Abstract of Doctoral Thesis

Synthesis, characterisation, and functionalisation of colloidal semiconductor nanoparticles displaying nonlinear optical activity

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The dissertation discusses semiconductor nanomaterials, their interaction with light and the impact of their size and shape on the strength of the phenomena occurring within or involving subjected nanomaterials, especially charge separation and NLO properties. Several functionalisation approaches are also presented aimed for enhancement, introduction or inhibition of certain physicochemical properties along with simultaneous preservation of desired behaviour.

In the experimental part, CdS QDs and CdSe NPLs of different thicknesses were synthesised, characterized, and subjected to functionalisation. Hydrophilic penicillamine-capped CdS QDs were decorated with gold nanostructures in order to entrap electrons after light-induced excitation and employ them or separated holes for reduction or oxidation reactions, respectively. The concentration of embedded gold was optimized for preservation of nonlinear optical (NLO) properties with the twophoton absorption (TPA) cross section of 15.8×10^3 GM, making the resulting CdS-Au nanohybrids a model multifunctional nanomaterial exhibiting both photocatalytical and NLO properties in line with an important new direction for nanomedicine - theranostics - which combines therapeutic and diagnostic functionalities. CdSe NPLs of three different thicknesses were synthesised and their optical properties were investigated, leading to determination of thickness-dependent exciton binding energy with a new method that combines optical absorption spectroscopy and photoacoustic spectroscopy. 5.5 ML CdSe NPLs with the TPA cross section of 8.0×10^4 GM were chosen as a model material for functionalisation towards biological application, especially in bioimaging. Encapsulation in polymeric NCs was selected as a hydrophilization method, which also provided cell viability after incubation without any significant change in optical spectra and preserving nonlinear absorption and two-photon excited emission (TPEE) properties as well as being visible through a two-photon microscope. The TPA cross section of polymeric NCs filled with 5.5 ML CdSe NPLs was estimated as 2.0 × 108 GM. 4.5 ML CdSe NPLs were chosen for studies on the relation between noble metal doping and NLO properties. Doping with silver and copper ions led to the TPA cross sections of up to 5.44×106 GM and 1.33×107 GM, respectively, and thus appears to be a method for enhancement of NLO properties of semiconductor NPLs without increasing their volume.

The above-mentioned examples highlight functionalisation as a promising method to improve desired parameters of semiconductor nanoparticles. In particular, the accent was put on NLO properties and, indeed, exceptionally high TPA cross sections and intensive following emission was achieved which opens a range of currently essential applications possibilities including multiphoton microscopy for biology or encryption. Moreover, more than one function may be introduced to a nanomaterial to aim at such specialized applications as theranostics, complex anti-counterfeiting and future advanced photovoltaic systems.