

# Dye-Sensitized Solar Cell Goes Solid

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Dye-sensitized solar cells (DSCs), invented by Grätzel and O'Regan in 1991, offer the prospect of replacing conventional solid-state photovoltaic devices made with a significant amount of the semiconductor material silicon.<sup>[1,2]</sup> DSCs have generated excitement because they consist mainly of non-toxic materials and offer a low-cost processing route (such as coating or printing) to thin-film device fabrication. Furthermore, they can be adapted for a variety of indoor and outdoor applications, and achieve high performance with minimal environmental impact. A DSC operates based on the interactions between the cell's anode and cathode, and a film of titanium oxide nanoparticles covered with light-sensitive dye molecules. An electrolyte, usually in form of iodide, fills the space between the TiO<sub>2</sub> nanoparticles, and helps transfer electrons from the cathode to the dye molecules. The fabrication of DSCs typically requires an electrolyte that enables high charge-collection efficiencies and high open-circuit voltages. The iodide electrolyte is particularly attractive in this regard as its oxidized form, I<sub>3</sub><sup>-</sup>, does not readily accept electrons from the titania surface. This minimizes charge recombination in functioning cell devices. Despite all the benefit and relatively high conversion efficiencies for solar energy, DSCs typically have durability issues associated with the liquid electrolyte, such as electrode corrosion or electrolyte leakage. These issues have led to a significant decrease in conversion efficiency, making these solar cells unsuitable for long-term use.

Although numerous attempts have been made to replace the liquid electrolytes with a wide range of materials, including *p*-type semiconductors, organic hole-conducting polymers, organic ionic crystals, and ionic gel electrolytes, the efficiency is compromised as a result of either poor

filling of solid electrolytes or the low conductivity nature of the polymers.<sup>[3-6]</sup> For example, in 2010, Feldt et al. reported iodide-free electrolytes using cobalt polypyridine complexes for DSCs. The best efficiency obtained from this study was only 6.7%.<sup>[7]</sup> An energy-conversion efficiency of 7.5% was reported in 2011 by Daeneke and co-workers,<sup>[8]</sup> who utilized ferrocene-based electrolytes combined with a novel metal-free organic donor-acceptor sensitizer. Very recently, Yella et al. showed a power-conversion efficiency of 12.3% under one-sun illumination by utilizing electrolytes containing cobalt complexes.<sup>[9]</sup> However, the volatile and corrosive nature of the electrolytes still complicates the manufacture of the cells.

Writing in *Nature*, Kanatzidis and Chang and their colleagues<sup>[10]</sup> now provide a much needed solution. The authors demonstrated the use of a new type of DSC, created using a solid-state *p*-type semiconductor CsSnI<sub>3</sub> doped with fluorine. The CsSnI<sub>3</sub> compound adopts a distorted 3D perovskite structure and features a sharp optical absorption edge at 1.3 eV (**Figure 1**). A high hole mobility ( $\mu_h = 585 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) for this compound was obtained at room temperature. More importantly, the dye cell equipped with the CsSnI<sub>3</sub> compound instead of conventional liquid electrolytes containing the iodide/tri-iodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) redox couple enables a remarkable energy-conversion efficiency of ~10.2%.

The discovery of CsSnI<sub>3</sub>-based DSCs is especially notable because it provides for the first time an all solid-state DSC that may ultimately exceed the performance of conventional liquid electrolyte-based DSCs. The CsSnI<sub>3</sub> hole-conducting compound is made of inexpensive, Earth-abundant elements and is solution-processable. As an added benefit, this compound has enhanced absorption in the red and near-infrared spectral regions, increasing the cell's conversion potential.

To understand how the CsSnI<sub>3</sub>-based cell works, we must review the basics of the Grätzel cell. The Grätzel cell can be regarded as a photoelectrochemical cell where redox couples such as I<sup>-</sup>/I<sub>3</sub><sup>-</sup> or cobalt-based complexes are required. The charge-transport mechanism in the Grätzel cell is dominated by ionic conduction controlled by electrochemical diffusion. When a dye molecule injects an electron, it has to be replenished by a hole-transporting material, usually employing a redox couple. In stark contrast, the CsSnI<sub>3</sub>-based cell does not rely on the electrochemical process in the operation of the cell. The nature of the charge transport in the CsSnI<sub>3</sub>-based dye cell (referred to as the Kanatzidis-Chang cell) is mainly hole conduction (**Figure 2a**), which is influenced by charge-carrier mobility. The oxidized dye molecule, in the case of CsSnI<sub>3</sub>-based dye cells, can be quickly transported toward the cathode due to highly conducting *p*-type CsSnI<sub>3</sub> (**Figure 2b**). The hole-conducting CsSnI<sub>3</sub> helps electrons and holes escape

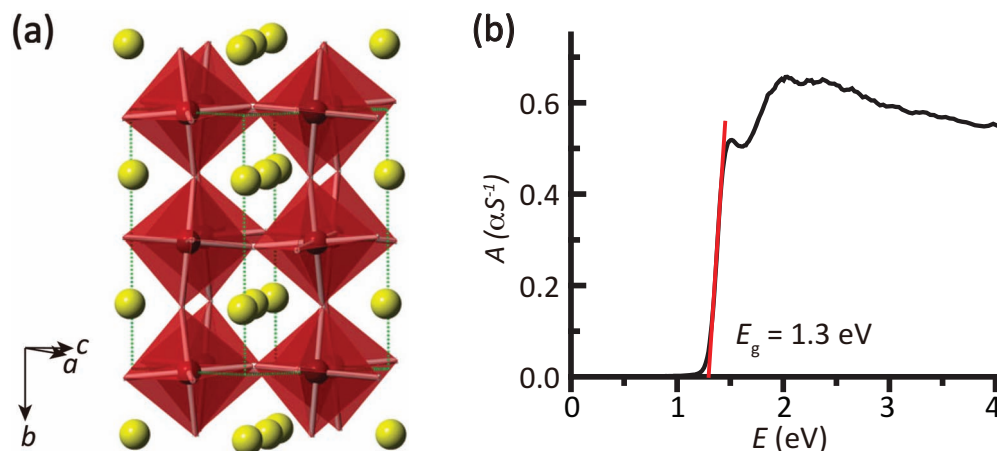
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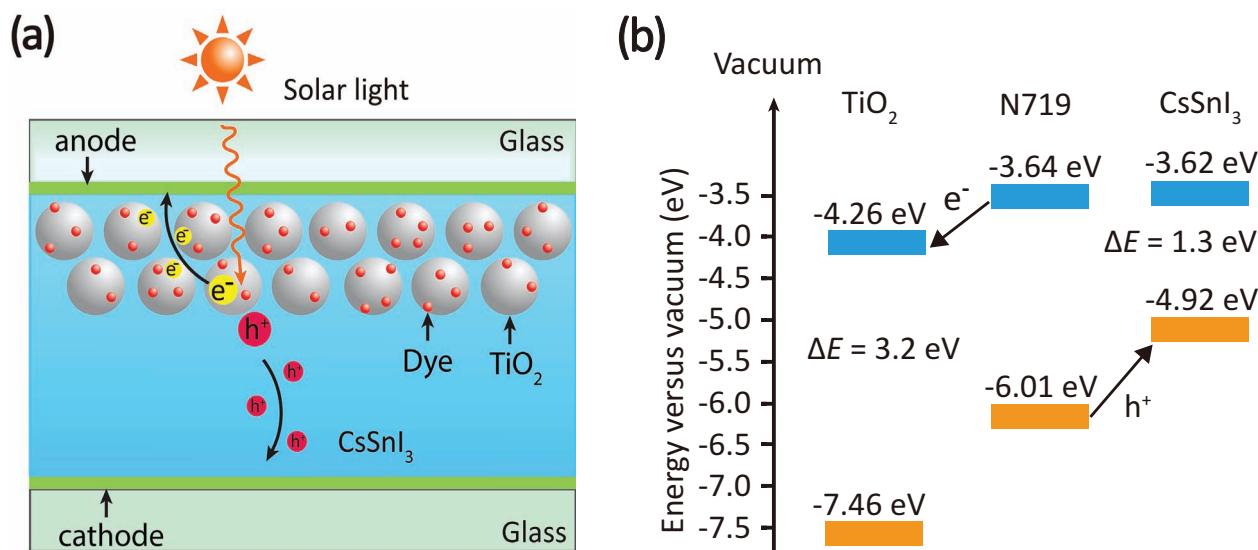
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**Figure 1.** a) Distorted 3D perovskite structure of CsSnI<sub>3</sub> at room temperature. Red polyhedron, [SnI<sub>6/2</sub>]<sup>-</sup>; yellow sphere, Cs. b) Absorption spectrum of CsSnI<sub>3</sub> showing a sharp edge at 1.3 eV. Reproduced with permission.<sup>[10]</sup> Copyright 2012, Nature Publishing Group.



**Figure 2.** a) Schematic of a Kanatzidis–Chang solid-state cell. The CsSnI<sub>3</sub> in place of the conventional liquid electrolyte can crystallize to fill the pores of the TiO<sub>2</sub> film and take part in both light absorption and sensitization. b) Relative energy levels of the key components of the CsSnI<sub>3</sub>-based solid-state dye cell showing excellent charge separation of the system. Reproduced with permission.<sup>[10]</sup> Copyright 2012, Nature Publishing Group.

from one other, thereby minimizing charge-recombination losses. Clearly, the Kanatzidis–Chang cell bypasses the electrochemical paradigm that has been used for so long in this field and points to a new direction in designing DSCs.

Despite the enticing prospects of enhanced device stability and power conversion efficiency offered by the solution processable CsSnI<sub>3</sub>, a number of challenges for this new technology remain. First, the energy-conversion measurements reported by Kanatzidis and colleagues were performed on small solar-collection devices, so the next step will be to build a large array of cells. More significantly, new materials (e.g., spectral converting lanthanide-doped nanomaterials<sup>[11,12]</sup>) need to be developed and integrated into this newly developed cell device for improved light harvesting in the near-infrared region, as this portion of energy is not effectively

used and is generally released as heat. If these challenges can be met, DSCs could become a real contender in the energy market.

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