Layered Nanostructures for Enhanced Light Harvesting in Dye-Sensitized Solar Cells

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Dye-sensitized solar cell (DSSC) is a promising alternative to conventional solar cells based on the p-n junction because DSSCs can be fabricated from inexpensive materials with low cost processes. The key component in a DSSC is the photoanode which is made by depositing a mesoporous nanocrystalline TiO$_2$ film on a transparent conducting oxide (TCO) glass. A monolayer of a photoactive dye adsorbed on the TiO$_2$ nanocrystal surfaces absorbs the light and generates photoexcited electrons. These electrons can reduce their energy by transferring into the TiO$_2$ conduction band and rapidly do so to provide an efficient charge separation mechanism. The electrons injected into the TiO$_2$ film diffuse to the TCO while the charged dye is regenerated by an electrochemical reaction with a redox couple (e.g., I$^-$/I$_3^-$) in an electrolyte interpenetrating the mesoporous film. Reduction, at the cathode, of the oxidized species by an electron that has traveled from the TCO through the load completes the circuit. To date, DSSCs with light-to-electric conversion efficiencies of ~7 to 11% have been demonstrated with ~10 µm thick electrodes made of 10–30 nm TiO$_2$ nanoparticles sensitized with ruthenium-based dyes.

Poor light absorption in the infrared region of the electromagnetic spectrum is one of the factors that limits further improvements in the DSSC efficiency. One way to improve the optical density of the photoanode in the infrared region is to make thicker films. However, the

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competition between electron diffusion in the TiO$_2$ film and electron recombination with I$_3^-$ in the electrolyte prevents one from increasing the photoanode thickness beyond the electron diffusion length. Increasing the transport rate of electrons by using aligned single-crystalline nanorods, nanotubes or nanowires in lieu of disordered nanocrystals is one possible way for increasing the diffusion length. However, the low surface area of these one-dimensional nanostructures limits the photocurrent and results in lower efficiencies than record DSSCs, -1.5% for ZnO nanowires and -3–8% for TiO$_2$ nanorods or nanowires. Another approach to improving the optical density is to enhance light absorption by increasing the optical path of photons through the dyed nanocrystals. This can be achieved by introduction of light scattering layers within the photoanode structure. Rayleigh scattering from the individual nanoparticles (10-30 nm) is too weak to enhance light harvesting by increasing the optical path of photons through the photoanode. For this reason, larger spherical or faceted TiO$_2$ particles, in the size range from 100 to 400 nm, are commonly used as light scatterers. However, introduction of these large and nonporous particles inevitably decreases the internal surface area and hence the roughness factor of the photoanode. Often, the loss of surface area counteracts the benefit of enhanced light scattering and optical absorption. Yet, another method to enhance light absorption is to couple a photonic crystal layer with the mesoporous nanocrystalline film. The photonic crystal layer acts as a dielectric mirror and modifies the dye absorption. Using this method, visible light harvesting in DSSCs has been increased by 26% but having to assemble an inverse opal photonic crystal layer complicates the DSSC fabrication.

Ideal DSSC photoanodes must be structured both in the micrometer and nanometer size scales to provide light scattering and high internal surface area at the same time. In this article, we describe how to achieve this in TiO$_2$ based DSSCs. Recently, porous films made of submicron-sized ZnO nanocrystal aggregates were used in constructing photoanodes for DSSCs. Enhanced power conversion efficiencies were observed and attributed to the synergistic
effect of high dye loading and improved light scattering. However, titanium dioxide is a better choice than ZnO for constructing DSSCs. Herein, we describe a two-step hydrothermal method for synthesizing mesoporous anatase TiO$_2$ microspheres and we demonstrate their use in constructing layered structures for improving the performance of DSSCs.