

Sensitizing TiO₂ with CQDs

Attaching Colloidal, TOPO-capped CdSe Quantum Dots to thin films of TiO₂

The procedure described in detail below is taken from the following publication. If this procedure is followed, please cite appropriately.

Pernik, D. R.; Tvrdy, K.; Radich, J. G.; Kamat, P. V., Tracking the Adsorption and Electron Injection Rates of CdSe Quantum Dots on TiO₂: Linked versus Direct Attachment. *The Journal of Physical Chemistry C* **2011**, *115* (27), 13511-13519.
<http://pubs.acs.org/doi/suppl/10.1021/jp203055d>

Without Molecular Linker

Mesoporous TiO₂ films may be simply introduced to a colloid of TOPO-capped CdSe quantum dots for about ten hours to achieve sensitization of the films. However, sensitization by this method is only possible if the quantum dots have been properly prepared. Two important preparation considerations must be taken:

1) Washing Pre-treatment. The following procedure removes excess TOPO from the quantum dot surface, freeing more CdSe surface area to interact with TiO₂. One washing step entails (a) adding methanol to the colloidal dispersion until it appears cloudy (b) centrifugation (c) decanting and (d) resuspension of the quantum dots in fresh colloidal solvent. Using several washing cycles makes it easier to adsorb quantum dots onto TiO₂, however too many washing cycles will cause the quantum dots to lose colloidal stability. Our studies (see reference below) found five washing cycles to be optimal.

2) Storage. Colloidal CdSe quantum dots need to be stored in an oxygen-deplete atmosphere. If stored in oxygen-rich conditions, quantum dot aggregation and flocculation from the colloid solvent (toluene is used in many of our studies) is observed on the order of days.

With Molecular Linker

To improve the coverage of TiO₂ with quantum dots, a molecular linker such as 3-mercaptopropionic acid (MPA) may be used. Considerations about storage and washing (above) are still very important when using MPA. Below is an outline of the steps for using MPA.

1) Inside a nitrogen glovebox, immerse a TiO₂ film in a pH 2 solution (HCl in deionized water) for 20 minutes.

2) Rinse the film with deionized water and then anhydrous acetonitrile. It is very important that the acetonitrile has not been sitting out in ambient conditions for a lengthy period of time where it could absorb water.

3) Immerse the TiO₂ film in an MPA solution (1 M 3-mercaptopropionic acid, 0.1 M H₂SO₄ in anhydrous acetonitrile) for five hours. Again, it is important that the acetonitrile is fresh.

4) Rinse the film with acetonitrile and then with deaerated solvent (use the same solvent that the colloidal quantum dots are stored in).

5) Introduce the films to the colloidal quantum dot solution. Adsorption times on the order of 10 hours are sufficient to sensitize the TiO_2 .

The following reference is an in-depth study of this CdSe quantum dot- TiO_2 adsorption process with adsorption kinetics: