Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Phase-transfer of CdSe@ZnS quantum dots using amphiphilic hyperbranched polyethylenimine

by Thomas Nann

1. Preparation of quantum dots (QDs)

CdSe@ZnS QDs were prepared in a two-step process: First, CdSe core particles were synthesised, precipitated and washed. Subsequently, these cores were redispersed in a coordinating solvent and the ZnS shell was added. A typical synthesis works as follows: 224 mg (330 µmol) cadmiumstearate were dissolved in 4 g tri-n-octylphosphinoxide (TOPO) at 70° to 100° C. The solution was degassed and aerated with nitrogen. 284 mg of selenium (360 µmol) were mixed with 4 g hexadecylamine (HDA) and 2.4 g tri-n-octylphosphin (TOP) within a glove-box environment. The mixture was sealed and homogenised at 50° - 60° C in a ultrasound bath. After one hour, the mixture was quickly injected into the cadmiumstearate solution at 280° C by means of a syringe. The reaction mixture was stirred for 10 minutes at 240° C, yielding a deep red solution of CdSe nanocrystals. The mixture was allowed to cool down to 60° C and the nanocrystals were precipitated by addition of 5 mL buthanol. The nanoparticles were subsequently dissolved in chloroform and characterised by means of absorption- and photoluminescence spectroscopy.

These CdSe nanocrystals were passivated with the following procedure: One batch CdSe nanocrystals were dissolved in 4 g TOPO and 2 mL TOP under inert gas atmosphere at 90° C. When the solution was clear, the temperature was raised to 140° C. A solution of 31 µL diethylzink and 61 µL 1,1,1,3,3,3-hexamethyldisilathiane ($(TMS)_2S$; Aldrich) in 2 mL TOP was prepared in a drybox and transferred into a syringe. The Zn-solution was slowly injected into the nanocrystal-solution under Schlenk conditions, and the mixture was stirred overnight at 90° C. Subsequently, 5 mL dry buthanol were added and the reaction mixture stirred for another several hours at 60° C. The flask was allowed to cool down to room temperature, and the nanoparticles were precipitated with dry methanol. After centrifugation, the precipitate was washed several times with dry methanol and used directly for the subsequent steps.

2. Phase-transfer with polyethylenimine (PEI)

Phase-transfer was conduced by redissolving 0.1 nmols of freshly precipitated QDs in 1 mL chloroform and 10 mg PEI (800 D). The solution was given several hours for the surface derivatisation with PEI to happen. Subsequently, the PEI-coated QDs were precipitated with 0.3 mL of cyclohexane and redispersed in water, buffer solution or any short-chained alcohol. Precipitation from alcohols can be done by addition of a 1:1 mixture of chloroform and cyclohexane. The procedure for high molecular weight PEI works analogously, but more cyclohexane is needed for precipitation of the derivatised QDs.

3. Photoluminescence/Absorbance-spectra of PEI-derivatised QDs

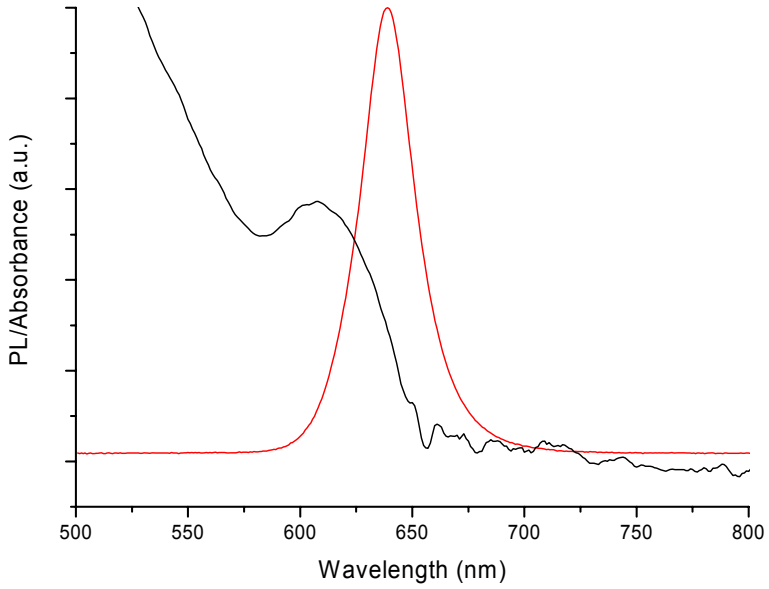

Fig. 1: Photoluminescence- and Absorbance-spectra of PEI (25kD) derivatised QDs in water.