Inorganic Chemistry

Semiconductors Go Green

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A relatively new, but growing, field of study focuses on synthesizing semiconducting materials from benign, Earth-abundant elements (see “What’s Earth-Abundance?”). Many commercial semiconductors contain cadmium, mercury, lead, arsenic, or selenium. The use of these toxic elements is facing stringent limitations in an increasingly restrictive regulatory environment.

Challenges for developing green semiconductors include bringing their performance up to par and narrowing their emissions bands by increasing particle uniformity. Four recent papers illustrate ways to accomplish these goals.

What’s Earth-Abundance?

Earth-abundance refers to the total percentage of an element within the Earth’s crust. However, some of these Earth-abundant elements are not easy to obtain in commercial quantities. Indium and some rare earth elements are as abundant as nickel or copper, but separating these elements from the native ore requires complex procedures. Some rare earth elements are available only from a few areas in the world. Thus, “green” semiconductors are made from elements that are not only Earth-abundant but also easily obtained.

Green alternatives in quantum dots

Peter Reiss and colleagues at the University of Grenoble (France) and Sikkim University (India) reviewed the state of the art in quantum dot semiconductors made from benign, abundant elements. One notable example is nanostructured carbon, which exhibits semiconducting behavior, even though bulk carbon does not.

The fullerenes C_{60} and C_{70} have band gaps of 1.86 eV and 1.56 eV, respectively (see “Semiconductor Band Gaps”).

Graphene with adsorbed hydrogen and graphene quantum dots are also semiconducting. Carbon nanodots can be made from food and agricultural waste. They are strongly luminescent and biocompatible, and they have good chemical and photostability. (*Chem. Rev.* DOI: 10.1021/acs.chemrev.6b00116)

Semiconductor Band Gaps

Using silicon (band gap 1.12 eV at 300 K) as a reference point, narrow semiconductor band gaps are less than ≈1 eV; intermediate band gaps are ≈1–2, eV; and wide band gaps are on the order of 2–3 eV.

Tin (II) sulfide

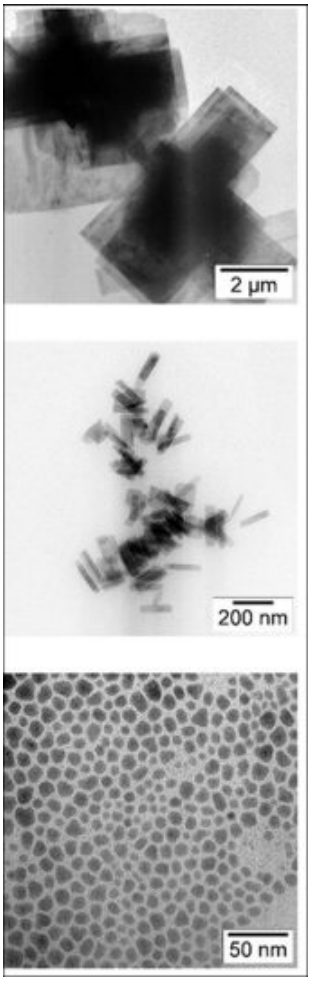

Figure 1

Tin monosulfide (SnS) has optical properties similar to those of silicon. It has an intermediate-width band gap, and it absorbs visible light. This material is a potentially strong candidate for optoelectronic devices, but small carrier diffusion lengths within the absorber SnS layers and poor alignment between SnS layers and the adjacent charge-transport layers have limited its application so far.

Edwin Heilweil and co-workers at NIST (Gaithersburg, MD) determined the charge carrier mobility and dynamics for films composed of SnS colloidal particles. They used time-resolved terahertz spectroscopy, which can track charge separation, relaxation, and trapping processes with subpicosecond resolution.

Instead of using vapor deposition to make colloidal SnS films, they used solution chemistry to form spherical nanoparticles, 2-D nanosheets, and 2-D micrometer-size sheets. Particles irradiated with 800 nm (near-infrared) light had initial relaxation

times that were slightly longer than for other reported nanoscale semiconductors. This allows the SnS charge carriers to produce more electrical current and generate less heat.

Figure 1 shows transmission electron microscopy images of the nanoparticles (bottom), nanosheets (center), and microsheets (top).

The authors found that particle size has a strong influence on charge carrier dynamics and mobility. Annealing the film to remove the surface-stabilizing oleylamine ligands and sinter adjacent crystallites together improved charge carrier mobility by as much as 5-fold for films made from nanospheres and nanosheets, and as much as 20% for films made from the micrometer-size sheets. (*J. Phys. Chem. C* DOI: 10.1021/acs.jpcc.6b01684)

Tin(IV) sulfide

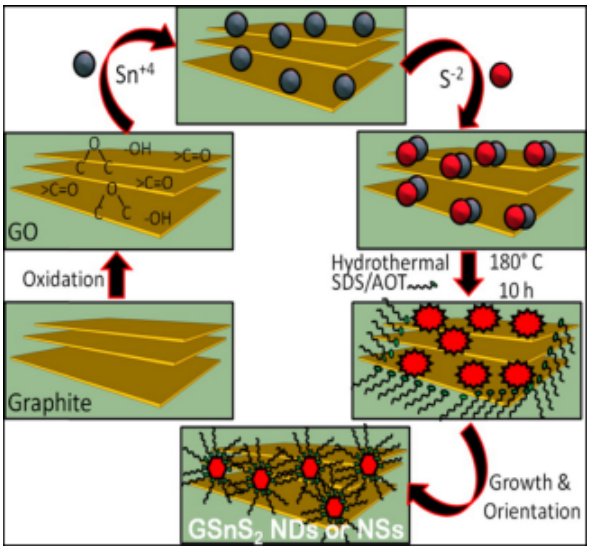

Figure 2

Tin disulfide (SnS_2) has potential uses in sensing, photovoltaics, and energy storage materials. It has a moderate optical band gap; and it absorbs in the visible light range, making it a candidate for applications that use solar energy.

Sasanka Deka and colleagues at the University of Delhi used a one-pot hydrothermal synthesis to make layered composites with SnS_2 nanodisks and nanosheets sandwiched between sheets of graphene. These composites combine the exciton generation and charge separation of SnS_2 with the charge-transport capabilities of graphene. Figure 2 is a schematic view of their synthesis procedure.

The authors used their SnS_2–graphene composite as a heterogeneous photocatalyst to convert nitrobenzene to aniline with a 99.9% yield and absolute selectivity. The composite also reduces toxic Cr(VI) to nontoxic Cr(III) and decomposes the mutagenic organic dyes methylene blue and rhodamine blue under visible light and ambient conditions. (*ACS Omega* DOI: 10.1021/acsomega.6b00042)

Adding complexity

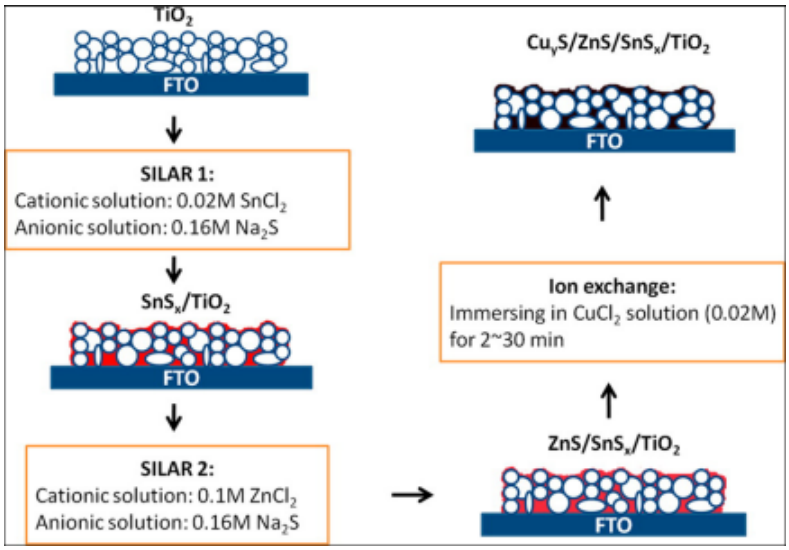

Figure 3

Copper zinc tin sulfide (Cu_2ZnSnS_4, CZTS) is a candidate to replace toxic copper indium gallium selenide; but because of its complexity, it tends to form secondary phases and crystal inhomogeneities. CZTS, however, has a possible application as a light absorber in devices that use a second material as a conductor. Such devices can perform well even when their components have some defects and impurities.

Zhuoran Wang and George Demopoulos* at McGill University (Montreal) demonstrated the feasibility of this strategy by making photoanodes from conducting films of mesoporous anatase (TiO_2) coated with nanoscale CZTS. To ensure good adhesion between the two layers, they used a three-step solution deposition–exchange process to grow the CZTS in situ onto the anatase substrate. They then annealed the film to crystallize it. Figure 3 shows a schematic of their process; “SILAR” is successive ionic layer adsorption and reaction.]

The authors removed impurity phases by etching the CZTS film with aqueous HCl, which increased the carrier lifetime from 7.9 to 8.7 ns. Their etched thin films show an excellent light absorption response and a band gap that approaches the theoretical value of 1.5 eV. (*Cryst. Growth Des.* DOI: 10.1021/acs.cgd.6b00033)

Green is looking good

Much remains to be done to bring materials like tin sulfide and carbon up to the standards of cadmium sulfide, indium arsenide, and other toxic or expensive semiconductors. Improved synthesis and processing techniques, however, have generated some very promising performance gains. Coupling “green” semiconductors with equally green conducting layers makes it possible to use less-than-perfect materials efficiently while opening up a wide variety of possible absorber–conductor combinations.

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