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A Solid Advancement for Dye-Sensitized Solar Cells**

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Concerns about global warming and depleting fossil fuel reserves are currently defining a pressing need to fundamentally change our energy sources and the way we use energy. Solar energy, available in great abundance, will most likely play a central role in this transformation. While crystalline silicon modules still dominate today's photovoltaics market, new solar cell technologies relying on thin films are on the rise. Dye-sensitized solar cells (DSCs) are one of these emerging concepts. As they are based on low-cost materials and high-throughput, low-tech fabrication techniques such as roll-to-roll printing, they show great promise to be highly competitive in both cost- and energy-payback time.

In DSCs a monolayer of dye molecules is sandwiched at the interface between an n-type semiconductor, typically TiO_2, and a hole-transport material. Analoguous to photosynthesis, charge separation in DSCs is initiated by the electronic excitation of a molecular dye, followed by fast electron transfer. In DSCs, TiO_2 acts as the electron-accepting medium. The excess positive charge remaining on the dye is then transferred to the hole-transport material. To form the junction, a dye-sensitized mesoporous TiO_2 film several microns thick is infiltrated with the hole conductor, resulting in the formation of a bicontinuous network where photogenerated charge carriers are transported to the respective collecting electrodes through the TiO_2 (electrons) and hole-conductor (holes) networks. Each of the networks hosts only majority charge carriers, leading to a strict separation of charges, such that charge recombination can be limited and proceeds exclusively across the junction interface.

DSCs were developed more then two decades ago[1] and respectable efficiencies of up to 10 % were reported already at a very early stage.[2] Today the first DSC products are entering the market, powering and charging portable electronic consumer products such as mobile phones and external keyboards for tablet computers. The long lead time between the discovery of DSCs and the onset of their commercialization has, to a large extent, been caused by engineering issues linked to the unfavorable properties of the liquid electrolyte used in conventional DSCs. Vital for the fabrication of highly efficient DSCs, this corrosive, volatile, iodine-containing electrolyte posed a major challenge in the mass production of these devices. Recently major progress has been achieved through the development of DSCs based on liquid electrolytes containing noncorrosive redox mediators, which afford record efficiencies of up to 12.3 %.[3] However, replacing these liquid electrolytes with a solid noncorrosive, nonvolatile hole-transport material would help to further eradicate most problems with fabrication and product lifetime.

In a recent publication in *Nature*, Chung et al.[4] describe a novel inorganic solution-processable p-type semiconductor, $CsSnI_3$, that yields energy-conversion efficiencies of up to 10.2 % (8.51 % with a mask) when used as a hole conductor in solid-state DSCs (s-DSCs, see Figure 1). Compared to the

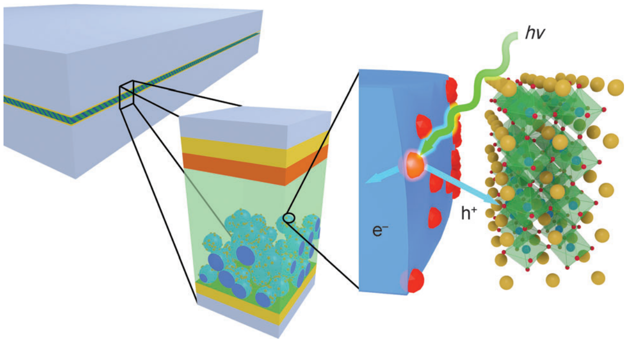

Figure 1. Schematic cross-section of a novel solid-state dye-sensitized solar cell based on $CsSnI_3$ as a p-type charge-transport material. Left: The solid-state dye-sensitized heterojunction is sandwiched between two charge-collecting FTO electrodes (F-doped SnO_2 (yellow) on glass (gray)). First enlargement (middle): The bottom electrode is coated with a 10 μm thick mesoporous TiO_2 film composed of TiO_2 nanoparticles (blue spheres), sensitized with a ruthenium polypyridyl sensitizer (N719, red hemispheres). $CsSnI_3$ (light green) infiltrates the sensitized mesoporous TiO_2 film and also bridges the gap to the top electrode, consisting of Pt-coated (orange) FTO glass. The second enlargement (right) shows the mechanism of charge separation and the structure of $CsSnI_3$. Light absorption by a sensitizer (red), is followed by electron injection into the TiO_2 layer (blue) and hole transfer to $CsSnI_3$ shown as a distorted perovskite crystal structure (yellow spheres: Cs^{+}; blue spheres: Sn^{2+}; red spheres: I^{-}).

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plethora of available organic charge-transport materials, with their highly tunable chemical and electronic structure, only a very limited number of inorganic p-type materials, suitable for their application in s-DSCs are known to date. Chung et al. not only successfully add a new candidate to the short list of appropriate inorganic p-type materials but also show that $CsSnI_3$, despite its very early stage of development, clearly outperforms all previously reported materials. This achievement comes at a time when renewed interest in the field has brought about a number of efficient s-DSCs based on materials such as nickel hexacyanoferrate ($\eta = 4\,\%$),[5] CuI ($\eta = 7.4\,\%$),[6] and CuSCN ($\eta = 3.4\,\%$).[7] For comparison, the highest efficiency ever reported for a s-DSC based on organic hole-transport materials such as poly(3,4-ethylenedioxythiophene) (PEDOT) and 2,2′,7,7′-tetrakis-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) are around 7.1–7.2 %.[8]

The infiltration of the sensitized mesoporous TiO_2 film with a p-type conductor is usually straightforward for liquid electrolytes but poses a major challenge for solid-state materials. Chung et al. have taken an unusual approach by first sealing the working and counter electrodes together using a spacer to control the cell gap. A solution of $CsSnI_3$ in a polar organic solvent is then injected into this gap though an entry port and left to evaporate. Using SEM cross-section analysis and elemental mapping, the authors show that $CsSnI_3$ homogeneously infiltrates the entire 10 μm thick TiO_2 film, forming an intimate contact to the dye-sensitized TiO_2. The high mobility of the charge carriers within $CsSnI_3$ makes it possible to utilize these thicker than usual working electrodes, resulting in more efficient light harvesting. The excellent photovoltaic properties reported by the authors also give evidence that $CsSnI_3$ efficiently bridges the gap between the two electrodes.

The use of pristine $CsSnI_3$ in s-DSCs yields reasonable solar energy conversion efficiencies of up to 3.72 % (in the absence of a mask). In their work Chung et al. show that by doping $CsSnI_3$ with 5 % SnF_2 the efficiency can be further increased to 6.81 % (in absence of a mask). By pretreating the TiO_2 electrode with a fluorine plasma and introducing a photonic crystal over the counter electrode, they were able to construct the highest performing s-DSC. This device yielded an efficiency of 10.2 % when measured without a mask and 8.52 % when measured with a mask. Ito et al. previously studied the effect of measuring high-efficiency DSCs with and without shadow masks.[9] In their experiments they observed a significant (13 %) overestimation when no shadow mask was used to cover the solar cell during characterization. At the same time they observed considerable (18 %) underestimation of the solar conversion efficiency when a shadow mask was used with an aperture of identical size and shape to the active area of the solar cell. The efficiency values reported by Chung et al. in the absence and the presence of a shadow mask therefore represent a good estimation of the lower and upper limits of the energy conversion efficiency achievable with these novel s-DSCs.

Fabricating efficient solid-state devices is one major challenge in DSC research; capturing solar energy from the IR region represents a second challenge. The new material described by Chung et al. scores in both aspects. With a direct bandgap at 1.3 eV, $CsSnI_3$ is ideally suited to absorb solar radiation well into the near IR, where conventional DSC sensitizers do not absorb. Unfortunately with the experimental setup used by Chung et al., the external quantum efficiency (IPCE) can be measured only up to a wavelength of about 670 nm (1.85 eV). An increased response in the red spectral range ($\lambda = 550$–670 nm), compared to that of a conventional liquid I^-/I_3^- electrolyte based DSC, provides some exciting evidence that $CsSnI_3$ could indeed contribute to the overall photocurrent.

Conventional DSCs based on liquid electrolytes have shown excellent stability in accelerated lifetime testing. At the same time, moving to a noncorrosive solid-state electrolyte would inherently simplify the large-scale fabrication of stable commercial solar panels. Inorganic p-type semiconductors such as $CsSnI_3$ are a promising class of materials that could hold the key towards the realization of durable low-cost DSCs as a viable alternative to conventional semiconductor technologies. Given the very early development stage, the performance results reported by Chung et al. are highly impressive. The current world-record DSCs are the result of two decades of intense research. The initial results reported by Chung et al. will very likely stimulate major research efforts in this area. Never before have s-DSCs been closer to matching the performance of their liquid-electrolyte-containing counterparts. Further research in this area, in particular the combination of the new solid electrolyte system with recently developed high-performance sensitizers, is likely to lead to further improvements, pushing the overall efficiency of solid-state DSCs to be at par with that of their liquid-electrolyte counterparts.

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