Popcorn-style dye-sensitized solar cells

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Photovoltaics with porous electrodes made of nanocrystallites can convert power more efficiently than current dye-sensitized devices.

As the primary energy source for life, solar power is considered the ultimate carbon-neutral solution to the important energy and environmental challenges of today. Every hour the Sun deposits $4.3 \times 10^{20}$ J on Earth, more than the global annual energy consumption (estimated at $4.1 \times 10^{20}$ in 2001, corresponding to a consumption rate of 13TW). Solar photovoltaic cells convert sunlight into electricity. Crystalline-silicon-semiconductor solar photovoltaics were invented more than 50 years ago and currently make up 94% of the market. However, to date cost issues have limited their widespread use.

Dye-sensitized solar cells (DSSCs) first achieved a 4% power-conversion efficiency (PCE) in the early 1990s. They are much cheaper and easier to produce in bulk than their crystalline-silicon counterparts, however, and have thus attracted significant research efforts to meet the long-term goal of manufacturing very low-cost and high-efficiency solar cells. These photovoltaics are similar to traditional electrochemical cells. Their key electrodes have a high porosity of $\sim 50\%$, specific surface areas of order $\sim 100 \text{m}^2 \text{g}^{-1}$, and pores of $\sim 20 \text{nm}$ diameter. They are made of titanium-dioxide (TiO$_2$) nanocrystallites with a self-assembled monolayer of dye molecules on the surface. When illuminated, the dye captures the incident photons and generates electrons and holes. The free electrons are immediately (within 100fs) injected into the TiO$_2$ conduction band and transported to the electron-collecting electrode. Regeneration of dye molecules is accomplished by capturing electrons from the liquid electrolyte that fills the entire void of the porous TiO$_2$ electrode and is connected to the counterelectrode.

The PCE depends on the efficiency of capturing photons, generating electron–hole pairs, and transporting the electrons and holes. Nanocrystals are critical for the formation of nanoporous electrodes with the desired surface area for dye-molecule adsorption. If more molecules are adsorbed, more photons can be captured and more electron–hole pairs generated. Because the electron traveling distance is only $\sim 10 \mu\text{m}$, increasing the thickness of the nanoporous electrode will not improve the PCE. Admixing submicron-sized particles can effectively increase the photon traveling distance within the electrode due to light scattering and thus enhance the photon-capture probability. However, incorporating such large particles results in a decreased surface area, and fewer photon-capturing dye molecules can be adsorbed. As a consequence, the increased efficiency due to light scattering is compromised by the smaller number of dye molecules, and the PCE does not increase.

TiO$_2$ and zinc oxide (ZnO) are wide-bandgap (3.2eV) semiconductors with the same electronic structure. They are the preferred choices for the production of porous photovoltaic electrodes for...
DSSCs. TiO$_2$ is chemically more stable and has therefore been studied extensively for this purpose. But ZnO is characterized by higher electron mobility, and the material is easier to manipulate chemically.

We recently fabricated DSSCs with porous electrodes made of micron-sized aggregates ('popcorn') of both ZnO nanocrystals and TiO$_2$ nanotubes. We achieved significantly enhanced PCEs (see Figure 1). ZnO nanocrystallites and TiO$_2$ nanotubes ensure availability of the desired high specific surface area for dye-molecule adsorption, while the micron-sized aggregates serve as light scatterers without sacrificing the specific surface area. The scattering resulted in an increase of the PCE from 2.4% for ordinary porous electrodes made of dispersed ZnO nanocrystallites using red N3 (Ruthenium 535) dyes to 5.4% for electrodes made of aggregates of ZnO nanocrystallites (for otherwise identical configurations).$^{1-3}$

A PCE of 6.2% was accomplished by modifying the surface chemistry,$^4$ while an increase to 9.9% was demonstrated using aggregated TiO$_2$ nanotubes as photoelectrodes sensitized with dark purple N719 (Ruthenium 535-bis-tetrabutylammonium or ‘dye salt’) dyes.$^5$ An efficiency of 9.9% is still lower than the certified record of 11% for TiO$_2$ DSSCs. However, we did not apply any commonly used modifications or enhancement procedures (including antireflection coatings, adhesion layers, and titanium-tetrachloride treatment) to the popcorn-style photovoltaics, although they can each increase the PCE by up to 10%. We plan to further optimize the aggregated photoelectrode films and combine this with a variety of common treatments to achieve an expected PCE exceeding the current record of 11%.

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**References**