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## Introduction

The technologies for harnessing sunlight have evolved and photovoltaics have become a major focus in today's politics and research. One very promising alternative to classical, inorganic p-n-junction solar cells lies in the concept of using a liquid electrolyte conjunction with a sensitizer on a metal oxide semiconductor as described by Gerischer and realized by Grätzel.<sup>[1,2]</sup> The dye-sensitized solar cells (DSCs) work on very different principles. The dyes are responsible for absorbing light and charge separation and therefore for the energy conversion. Dyes are bound to the nanoporous semiconductors, which are only used to transport the resulting electrons and pass them along as current. Electrons flow back into the system through a redox mediator, which regenerates the dye molecules, allowing the cycle to close. Those cells exhibit impressive energy efficiencies of up to 14% under full sun illumination. Further, they are based on cheap starting materials and simple production techniques.

Currently, though dye sensitized solar cells are highly cost efficient, the drop in the price of silicon panels has made the price difference insignificant. While otherwise promising, the commercialization of DSCs faces problems arising from the corrosive, toxic, flammable and volatile nature of the liquid electrolyte used in such cells. While the sealing of silicon solar cells towards water and oxygen is a standard and industrialized, the sealing of liquid junction solar cells is a much more difficult task. The requirement of dye sensitized solar cells on the liquid electrolytes is the limitation for production of DSCs modules. The practical advantages have therefore to be gained by the replacement of the liquid electrolyte with a solid charge transport material, resulting in so called solid-state dye-sensitized solar cells (ssDSCs).

### **Structure and Working Principles of DSCs**

The DSC consists of two main electrodes, the photoanode and the counter electrode (CE). The photoanode consists of nanoporous metal oxide deposited onto fluorine doped tin oxide (FTO) coated glass substrate. Usually a blocking layer, commonly a compact layer of  $TiO_2$  is deposited on top of the FTO layer to avoid direct contact the with the redox mediator. The high surface area of the mesoporous semiconductor, such as  $TiO_2$  with particle size around 20 nm is a perquisite to absorb a large amount of sensitizer. There is a large variety of sensitizers for DSCs, which can be classified in metalorganic complexes and organic dyes.

A redox electrolyte or hole transporting material infiltrates the porous metal oxide between the photoanode and the CE. The counter electrode usually consists of metal (Pt, Au, Ag) or carbon-based materials deposited by drop casting or by evaporation. A schematic representation of a DSCs is given in Figure 1 a. The basic working principle of a DSCs is shown in Figure 1 b. The dye, is bound to a semiconductor nanoparticle. Upon illumination, the dye can be excited from the ground state. In the excited state, the dye can inject an electron above the conduction band of the semiconductor, which can rapidly transfer the electrons through the mesoporous network to the conductive fluorine dope tin oxide (FTO) electrode. The oxidized dye is consequently being regenerated by the redox mediator or hole transport material (HTM). The mechanisms of electron transport in an HTM is by electronic conduction. Redox electrolytes are ionic conductors in which charges are transported via diffusion. The ultrafast electron injection from the excited state dye into the TiO<sub>2</sub> conduction band is the fastest process in a dye sensitized solar cell and occurs in a timescale of fs to ps, as shown in Figure 2.

After the excitation (1), electrons are injected into the  $TiO_2$  conduction band on a picosecond timescale (2), followed by extraction towards the anode contact (3). On the other hand, the dye regeneration step (4) as well as the renewal of the redox species at the cathode (5) rely on diffusion within the redox electrolyte and thus yield the limiting step for DSC-performance with  $\mu$ s-ms timescales. However, undesirable electron transfers occurring in a DSC can severely affect the power conversion efficiency. While the electron injection into the TiO<sub>2</sub> conduction band largely extracts electrons from the dye molecules on a faster timescale than possible recombination to the ground state (6) as well as to the electrolyte (7), electron transitions from TiO<sub>2</sub> to both the oxidized dye (8) as well as the redox species (9) do compete with the diffusive current through the mesoporous TiO<sub>2</sub> layer. Excited electrons lost due to recombination will not contribute to the photocurrent and thus impede the device performance.

## **Copper Complexes as Redox Mediators**

In the early 2000s, Fuzumi and coworkers reported that copper complexes a series of blue copper model complexes (([Cu(SP)(mmt)]<sup>0/-</sup>, [Cu(dmp)<sub>2</sub>]<sup>2+/+</sup> and [Cu(phen)<sub>2</sub>]<sup>2+/+</sup>) were tested as redox shuttles in DSCs. They afford a maximum IPCE of 40%, which is thought to stem from a slow regeneration of the N3 ruthenium photosensitizer owing to the large reorganization energies of copper(I/II) complexes.<sup>[3]</sup> Promising results were obtained under the weak solar light irradiation of 20 mW/cm<sup>2</sup> intensity, the maximum  $\eta$  value was obtained as 2.2% for DSC using [Cu(dmp)<sub>2</sub>]<sup>2+/+</sup>. Peng Wang and coworkers further improved the system using the [Cu(dmp)

 $_2$ ]<sup>2+/+</sup> redox shuttle with a high-absorption-coefficient organic dye C218, generating an impressive power conversion efficiency of 7.0%. Recently, Freitag et.al. surpassed the 10.0% efficiency mark at 100 mWcm<sup>-2</sup>AM 1.5G light for this family of alternative redox mediators.<sup>[4,5]</sup> The important achievement of the copper based electrolytes is the ability to regenerate the dye near quantitatively with a very small driving force of 0.1 V. A new DSC design was introduced with copper polypiridyl complex (Cu<sup>(II/I)</sup>(tmby)<sub>2</sub>) as a redox couple, capable of successfully regenerating dyes at only 0.1 eV driving force. Strikingly, under 1000 lux indoor illumination, the PCE is 28.9 %, resulting in a power output of 88.5  $\mu$ W/cm<sup>2</sup>.<sup>[6,7]</sup>

#### **Copper Complexes as Hole Transport Materials**

HTMs based on organic small molecules or conducting polymers are less efficient to date. Inorganic widebandgap p-type semiconductors such as CuSCN and CuI show higher conductivity than their organic counterparts, but yielded thus far lower PCE in ssDSC devices. More recently, the dark-colored Sn<sup>4+</sup> compound Cs<sub>2</sub>SnI<sub>6</sub> was successfully used as a hole conductor in ssDSC, reaching PCE-values of up to 7.8 %.<sup>[8]</sup> Interestingly, the open-circuit potentials for ssDSC that use inorganic p-type semiconductors is thus far significantly lower (~0.6 V) than that obtained with spiro-OMeTAD (~0.9 V). Recently a new type of HTM was discovered, based on earth abundant and very stable copper complexes in solid-state DSC, resulting in recordbreaking solar cell efficiencies.<sup>[9]</sup> Considering the rapid electron self-exchange rate in rigid copper complexes,  $[Cu(dmp)_2]^{2+/+}$  molecules were used as an HTM for solid-state DSCs (ssDSCs). The so called "zombie" ssDSCs were simply fabricated by evaporating volatile solvents from the copper based redox electrolyte in ambient air, <sup>[10]</sup> resulting in stable ssDSC with PCE of 11.0% under standard AM1.5G conditions. fabricated using a blend of  $[Cu(tmby)_2](TFSI)_2$  and  $[Cu(tmby)_2](TFSI)$  (tmby = 4,4',6,6'-tetramethyl-2,2'-bipyridine; TFSI=bis (trifluoromethylsulfonyl)imide) as a HTM, Y123 as a sensitizer and electrodeposited PEDOT as a counter electrode, Figure 11. Further studies showed that the conductivity and mobility is highly dependable on the morphology and christality of the material. Nevertheless, the performance is superior to those of counterparts made using CuSCN (2%), CuI (4.5%),<sup>[11-13]</sup> or cobalt complexes as HTMs.<sup>[14]</sup> Current solid hole transport materials still face several major challenges in terms of efficiency with low Jsc. The pore filling problem is difficult to overcome and can never be completed when solvent evaporates living space, which greatly influences charge separation and collection.

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