

Quantum Dot Sensitization of Single Crystal TiO₂:
Surface Chemistry, Stability and Multiple Exciton Collection
J. Sambur

Surface Chemistry

Sensitization of mesoporous nanocrystalline TiO₂ solar cells with quantum confined semiconductor nanocrystals (QDs) has some advantages over organic dyes or inorganic complex sensitizers, yet the reported efficiencies of laboratory devices are not currently competitive with those of dye sensitized cells. Several methods previously utilized to bind CdSe QDs to mesoporous TiO₂ films were investigated using low index faces of both anatase and rutile TiO₂ polytypes as model systems. The in situ ligand exchange method, where 3-mercaptopropionic acid (MPA) covered TiO₂ crystal surfaces are treated with trioctylphosphine (TOP)/trioctylphosphine oxide (TOPO) (TOP/TOPO)-capped CdSe QDs, resulted in very irreproducible and usually low sensitized photocurrents. The ex situ ligand exchange method, whereby MPA-capped QDs are synthesized and directly adsorbed onto bare TiO₂ single crystals, resulted in both reproducible sensitized photocurrents and surface coverages that are verified with atomic force microscopy (AFM). Purification of the nanocrystals and adjustment of the pH of the sensitization solution to >10.2 was found to prevent QD agglomeration and takes advantage of the dual chemical functionality of MPA to directly link the QDs to the TiO₂ surface. The spectral response of the incident photon to current efficiencies of CdSe QDs was directly compared to the commonly used sensitizer cis-di(thiocyanato)-bis(4,4'-dicarboxy-2,20-bipyridine) ruthenium(II) (N3) on the same single crystals.

Stability

It is thought that the inorganic nature of QDs should provide enhanced stability over the entirely organic or inorganic complex dyes, yet the long-term stability of laboratory QD-SSC devices has not been investigated in detail. A general approach to synthesize high stability QDs involves coating the core material with a wide band gap inorganic shell material (type-I CS QD). However,

the electronic structure of the resulting core/shell (CS) structure has potential barriers for both electron and hole transfer, suggesting inefficient charge carrier separation for type-I CS QDs. Herein we demonstrate that type-I CdSe/ZnS CS QDs can effectively sensitize single crystal TiO₂ electrodes and continue to operate in a regenerative mode in an aerated iodide electrolyte for more than 20 hours. Core CdSe QDs degrade rapidly in the same electrolyte. The possibility of exploring new core/shell nanomaterials in a variety of electrolyte/mediator combinations may result in more efficient and stable QD-SSCs.

Multiple Exciton Collection

Multiple exciton generation, the creation of two electron-hole pairs from one high-energy photon, is well established in bulk semiconductors, but assessments of the efficiency of this effect remain controversial in quantum-confined systems like semiconductor nanocrystals. We used a photoelectrochemical system composed of PbS nanocrystals chemically bound to TiO₂ single crystals to demonstrate the collection of photocurrents with quantum yields greater than one electron per photon. The strong electronic coupling and favorable energy level alignment between PbS nanocrystals and bulk TiO₂ facilitate extraction of multiple excitons more quickly than they recombine, as well as collection of hot electrons from higher quantum dot excited states. Our results have implications for increasing the efficiency of photovoltaic devices by avoiding losses resulting from the thermalization of photogenerated carriers.