

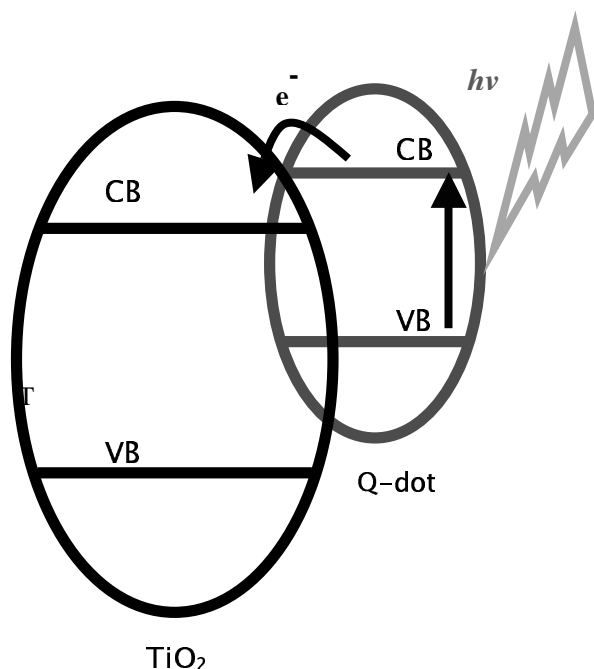
Self-assembled Semiconductor Q-dots for
Photosensitization of Nanocrystalline TiO₂

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Exciting features of quantum-confined materials arise from the fact that it is possible to fabricate structures with their radius smaller than the electron-hole-pair exciton Bohr radius. Decreasing the particle radius below the Bohr radius results a separation of electronic levels (*i.e.* electron affinity and optical bandgap) and the ultra-small particles of this nature are commonly referred to as quantum dots (Q-dots). In recent years semiconductor Q-dots have attracted much attention from the scientific community because of their strong size-dependent physical and chemical properties. Potential applications of semiconductor Q-dots have been reported recently in superior biological labels, white-light laser sources, tunnel diodes, near-IR emitters, organic-inorganic hybrid and nanocrystalline solar cells and molecular electronics owing to their size-dependent absorption and emission properties [1].



The dye-sensitized nanocrystalline TiO₂ solar cell which was proposed as a cheap alternative to crystalline silicon solar cells, gives peak light harvesting efficiencies approaching 100% by monolayer adsorption of the sensitizer organic dye, 'N3' (cis-di(thiocyanato)-N,N-bis(2,2'-bipyridyl dicarboxylate) Ru(II)) via its carboxylate ligands on high-surface area nanocrystalline TiO₂[2]. Current approaches to enhance cell efficiency involve tuning the absorption spectrum and the redox properties of different dyes. Other sensitizer dyes such as 'N719' (bis(tetrabutylammonium) cis di(thiocyanato) bis(2,2'-bipyridine-4,4'-carboxylic acid) Ru(II)) and 'black dye' (tri(cyanato)-2,2',2''-terpyridyl-4,4',4''-

tricarboxylate) Ru(II)) are being used in this direction. However, synthesis of these organic dyes involves rather difficult routes resulting in very high cost.

Therefore, further research towards replacing the dye in dye-sensitized nanocrystalline solar cells by other suitable alternative light harvesting materials is highly demanding. Our interest in studying inorganic semiconductor Q-dots has mainly centered on this target because of their unique features such as the ability of tuning the optical bandgap by material and size selection, high absorption coefficients, steep onset absorption and well established methodology for other applications.

CdS has been widely studied and methods of controlling the size of CdS Q-dots are well established. The tunability of optical absorption by particle size selection allowed us to show efficient photosensitization of nanocrystalline TiO₂ with self-assembled layers of CdS Q-dots [3]. Spectroscopic and photoelectrochemical properties of these electrodes have extensively studied [3]. CdS Q-dots were self-assembled in situ on TiO₂ electrodes by arrested precipitation. 3-mercaptopropionic acid was chosen as the stabilizer in order to facilitate assembly on the TiO₂ substrate via the carboxylic moiety. The size of the CdS Q-dots was adjusted by controlling the stabilizer concentration in the colloidal synthesis step.

However, any prospective inorganic Q-dot material that could possibly challenge the existing organic sensitizer dyes must have an optical absorption edge close enough to near IR region so that the spectral response of the sensitized device matches the incident solar radiation. Therefore, currently we are trying to self-assemble other inorganic semiconductor Q-dots such as Bi₂S₃, which has a fundamental absorption edge close to 800 nm on nanocrystalline TiO₂ electrodes, and use them in photosensitization. We have successfully extended the self-assemble methodology to graft Bi₂S₃ Q-dots on nanocrystalline TiO₂ electrodes. These electrodes have investigated for photoelectrochemical and optical properties. Further work in progress on the use of other semiconductor Q-dots for the photosensitization of nanocrystalline TiO₂ electrodes and use them in solar energy conversion devices. Our recent attempts on photosensitization of nanocrystalline TiO₂ electrodes with self-assembled semiconductor Q-dots and their photoelectrochemical and optical properties will be presented.

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