeration on the TEM grids, the suspension is diluted a minima by a factor of ten and sonicated 2 minutes in an ultrasonic bath just before deposition. High-resolution scanning transmission electron microscopy (HR-STEM) pictures have been acquired using a JEOL JEM-ARM200F Cold FEG NeoARM operating at 200kV.

X-ray Diffraction experiments. Powder X-Ray Diffraction (XRD) analyses were performed with a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu K α ceramic tube, operating at 45 kV and 40 mA and a PIXcel3D 2x2 area detector.

Simulation of X-ray Powder Diffraction. Atomic models of In₂S₃ nanoribbons are generated using the Crystal Maker software as follows. A new crystal is created and the corresponding space group, lattice parameters and position of the atoms in the unit cell are entered following Pistor *et al.*, (21) The unit cell is expanded along the principal crystallographic directions with ratios 1 $\times$ 10 $\times$ 100. The structure is then exported as a xyz coordinate text file which serves as input for calculation of the X-ray diffractogram using the Debye program (<https://github.com/wojdyr/debyer>) which calculates the scattering pattern from atomic coordinates using Debye's scattering equation.

Small Angle X-ray Scattering. Synchrotron SAXS experiments were performed on the SWING beamline at the SOLEIL synchrotron (Saint-Aubin, France) using an X-ray energy of 16 keV with a sample to detector distance of 1 m. The 2D scattering patterns were radially averaged using beamline specific procedures. The I(q) data were fitted using SasView (<http://www.sasview.org/>).

UV-visible spectroscopy. UV-vis absorption spectra were measured on a Lambda 750 Perkin-Elmer and a Jasco V-770 spectrophotometers. For the measurements, NR are dispersed in THF (0.027 g.L⁻¹) in 1 mm thick quartz cuvettes (Hellma).

Assessment of the gelling power and polarized-light microscopy. Samples of dispersions of In₂S₃ nanoparticles in various organic solvents at different concentrations were filled into 2 mL glass vials and placed upside-down to assess

their gel properties, and photographed with an Olympus XZ-1 digital camera.

Samples of dispersions were also filled into optical flat glass capillaries (Vitrocom, NJ, USA) of 100 μ m thickness and 200 μ m width to examine their textures with a polarizing microscope (Olympus BX51). When necessary, a wave-plate was inserted to determine the direction of the slow axis of well-defined birefringent domains. The optical textures were recorded with a sCMEX-20 (Euromex, Netherlands) camera.

Results and discussion

Indium sulfide NR are synthesized from molecular precursors by a fast and simple solvothermal method. Briefly, anhydrous indium (III) chloride is mixed with sulfur powder, water, and oleylamine in a Teflon-lined autoclave (see Figure S1 and experimental section for more details). The autoclave is then sealed and heated for two hours at 215°C in an oven. The resulting yellow viscous product is then washed with ethanol and toluene. Transmission Electron Microscopy (TEM) images of the resulting product show highly anisotropic nanoparticles with an average length of 1162 ± 44 nm and 8.7 ± 0.1 nm in width, as measured for an ensemble of 500 particles (Figure 1 and SI for uncertainty calculations). The homogeneous contrast between the particles lying flat and the TEM grid proven by the bimodal gray level distribution (inset of Figure 1.a.) points towards flat objects with a well-defined thickness for all the NR. Indeed, atomic resolution STEM examination of NR lying on their side (Figure 4.d.) shows a unique thickness for all the NR (0.71 nm). This highlights a very large aspect ratio of respectively 10 and 1000 between their length and their width compared to their thickness, respectively. Additionally, UV-visible spectroscopy was performed on the NR dispersed in THF and highlights an absorption peak centered at 247 nm, with a broad absorption tail up to the visible range (550 nm, Figure S2).

In order to identify the exact composition of the as-synthesized NR, we performed Rutherford Backscattering Spectrometry (RBS) experiments. This technique has already been used for CdSe nanoribbons (27) and is known to yield reliable and accurate results for the composition of inorganic materials, in particular for heavy elements. The powder material is irradiated by α -particles which are backscattered after interaction with the nucleus of the atoms composing the material. The energy of each backscattered ion is proportional to the initial energy of the α -particles by a factor k named kinematical factor, which depends of the atomic number of the chemical element. RBS analyses indicate that the NR are composed at (60 ± 1) % of sulfur and (40 ± 1) % of indium (Figure 2.a.). The stoichiometric ratio between indium and sulfur is thus of 2:3, so that the empirical formula of the NR is In₂S₃.

Further insight on the surface chemistry of the NR is brought by X-Ray Photoelectron Spectroscopy (XPS) (Figure 2). The interpretation of the survey spectrum gives the following atomic composition: C (65.9%), O (0.5%), S(18.6%), In

Fig. 1. TEM images at different magnifications of In_2S_3 NR lying flat. The inset in (a.) is a grey-scale histogram of the underlying image, showing the uniform thickness of the NR as only two peaks are seen (background and NR)

Fig. 2. RBS and XPS analyses. (a.) RBS spectrum for indium sulfide nanoribbons. The experimental data are fitted in order to obtain the chemical composition of the sample: 60% of sulfur and 40% of indium, yielding a In_2S_3 empirical formula. (b.) Survey XPS spectrum, proving the atomic composition: In(12.2%), S(18.6%), O(0.5%), C(65.9%), N(2.8%). High-resolution XPS spectra highlighting the presence of (c.) indium in the form of indium sulfide (peak centred at 444.7-444.9 eV) and (d.) sulfur in the sulfide form (peak centred at 162.5 eV).

(12.2%) and N (2.8%). The analysis was carried on two different spots, revealing the same distribution in elements in both spots. Indium and sulfur are linked together, forming indium sulfide material as expected, with an In to S atomic ratio of 1.52. This stoichiometry is consistent with the one obtained from RBS analysis and it confirms the empirical formula of In_2S_3 . Oxygen is involved only in C-O bonds, proving it is solely part of ethanol molecules that may remain physisorbed on the surface of the NR during the different purification steps. Nitrogen comes only from the oleylamine surface ligands (2.3 molecules.nm⁻²) and its content yields the following formula: $\{\text{In}_2\text{S}_3[\text{oleylamine}]_{0.46}\}$ (see SI for calculation details). The NR coverage in amine is analogous to coverages reported for instance on wurtzite $\{\text{CdSe}[\text{n-octylamine}]_{0.53}\}$ quantum belts (28, 29).

To identify the NR crystalline structure, we performed X-Ray diffraction (XRD) experiments and compared the pattern with computed diffraction patterns of indium sulfide (Figure 3). Experimentally, we observe a broad peak at 19.5°, a low intensity peak at 24.6°, an intense thin peak at 27.3° followed by two broader reflections at 30.5 and 31.8°. Finally, we observe a series of 3 peaks with one centered at 48° and two lower intensity peaks located at $\pm 1^\circ$ (i.e. 47° and 49°) from the center peak. Low intensity peaks can be seen at 56.1°, 75.2° and 78.3°. Very similar diffraction patterns have been reported in several publications (4, 7, 11, 13, 30–32). How-

Fig. 3. X-ray diffraction of In_2S_3 NR. Experimental X-ray diffractogram for In_2S_3 nanoribbons (blue curve, bottom panel) overlaid with the theoretical bulk diffraction peaks of the γ -trigonal In_2S_3 (vertical red lines). Computed X-ray diffractograms (red, green, and black lines) for γ - In_2S_3 NR with a 1, 10, 100 aspect ratio in the three crystallographic orientations.

ever, the indexation of the peaks varied in the different reports. The 27.3° peak has been attributed to the [311] reflection of the β phase in references (11, 31–33) but to the [109] peak of the same phase in references (4, 7) while other reports (13, 30) assign this peak to the [110] reflection of the ϵ phase. These seemingly contradictory findings can be explained by the fact that the α cubic phase has been relabelled by some authors as the β phase because it appears at a higher temperature. (21) The peak at 19.5° has previously been attributed to impurities (7). This is consistent with our observation of batch-to-batch variability in the relative intensity of this peak compared to the others. To check if this peak could be due to organometallic impurities we acquired X-ray diffractograms for indium chloride, sulfur powder, a mixture of indium chloride in oleylamine and oleylamine alone. The broad peak at 19.5° is present for oleylamine alone (Figure S3). We thus concluded that the solvent oleylamine is responsible for the presence of this peak.

Indexing the peaks and attributing the correct crystallographic structure can be made difficult in the case of nanostructures because the limited particle dimensions in some crystallographic directions induce a broadening of the diffraction peaks. In order to take this into account, we simulated the X-ray diffraction patterns of different atomic models of In_2S_3 NR. We generated atomic models of In_2S_3 nanoparticles whose dimensions match those observed using electron microscopy and we computed their diffraction patterns from the atomic positions using the Debye formula (Figure 3). For the different allotropes, we changed the orientation of the edges with respect to the principal crystallographic axes to evaluate their influence on the X-ray diffractogram. The width of the peaks depends on the orientation of the crystalline lattice with respect to the edges. Let us consider a plate-like particle with dimensions $10 \times 100 \times 1$ unit cells along the three a , b , c principal crystallographic axes. All the $(hk0)$ reflections will be sharp since the crystallographic order along the a and b directions extends over a relatively long range. We also expect that the $(0k0)$ reflections will be sharper than $(h00)$ ones. Similarly, the $(00l)$ reflections will be very broad or even undetectable since only one or a few unit cells are found along the c principal direction (20).

We have simulated three different structures that are likely to match the experimental patterns: the α (Figure S4), β (Figure S5) and γ phases (Figure 4) with edge orientation along the principal crystallographic directions. For symmetry reasons, among six possibilities, only three yield a different diffraction pattern for the γ and β phases since the a and b axis are equivalent. Hence, only the number of unit cells along the c direction (n_z) influences the diffraction pattern. For the α phase, all three axes being equivalent, the orientation of the NR edge does not influence the diffraction pattern. The comparison of the computed α diffraction pattern to the experimental one shows that two predicted salient features are missing: the sharp [400] reflection (32°) and the [511] peak (43°). The same holds true for the β phase for which several peaks in the $40\text{--}45^\circ$ range are visible in all computed patterns but are absent in our experimental data. In contrast, the

computed diffractograms of the γ phase do not display sharp intense peaks that are not visible experimentally with the exception of the [002] in the case of $n_z=100$ at around 20° . The experimental 27.3° and 48° reflections are well reproduced by theory for all the different orientations of the γ phase but our model does not predict the two broader reflections at 30.5 and 31.8° and the three peaks centered at 48° .

In order to determine unambiguously the crystalline structure of the NR, we performed high-resolution electron microscopy experiments which show the presence of a ternary symmetry axis in the direction parallel to the thickness (Figure 4.a.), pointing towards the γ phase which contains this element of symmetry. We thus compared this crystallographic model and experimental observations from HAADF-STEM images (Figure 4). Let us first consider NR lying flat on TEM grids (Figures 4.a. to c.). Atoms are aligned in rows oriented at $58 \pm 3^\circ$ (averaged from 55 measurements) from the edge of the particle (measurement $n^\circ 3$ in Figure 4). Within this row, atoms are separated by 0.39 ± 0.01 nm (averaged from 155 measurements) whereas two atoms vertically aligned (from different rows) are distant by 0.40 ± 0.01 nm (averaged from 174 measurements, respectively measurements $n^\circ 1$ and 2). Computed distances on modelled $\gamma\text{-In}_2\text{S}_3$ NR viewed along the normal vector of their (001) plane (i.e. simulation of a NR viewed lying flat, with its thickness along the c axis) are in good agreement with these experimental observations: atoms are aligned in rows oriented at 60° with respect to the edges, whereas in-row atoms and vertically-aligned atoms are distant by 0.38 nm (resp. measurements $n^\circ 3$, 1 and 2). Fast Fourier transforms (FFT) from In_2S_3 NR HAADF-STEM images match with modelled electron diffraction patterns of $\gamma\text{-In}_2\text{S}_3$ (Figure 4.c. and 4.f.). Indeed, a 6-fold symmetry is observed on the FFT of HAADF-STEM images of In_2S_3 NR lying flat on the grid. d-spacing measurements are equal to those of modelled electron diffractogram of $\gamma\text{-In}_2\text{S}_3$ viewed along the [001] direction ($d=0.33$ nm for the first ring spots, $d=0.19$ nm for the second ring spots). All this confirms our hypothesis that the In_2S_3 NR are in the γ phase, with their thickness along the c -direction. HAADF-STEM images of In_2S_3 NR lying on their edge show an atomically bilayered thickness, that is also well reflected in our crystallographic model (Figure 4.d. to f.). The experimental thickness of this double layer ((0.71 ± 0.04) nm, averaged from 30 measurements) is close to the one given in our model (measurement $n^\circ 4$ in Figure 4.e., 0.64 nm). We stress, however, that although multiple experimental observations strongly suggest this attribution, our basic modelling of the X-ray diffractogram does not explain some experimental features such as the broad peaks found between 30 and 35° and the triple peak around 47° . We assume that this could be due to strain affecting the nanostructure, which is not taken into account in our modelling. This issue will require further investigation and will be reported later.

We now focus on the experimental conditions of the synthesis and more specifically on the role of the hydration of the

Fig. 4. (a.) HAADF-STEM images, (b.) crystallographic model viewed along the normal to the (001) plane, and (c.) Fourier transform of TEM images (yellow box) of In_2S_3 NR lying flat. - (d.) HAADF-STEM images, (e.) crystallographic model viewed along the normal to the (100) plane, and (f.) Fourier transform of TEM images (yellow box) of In_2S_3 NR lying on edge. Atomic models of $\gamma\text{-In}_2\text{S}_3$ NR have a thickness along the c-axis of a single conventional unit-cell. The Fourier transforms of the TEM images match the computed electron diffractograms of $\gamma\text{-In}_2\text{S}_3$ the modelled structure is observed respectively along the normals of the (001) and (100) planes. (g.) HAADF-STEM images of In_2S_3 NR. - (h.) Trigonal ($P\bar{3}m1$) $\gamma\text{-In}_2\text{S}_3$ conventional-cell crystallographic representation, along with bulk referenced cell parameters.

indium precursor. By using an aged batch of indium chloride that had taken up water during storage, we found that the amount of water in the synthesis determines the shape of the final nano-objects. When indium chloride is a minima octahydrated, long ultrathin In_2S_3 nanoribbons, as described before, are obtained. In contrast, when indium chloride is anhydrous, hexagonal nanoribbons (NR) are obtained (Figures 5.a. and S4). These hexagonal NR are regular, with an average apothem of (26.9 ± 0.5) nm (measured on 200 NR), although some are elongated along one direction (Figure S7). Hexagonal NR have the same composition as nanoribbons, as RBS measurements give a composition of the hexagons of 57 ± 1 % of sulfur and 43 ± 1 % of indium. The small excess of indium might reveal the presence of unreacted indium chloride from the reaction along In_2S_3 NR. To further understand the evolution of shape from hexagons to nanoribbons, we realized a series of syntheses varying the amount of water in the initial mixture. For one equivalent of anhydrous

indium (III) chloride, we added 0, 2, 4, 6, 8, and 10 equivalents of water. TEM images of the products of each synthesis are shown on Figure 5 and show various nano-objects with shapes depending on the amount of water added. Upon increasing water amount, the hexagons become smaller (up to twice smaller, with an average apothem of (14 ± 1) nm for 2 water equivalents added), before they completely disappear when 4 and more equivalents of water are added. NR with triangular shapes appear alongside hexagons for 2 to 6 equivalents of water (Figure 5.b.). The size of these equilateral triangles also decreases with increasing water amount, from an average side of 95 ± 3 nm to 16.8 ± 0.8 nm. As soon as 2 equivalents of water and more are present in the initial mixture, long nanoribbons appear and form bundles. According to TEM images, the number of long NR clearly increases with the amount of water in the medium. This agrees with a crude solution becoming gradually more and more viscoelastic as the water content increases. The NR length reaches

Fig. 5. TEM images of products of syntheses where only the amount of water is varied with respect to the amount of indium (III) chloride.

a maximum for 4 equivalents of water added (average length of $(1.2 \pm 0.1) \mu\text{m}$ and average width of $(7.3 \pm 0.2) \text{ nm}$, Figure 5.c.). When we increased further the water content from 6 to 10 equivalents we observed dispersions of pure NR with length of the same order of magnitude.

Water is thus a strong shape-directing agent as it triggers the anisotropic growth from hexagons to long 1D ribbons. We can therefore tune the aspect ratio of colloidal In_2S_3 nanoribbons by a factor of 20, from 50 to more than 1000. Although elucidating the atomic mechanism leading to this water-induced anisotropic growth will need further inquiry, previous reports have shown a strong effect of water on the synthesis of other materials. Bertrand *et al.* (34) have shown that water tunes the lateral aspect ratio for CdSe NR but in a trend opposite to ours since, in their study, increasing the water content decreases the aspect ratio. Trace amount of water has also been shown to inhibit the growth of InP quantum dots (35). In both cases, water is thought to be a source of hydroxyle ions which are known to bind strongly on semi-conducting nanoparticle surfaces (36). Hydroxyle adsorption on selected facets could slow down or enhance growth in a

preferred direction and thus explain the increase of the particle aspect ratio when water is present. In our case, the basic nature of the reacting medium where an excess of amine is present will indeed favor the formation of hydroxyles from water. Temperature and reaction time can be used to control the aspect ratio and length of the nanoribbons. Increasing one of these parameters engenders an increase in the length, width and number of NR (see SI).

When redispersed after synthesis in toluene, the NR appear bundled, as shown in Figure 6.a. Long aggregates of NR as large as $10 \mu\text{m}$ in length and 1 to $2 \mu\text{m}$ in width are observed in electron microscopy. These aggregates make the toluene dispersion hazy and sediment with time. The Small Angle X-ray Scattering (SAXS) patterns of NR dispersions in toluene (Figure 6.c.) display several sharp peaks which give information on the structure of the bundles. A first series of peaks at q^* , $2q^*$, and $3q^*$ where $q^* = 1.359 \text{ nm}^{-1}$, related to a period $d^* = 2\pi/q^* = 4.62 \text{ nm}$, is due to the lamellar stacking of the NR within the bundles. This stacking period is consistent with the length ($\ell \simeq 2 \text{ nm}$) of two oleylamine molecules plus the thickness of the NR. Then, two broad

Fig. 6. Bundling and unbundling of In_2S_3 NR dispersion, depending on the solvent for a concentration of 3.6 mg/mL (a.) TEM images of the dispersion at the same NR concentration in (a.) toluene and (b.) THF. Insets are pictures of the colloidal dispersions. (c.) SAXS patterns of a NR dispersion in a non-bundling solvent (THF, red symbols) and a bundling solvent (toluene, blue symbols). The former SAXS pattern is fitted to a model (black line) of polydisperse board-like parallelepipeds.

peaks at smaller angles (0.41 and 0.87 nm^{-1}), corresponding to periods of respectively 15.4 and 7.2 nm , arise from some short-range positional order within the plane of the NR. The corresponding distance is larger than $w + 2\ell = 12.7 \text{ nm}$ where w is the width of the NR. Therefore, the NR are loosely packed in the direction parallel to their width within the bundles. When tetrahydrofuran is used instead of toluene to disperse the NR, a clear and stable dispersion is obtained readily, indicating that the NR bundle do not form initially at this concentration (3.6 mg/mL) (Figure 6.b.). This is confirmed by the SAXS pattern shown on Figure 6.c. that does not display any peaks. Instead, the scattered intensity decreases regularly with increasing scattering angle, as expected for the form factor of isolated objects in solution. A fit of the SAXS pattern to a model of polydisperse board-like parallelepipeds (Figure 6.c.) displays excellent agreement with the data. The corresponding NR dimensions are 0.92 nm in thickness, 13.2 nm in width, and $1.2 \pm 0.34 \mu\text{m}$ in length, which agrees with the TEM measurements.

Dispersions of In_2S_3 nanoribbons in various organic solvents such as tetrahydrofuran, chloroform, and cyclohexane, were readily obtained and their most salient property is that they form gels at relatively low concentrations (Figure 7.a.,b.). With the density of bulk In_2S_3 of 4900 kg/m^3 , the last gel sample in the dilution series of Figure 7b has a volume fraction of 0.07% and, occasionally, a sample of volume fraction of only ca 0.01% was also found to form a gel (Figure S8). Such gelation thresholds are much lower than those ($\simeq 1\%$) reported for other (hydrophilic) mineral systems like swelling clay nanosheets, imogolite nanotubes, and V_2O_5 nanoribbons. (37–39) In fact, In_2S_3 nanoribbons have such a high gelling power for THF that they belong to the small class of so-called “supergelators” (i.e. below 0.1%) encountered with self-assembled fibrillar systems. (40–42) The low value of the percolating threshold in this system directly reflects the huge particle aspect ratio. Indeed, considering rod-like cylindrical particles, with $L = 1 \mu\text{m}$ and effective diameter $D = (1 \times 10)^{1/2} \simeq 3 \text{ nm}$, percolation is theoretically expected (43) at $D/2L = 0.15\%$, in good agreement with our estimates. These values are also similar to those experimentally observed ($\simeq 0.2\%$) with single-wall carbon nanotubes, which is another case of extremely anisotropic nanoparticles. (44) Observations by polarized-light microscopy of concentrated (20.5 g/L) gels in THF reveal a birefringent texture (Figure 7.c.) that is highly reminiscent of the threaded texture of nematic lyotropic liquid-crystals. (45) However, no clear isotropic/nematic biphasic domain could be detected, which is probably due to gelation. Observations of the same samples in natural light (Figure 7.d.) show a strong density contrast, which is usually not observed with nematic samples. This is most probably due to the existence at high concentration of a network of fibrils made of stacked In_2S_3 nanoribbons, reminiscent of the previously described NR bundling in toluene. (Figure 6) Moreover, taking advantage of the gel syneresis that occurred over 1-2 years, we investigated the gel/solvent interface by optical microscopy

Fig. 7. Gelation and birefringence properties of In_2S_3 nanoribbons. a) Dispersions of In_2S_3 particles in tetrahydrofuran, chloroform, and cyclohexane form gels. b) Series of vials filled with dispersions of In_2S_3 nanoribbons in THF at concentrations decreasing from left to right. The first four samples are gels whereas the last one is a sol. c) Birefringent texture of a dispersion of In_2S_3 nanoribbons in THF at 20.5 g/L placed between crossed polarizers. d) Image of the same sample observed in natural light (i.e. both the polarizer and analyzer have been removed). e) High-magnification image of the same sample, recorded at the gel/solvent interface, showing small spindle-like birefringent objects. f) Image of the same area observed after insertion of a wave-plate of slow axis denoted γ . (In images c), e), and f), the perpendicular double-headed arrows represent the directions of the crossed polarizer and analyzer.)

and detected there the presence of small, Brownian, wispy birefringent objects (Figure 7.e.). These objects likely represent a first nanoribbon-stacking stage leading eventually to the large fibrillar objects that form the threaded texture (Figure 7.c.). Upon insertion of a wave-plate in the microscope optical path, the wispy objects that have their main axis parallel (resp. perpendicular) to the slow axis, γ , of the wave-plate appear blue (resp. red-orange) on the pink background (Figure 7.f.). This means that the slow axis of these objects is their main axis. Because the birefringence of In_2S_3 nanoribbons is most probably dominated by their form-birefringence, which leads to their highest refractive index oriented along their length, we infer that each wispy object is made of stacked nanoribbons aligned along its main axis. (25)

Conclusion

To summarize, we successfully synthesized and characterized, using a combination of several techniques, indium sulfide nanoribbons with aspect ratio reaching 1000. The crystallographic structure of these very long and ultrathin NR is the $P\bar{3}m1$ trigonal structure, known also as the $\gamma\text{-In}_2\text{S}_3$ phase. Our work report several findings. First, it points towards the critical role of water in the anisotropic growth of NR. The indium salt precursors being highly hygroscopic, we underline here that adventitious addition of an uncontrolled amount of water in the reacting medium can strongly impact the lateral dimensions of the NR. Second, we show that the dispersion state of the NR strongly

depends on the solvent. In toluene, the NR aggregate into bundles whereas they are well-dispersed in THF, except at high concentrations. Moreover, dispersions of In_2S_3 NR in organic solvents at very low volume fractions can form gels whose rheological properties are worth investigating further and underlines the influence of nanoparticle shape on the flowing properties of their dispersions. Finally, we believe our work could open valuable perspectives for the design of functional highly anisotropic and ultra-thin nanomaterials since it could serve as a starting point for further ion exchange with potential applications beyond toxic Cd and Pb based semiconductors.

ACKNOWLEDGEMENTS

We acknowledge SOLEIL for provision of synchrotron radiation facilities and we would like to thank Thomas Bizien for assistance in using beamline SWING. This article is part of a project that has received funding from the European Research Council (ERC CoG SENECA) under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 865995) and was supported by the LABEX IMUST of the University of Lyon (ANR-10-LABX-0064), created within the program Investissements d'Avenir set up by the french government and managed by the French National Research Agency (ANR). This work benefited from the use of the SasView application, originally developed under NSF award DMR-0520547. SasView contains code developed with funding from the European Union's Horizon 2020 research and innovation programme under the SINE2020 project, grant agreement No 654000.

Bibliography

1. N. Barreau. Indium sulfide and relatives in the world of photovoltaics. *Solar Energy*, 83(3): 363–371, March 2009. ISSN 0038092X. doi: 10.1016/j.solener.2008.08.008.
2. E. Turan, M. Zor, M. Kul, A.S. Aybek, and T. Taskopru. $\alpha\text{-In}_2\text{S}_3$ and $\beta\text{-In}_2\text{S}_3$ phases produced by SILAR technique. *Philosophical Magazine*, 92(13):1716–1726, May 2012. ISSN 1478-6435, 1478-6443. doi: 10.1080/14786435.2012.657708.

3. E. Dalas, S. Sakkopoulos, E. Vitoratos, G. Maroulis, and L. Kobotiatis. Aqueous precipitation and electrical properties of In₂S₃: Characterization of the In₂S₃/polyaniline and In₂S₃/polypyrrole heterojunctions. *Journal of Materials Science*, 28(20):5456–5460, October 1993. ISSN 0022-2461, 1573-4803. doi: 10.1007/BF00367815.
4. Kang Hyun Park, Kwonho Jang, and Seung Uk Son. Synthesis, Optical Properties, and Self-Assembly of Ultrathin Hexagonal In₂S₃ Nanoplates. *Angewandte Chemie International Edition*, 45(28):4608–4612, 2006. ISSN 1521-3773. doi: 10.1002/anie.200601031.
5. Sung-Hyu Choe, Tae-Hwan Bang, Nam-Oh Kim, Hyung-Gon Kim, Choong-Il Lee, Moon-Seog Jin, Seok-Kyun Oh, and Wha-Tek Kim. Optical properties of β -In₂S₃ and β -In₂S₃·Co²⁺ single crystals. *Semiconductor Science and Technology*, 16(2):98–102, February 2001. ISSN 0268-1242, 1361-6641. doi: 10.1088/0268-1242/16/2/307.
6. S. Gorai, P. Guha, D. Ganguli, and S. Chaudhuri. Chemical synthesis of β -In₂S₃ powder and its optical characterization. *Materials Chemistry and Physics*, 82(3):974–979, December 2003. ISSN 02540584. doi: 10.1016/j.matchemphys.2003.08.013.
7. Jiang Tang, Gerasimos Konstantatos, Sean Hinds, Stefan Myrskog, Andras G. Pattantyus-Abraham, Jason Clifford, and Edward H. Sargent. Heavy-Metal-Free Solution-Processed Nanoparticle-Based Photodetectors: Doping of Intrinsic Vacancies Enables Engineering of Sensitivity and Speed. *ACS Nano*, 3(2):331–338, February 2009. ISSN 1936-0851. doi: 10.1021/nn800718u.
8. Shinjita Acharya, Mrinal Dutta, Suresh Sarkar, Durga Basak, Supriyo Chakraborty, and Narayan Pradhan. Synthesis of Micrometer Length Indium Sulfide Nanosheets and Study of Their Dopant Induced Photoresponse Properties. *Chemistry of Materials*, 24(10):1779–1785, May 2012. ISSN 0897-4756. doi: 10.1021/cm3003063.
9. Ming Li, Xinglong Tu, Yanjie Su, Jing Lu, Jing Hu, Baofang Cai, Zhihua Zhou, Zhi Yang, and Yafei Zhang. Controlled growth of vertically aligned ultrathin In₂S₃ nanosheet arrays for photoelectrochemical water splitting. *Nanoscale*, 10(3):1153–1161, January 2018. ISSN 2040-3372. doi: 10.1039/C7NR06182J.
10. Yu Hee Kim, Jong Hak Lee, Dong-Wook Shin, Sung Min Park, Jin Soo Moon, Jung Gyu Nam, and Ji-Beom Yoo. Synthesis of shape-controlled β -In₂S₃ nanotubes through oriented attachment of nanoparticles. *Chemical Communications*, 46(13):2292, 2010. ISSN 1359-7345, 1364-548X. doi: 10.1039/b922366e.
11. Matthew A. Franzman and Richard L. Brutchey. Solution-Phase Synthesis of Well-Defined Indium Sulfide Nanorods. *Chemistry of Materials*, 21(9):1790–1792, May 2009. ISSN 0897-4756, 1520-5002. doi: 10.1021/cm9002004.
12. Shinjita Acharya, Suresh Sarkar, and Narayan Pradhan. Subnanometer Thin beta Indium Sulfide Nanosheets. *The Journal of Physical Chemistry Letters*, 3(24):3812–3817, December 2012. ISSN 1948-7185. doi: 10.1021/jz301796m.
13. Suresh Sarkar, Alice D. P. Leach, and Janet E. Macdonald. Folded Nanosheets: A New Mechanism for Nanodisk Formation. *Chemistry of Materials*, 28(12):4324–4330, June 2016. ISSN 0897-4756. doi: 10.1021/acs.chemmater.6b01279.
14. Bing Ni, Hailing Liu, Peng-peng Wang, Jie He, and Xun Wang. General synthesis of inorganic single-walled nanotubes. *Nature Communications*, 6(1):8756, December 2015. ISSN 2041-1723. doi: 10.1038/ncomms9756.
15. Peng-peng Wang, Yong Yang, Jing Zhuang, and Xun Wang. Self-Adjustable Crystalline Inorganic Nanocoils. *Journal of the American Chemical Society*, 135(18):6834–6837, May 2013. ISSN 0002-7863, 1520-5126. doi: 10.1021/ja403065z.
16. Yang Tian, Ligang Wang, Hanqin Tang, and Weiwei Zhou. Ultrathin two-dimensional β -In₂S₃ nanocrystals: Oriented-attachment growth controlled by metal ions and photoelectrochemical properties. *Journal of Materials Chemistry A*, 3(21):11294–11301, May 2015. ISSN 2050-7496. doi: 10.1039/C5TA01958C.
17. Hai-Yan Wang, Xiao-Feng Li, Lei Xu, Xu-Sheng Li, and Qian-Ku Hu. Phase Transition and Physical Properties of InS. *Communications in Theoretical Physics*, 69(2):211, February 2018. ISSN 0253-6102. doi: 10.1088/0253-6102/69/2/211.
18. Anuja Datta, Soma Gorai, Subhendu Kumar Panda, and Subhadra Chaudhuri. A Simple Route to the Synthesis of Crystalline InS Nanowires from Indium Foil. *Crystal Growth & Design*, 6(4):1010–1013, April 2006. ISSN 1528-7483, 1528-7505. doi: 10.1021/cg050649l.
19. S. Gorai, A. Datta, and S. Chaudhuri. Solvothermal synthesis and characterization of InS. *Materials Letters*, 59(24-25):3050–3053, October 2005. ISSN 0167577X. doi: 10.1016/j.matlet.2005.05.017.
20. Cameron F. Holder and Raymond E. Schaak. Tutorial on Powder X-ray Diffraction for Characterizing Nanoscale Materials. *ACS Nano*, 13(7):7359–7365, July 2019. ISSN 1936-0851. doi: 10.1021/acsnano.9b05157.
21. Paul Pistor, Jose M. Merino Álvarez, Máximo León, Marco di Michiel, Susan Schorr, Reiner Klenk, and Sebastian Lehmann. Structure reinvestigation of α -, β - and γ -In₂S₃. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials*, 72(3):410–415, June 2016. ISSN 2052-5206. doi: 10.1107/S2052520616007058.
22. R. Diehl, C.-D. Carpentier, and R. Nitsche. The crystal structure of γ -In₂S₃ stabilized by As or Sb. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry*, 32(4):1257–1260, April 1976. ISSN 0567-7408. doi: 10.1107/S0567740876005062.
23. Fabian Matter, Ana Laura Luna, and Markus Niederberger. From colloidal dispersions to aerogels: How to master nanoparticle gelation. *Nano Today*, 30:100827, 2020. ISSN 1748-0132. doi: 10.1016/j.nantod.2019.100827.
24. Zachary M. Sherman, Allison M. Green, Michael P. Howard, Eric V. Anslyn, Thomas M. Truskett, and Delia J. Milliron. Colloidal Nanocrystal Gels from Thermodynamic Principles. *Accounts of Chemical Research*, 54(4):798–807, 2021. ISSN 0001-4842. doi: 10.1021/acs.accounts.0c00796. Publisher: American Chemical Society.
25. Allison M. Green, Charles K. Ofosu, Jiho Kang, Eric V. Anslyn, Thomas M. Truskett, and Delia J. Milliron. Assembling Inorganic Nanocrystal Gels. *Nano Letters*, 22(4):1457–1466, February 2022. ISSN 1530-6984, 1530-6992. doi: 10.1021/acs.nanolett.1c04707. arXiv: 2112.05778.
26. Emanuela Zaccarelli. Colloidal gels: equilibrium and non-equilibrium routes. *Journal of Physics: Condensed Matter*, 19(32):323101, 2007. ISSN 0953-8984, 1361-648X. doi: 10.1088/0953-8984/19/32/323101.
27. Shalini Singh, Renu Tomar, Stephanie ten Brinck, Jonathan De Roo, Pieter Geiregat, José C. Martins, Ivan Infante, and Zeger Hens. Colloidal CdSe Nanoplatelets, A Model for Surface Chemistry/Optoelectronic Property Relations in Semiconductor Nanocrystals. *Journal of the American Chemical Society*, 140(41):13292–13300, October 2018. ISSN 0002-7863. doi: 10.1021/jacs.8b07566.
28. Yang Zhou, Fudong Wang, and William E. Buhro. Large Exciton Energy Shifts by Reversible Surface Exchange in 2D II–VI Nanocrystals. *Journal of the American Chemical Society*, 137(48):15198–15208, December 2015. ISSN 0002-7863. doi: 10.1021/jacs.5b09343.
29. Yang Zhou and William E. Buhro. Reversible Exchange of L-Type and Bound-Ion-Pair X-Type Ligation on Cadmium Selenide Quantum Belts. *Journal of the American Chemical Society*, 139(37):12887–12890, September 2017. ISSN 0002-7863. doi: 10.1021/jacs.7b05167.
30. Fangmin Ye, Cen Wang, Gaohui Du, Xubin Chen, Yijun Zhong, and J. Z. Jiang. Large-scale synthesis of In₂S₃ nanosheets and their rechargeable lithium-ion battery. *Journal of Materials Chemistry*, 21(43):17063–17065, October 2011. ISSN 1364-5501. doi: 10.1039/C1JM12937F.
31. Yan Xing, Hongjie Zhang, Shuyan Song, Jing Feng, Yongqian Lei, Lijun Zhao, and Meiyi Li. Hydrothermal synthesis and photoluminescent properties of stacked indium sulfide superstructures. *Chemical Communications*, (12):1476, 2008. ISSN 1359-7345, 1364-548X. doi: 10.1039/b717512d.
32. Ahmed Lutfi Abdelhady, Karthik Ramasamy, Mohammad A. Malik, and Paul O'Brien. Very narrow In₂S₃ nanorods and nanowires from a single source precursor. *Materials Letters*, 99:138–141, May 2013. ISSN 0167-577X. doi: 10.1016/j.matlet.2013.02.061.
33. Weimin Du, Jun Zhu, Shixiong Li, and Xuefeng Zhang. Ultrathin β -In₂S₃ Nanobelts: Shape-Controlled Synthesis and Optical and Photocatalytic Properties. *Crystal Growth & Design*, 8(7):2130–2136, July 2008. ISSN 1528-7483. doi: 10.1021/cg7009258.
34. Guillaume H. V. Bertrand, Anatolii Polovitsyn, Sotirios Christodoulou, Ali Hossain Khan, and Iwan Moreels. Shape control of zincblende CdSe nanoplatelets. *Chemical Communications*, 52(80):11975–11978, 2016. ISSN 1359-7345, 1364-548X. doi: 10.1039/C6CC05705E.
35. Lisi Xie, Daniel K. Harris, Mouni G. Bawendi, and Klavs F. Jensen. Effect of Trace Water on the Growth of Indium Phosphide Quantum Dots. *Chemistry of Materials*, 27(14):5058–5063, July 2015. ISSN 0897-4756, 1520-5002. doi: 10.1021/acs.chemmater.5b01626.
36. Danylo Zhrebetskyy, Marcus Scheele, Yingjie Zhang, Noah Bronstein, Christopher Thompson, David Britt, Miquel Salmeron, Paul Alivisatos, and Lin-Wang Wang. Hydroxylation of the surface of PbS nanocrystals passivated with oleic acid. *Science*, 344(6190):1380–1384, June 2014. ISSN 0036-8075, 1095-9203. doi: 10.1126/science.1252727.
37. E. Paineau, K. Antonova, C. Baravian, I. Bihannic, P. Davidson, I. Dozov, M. Impérator-Clerc, P. Levitz, A. Madsen, F. Meneau, and L. J. Michot. Liquid-Crystalline Nematic Phase in Aqueous Suspensions of a Disk-Shaped Natural Beidellite Clay. *The Journal of Physical Chemistry B*, 113(48):15858–15869, 2009. ISSN 1520-6106. doi: 10.1021/jp908326y.
38. Erwan Paineau, Marie-Eve M. Krapf, Mohamed-Salah Amara, Natalia V. Matskova, Ivan Dozov, Stéphan Rouzière, Antoine Thill, Pascale Launois, and Patrick Davidson. A liquid-crystalline hexagonal columnar phase in highly-dilute suspensions of imogolite nanotubes. *Nature Communications*, 7(1):10271, 2016. ISSN 2041-1723. doi: 10.1038/ncomms10271.
39. Patrick Davidson. Vanadium pentoxide gels: From “chimie douce” to “matière molle”. *Comptes Rendus Chimie*, 13(1-2):142–153, 2010. ISSN 16310748. doi: 10.1016/j.crci.2009.04.002.
40. Baiju P. Krishnan and Kana M. Sureshan. A Library of Multipurpose Supramolecular Supergelators: Fabrication of Structured Silica, Porous Plastics, and Fluorescent Gels. *Chemistry - An Asian Journal*, 13(2):187–193, 2018. ISSN 18614728. doi: 10.1002/asia.201701657.
41. Mladen Žinic, Fritz Vögtle, and Frédéric Fages. Cholesterol-Based Gelators. In *Low Molecular Mass Gelator*, volume 256, pages 39–76. Springer Berlin Heidelberg, Berlin, Heidelberg, 2005. ISBN 978-3-540-25321-1 978-3-540-31460-8. doi: 10.1007/b107171. Series Title: Topics in Current Chemistry.
42. Richard G Weiss and Pierre Terech. *Molecular Gels: Materials with self-assembled fibrillar networks*. Springer, Dordrecht, 2006. ISBN 978-94-017-7632-5.
43. I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner. Excluded volume and its relation to the onset of percolation. *Physical Review B*, 30(7):3933–3943, October 1984. doi: 10.1103/PhysRevB.30.3933.
44. Fangming Du, Robert C. Scogna, Wei Zhou, Stijn Brand, John E. Fischer, and Karen I. Winey. Nanotube Networks in Polymer Nanocomposites: Rheology and Electrical Conductivity. *Macromolecules*, 37(24):9048–9055, November 2004. ISSN 0024-9297. doi: 10.1021/ma049164g.
45. P. G. de Gennes. *The Physics of Liquid Crystals*. Clarendon Press, Oxford, 2 edition, 1995. ISBN 978-0-19-851785-6.