

Nano Focus

Sub-1-nm nanowires bridge inorganic and polymer-like properties

Inorganic materials including ceramics or metals are the main components of most functional devices used for energy conversion, catalysis, and electronic displays. Due to their crystalline nature and strong covalent ionic bonds, these materials are stiff and strong and require high temperatures or pressures to be processed. In contrast, organic materials like polymers and biomolecules are highly flexible and can exhibit liquid-like properties and self-assemble under ambient conditions.

Synthesizing inorganic materials with polymer-like properties would thus facilitate the fabrication of multifunctional devices for a variety of practical applications, especially in the optical and energy fields.

As described in *ACS Materials Letters* (doi:10.1021/acsmaterialslett.0c00149), S. Zhang and X. Wang from Tsinghua University, China, propose to realize such materials using sub-1-nm inorganic materials. Such nanomaterials have a high-aspect ratio with one dimension under 1 nm. With a higher number of atoms directly at the surface, as compared to bulk atoms, inorganic nanowires,

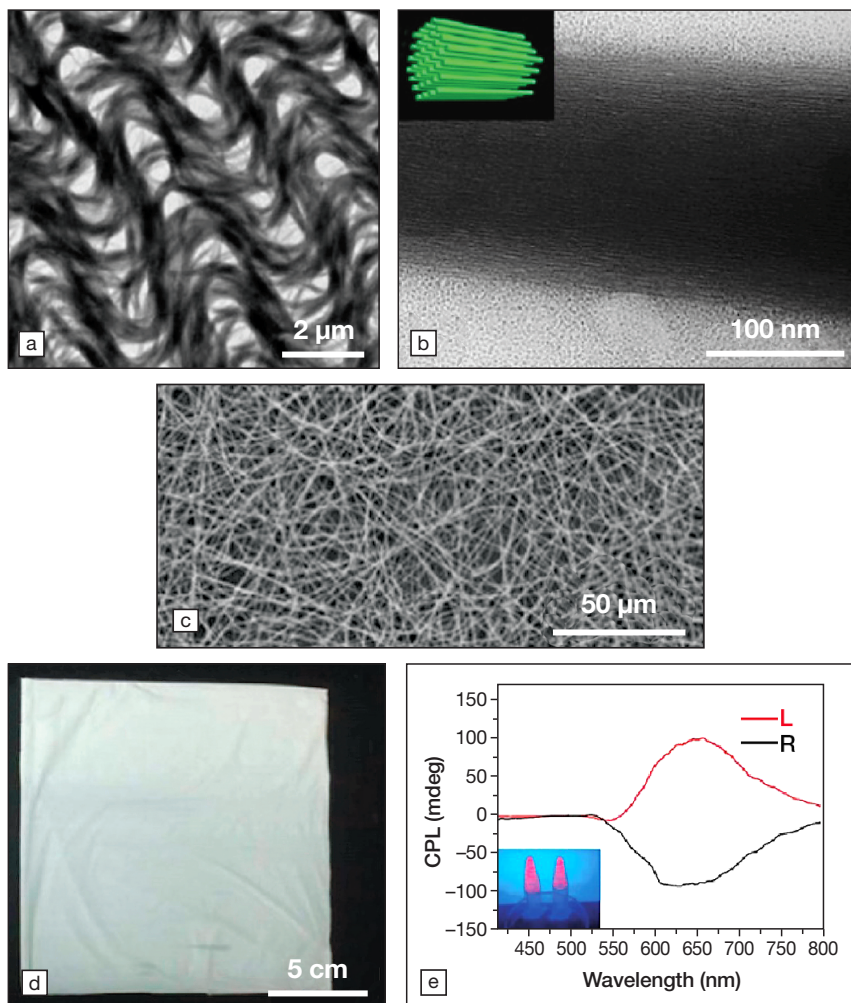
nanocoils, or nanohelices exhibit excellent optical and catalytic properties.

Similar to polymer chains, sub-1-nm materials have low crystallinity and low internal cohesive energy, of about tens of $\text{kJ}\cdot\text{mol}^{-1}$. This is orders of magnitude lower than the energies of covalent and ionic bonds of several hundreds and thousands $\text{kJ}\cdot\text{mol}^{-1}$, respectively. With such a low internal energy, sub-1-nm nanowires (SNWs) are not only flexible, they can also self-assemble via weak surface interactions such as Van der Waals and hydrogen bonds. Several recent studies have reported bendable and flexible ultra-high-aspect-ratio nanowires made of tungsten oxides, indium sulphide, gadolinium oxyhydroxide (GdOOH), to name a few, that can self-assemble into ordered structures (see Figures a and b).

With polymer-like morphologies and physical properties, SNWs also share similar processing methods. For example, when suspended in solvents, they form viscous fluids that can flow under shear. By applying wet methods like electrospinning or wet spinning, non-woven meshes can be obtained. Meshes fabricated using GdOOH SNWs retain the high modulus and tensile strength of each individual inorganic fiber, of 10.3 GPa and 712.5 MPa, respectively, while being flexible macroscopically (see Figures c and d).

The processability and flexibility of sub-1-nm inorganic materials make them particularly interesting for applications in optics. For example, the high anisotropy of SNWs and their inorganic character can be used to create age- and moisture-resistant films that are birefringent in the visible spectrum and polarized UV light. Some SNWs like those obtained with GdOOH also have chiral properties and self-assemble into macroscopic helices through evaporation-induced self-assembly. When the GdOOH SNWs are combined with a fluorescent dye, chiral fluorescence can be recorded from the helicoidal structures (see Figure e). This may open unexplored fields of research.

Combining functional performance from the inorganic components with the structural properties of polymers is expected to lead to many applications. For



Gadolinium oxyhydroxide sub-1-nm nanowires (GdOOH SNWs): Electron micrographs of (a) entangled SNWs, (b) an electrospun fiber with individual GdOOH SNWs aligned inside (see model in the inset), (c) an electrospun mesh. (d) Picture of a large-scale electrospun film. (e) Circularly polarized luminescence (CPL) spectrum of the macroscopic helicoidal assemblies of GdOOH SNWs containing a fluorescent dye. L and R stand for the left- and right-handed helicity, respectively. Credit: American Chemical Society.

example, “flexible solar cells have been limited in their applications due to their poor bending capacity. The approaches described by Zhang et al. have thus exciting implications for tailored support structures that improve the flexibility and durability

of solar cells,” say Michel Nasilowski and Dane deQuilettes from the GridEdge Solar research program at the Massachusetts Institute of Technology.

Sub-1-nm inorganic materials also have the potential to achieve multifunctionality

and performance with recyclability and less chemical waste. “The synthesis procedures of such nanomaterials are very simple ... while using ordinary equipment and nontoxic solvents,” Wang says.

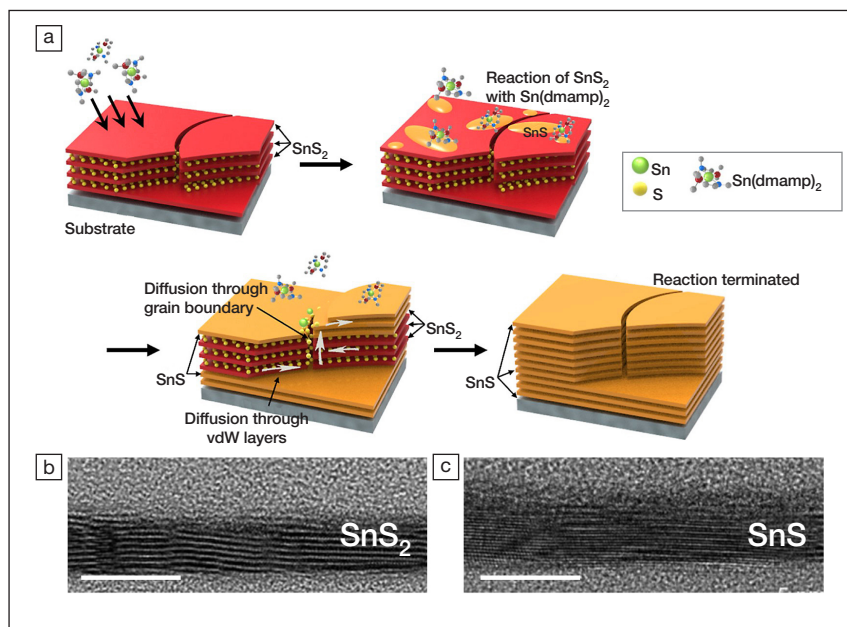
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Atomic layer deposition transforms SnS_2 into SnS

Song Keun Kim of the Korea Institute of Science and Technology, Republic of Korea, and co-workers have devised an *in situ* transformation as a new strategy to synthesize metal chalcogenides. They specifically demonstrated that exposing SnS_2 nanosheets to the vapor of bis(1-dimethylamino-2-methyl-2-propoxy)tin(II) ($\text{Sn}(\text{dmamp})_2$) reduced SnS_2 to SnS with a high purity yield. This finding has been published in *Chemistry of Materials* (doi: 10.1021/acs.chemmater.9b04387).

The SnS_2 -to-SnS transformation was accomplished using atomic layer deposition (ALD). ALD deposits thin films onto a substrate by stacking one atomic layer per reaction cycle. The researchers first grew a 4-nm-thick SnS_2 film onto a SiO_2 substrate, using $\text{Sn}(\text{dmamp})_2$ and H_2S as the sources of Sn and S, respectively. Subsequently, H_2S gas was eliminated, and they exposed the SnS_2 thin film to only the vapor of $\text{Sn}(\text{dmamp})_2$ (1.06 Torr) at 270°C. In each reaction cycle, the exposure lasted for 2 s followed by purging for 10 s. After at least 200 cycles, the researchers confirmed that SnS_2 was fully converted to SnS according to the lattice spacing measured by transmission electron microscopy, as well as a characteristic vibrational peak of SnS detected using Raman spectroscopy.

The discovery of this phase transformation occurred by serendipity. Kim, the corresponding author, says that the research team initially “... tried to fabricate vertical *p-n* junction diodes by stacking *p*-type SnS layers on *n*-type SnS_2 layers using ALD.” However, instead of a double-layered SnS_2/SnS heterostructure, they discovered that they had obtained a pure SnS thin film.



(a) The process of the transformation from SnS_2 to SnS, where (dmamp)₂ is bis(1-dimethylamino-2-methyl-2-propoxy)tin(II); transmission electron microscope images of (b) SnS_2 and (c) SnS. Scale bars represent 10 nm. Credit: *Chemistry of Materials*.

The mechanism of the transformation is associated with Sn^{2+} adsorption and S diffusion. Upon contacting SnS_2 , $\text{Sn}(\text{dmamp})_2$ adsorbed onto SnS_2 , and the dmamp ligands decomposed into volatile products, including acetone. The adsorbed Sn^{2+} then combined with the S atoms within the surface. With the reaction cycle repeated, the S atoms on the surface were mainly consumed, and those buried inside the SnS_2 thin film started to diffuse upward to replenish the surface through grain boundaries. The transformation self-terminated once all the S atoms were reacted and, therefore, thoroughly converted SnS_2 to SnS.

Yu Song of Northeastern University, China, whose research deals with two-dimensional (2D) metal dichalcogenides, says, “The *in situ* conversion strategy opens a new gate to the synthesis of

continuous, high-quality, and large-area 2D metal chalcogenide thin films with tunable electronic and optical properties.” Song was not involved in this study.

Projecting forward, Kim says that his research team is developing strategies to address the challenge of thickness uniformity of the SnS films. “The polycrystalline SnS_2 layer was adopted as the parent material to transform into SnS. The polycrystalline nature of the ALD-grown SnS_2 layer inevitably results in nonuniformity in the thickness of the transformed SnS and generation of defects in the SnS layer,” Kim says. He envisions that this ALD-based conversion will be useful to synthesize a plethora of transition-metal chalcogenide pairs, including $\text{SnSe}/\text{SnSe}_2$, $\text{BiTe}/\text{Bi}_2\text{Te}_3$, and Cu_2S & CuS .

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