

## Abstract

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Title: Colloidal Zinc Oxide Nanocrystals: Organometallic Synthetic Approach, Functionalisation, Characterisation and Applications

Colloidal semiconductor nanocrystals (NCs) composed of earth-abundant non-toxic elements are of great interest to catalysis, photovoltaics, electronics, and biomedicine. Among the semiconducting materials, ZnO NCs have been the subject of intense research on account of their unique catalytic and optoelectronic properties. However, preparing high-quality ZnO nanostructures, especially NCs in the quantum size regime (diameter < 10 nm) with desired physico-chemical properties, remains challenging. Establishing and controlling the ZnO NCs surface and the coating ligand shell are other issues of current interest since the ZnO organic-inorganic interfaces affect key properties of these colloids such as solubility and stability in an aqueous environment, catalytic activity, and photoluminescence efficiency. Moreover, despite the strong influence of both applied synthetic procedure and the ligand shell composition on NC properties, comprehensive studies on the surface coordination chemistry of ZnO NCs are still in their embryonic stage. This thesis addresses these challenges by providing contributions to (i) the design and preparation of high-quality luminescent water-soluble ZnO NCs, (ii) the in-depth characterisation and development of a structural model of the NC inorganic-organic interfaces, and (iii) the ultrafine post-synthetic engineering of the NC interfaces.

Here, a new synthetic strategy leading to colloidal ZnO NC is demonstrated alongside the development of original approaches for their further functionalisation. Through a comprehensive understanding of their structure and physicochemical properties, new applications for this class of materials were sought and shown in (photo)catalysis, photovoltaics, and cargo delivery. Initially, the controlled hydrolysis of organozinc precursors was developed and applied as a transformation pathway to ZnO NCs with size down to a quantum regime. Further post-synthetic modification of the interfaces of the resultant ZnO NCs with an ethylene glycol oligomer (OEG) provided excellent aqueous colloidal stabilisation of the resultant OEG-capped ZnO NCs. The described OEG modification of the NCs extended the lifetime of photo-excited electrons up to microseconds. The presented work also provides an important contribution to the picture of the structure and composition of the ligand shell of colloidal ZnO NCs in an aqueous environment. Comprehensive analysis of the interface structure and

composition of OEG capped-ZnO NCs, indicating dynamic processes taking place within them, is an integral part of this research. Moreover, the developed strategy for rational surface passivation allows for leaving coordinatively unsaturated centres at the NC surfaces – thereby leaving surface sites available for further functionalisation towards numerous applications.

Besides the synthesis of high-quality luminescent water-soluble ZnO NCs and their in-depth characterisation, the current work also aimed at developing methods of ultrafine interface modification *via* either a direct ligand exchange or a supramolecular approach. First, a viologen-based ligand ( $MV^{2+}$ ) was incorporated into the NC surfaces. Then, for the first time, the interface of ZnO NCs was reversibly decorated by cucurbit[8]uril (CB[8]) macrocycles interacting with the  $MV^{2+}$  through host-guest interactions. This combination of photoactive ZnO nanoparticulate building blocks with CB[8] paved the way for semiconductor-assisted light-modulation of supramolecular assemblies (SALSA) mediated by photo-generation of radical cationic species on the interfaces of the ZnO NCs. The SALSA processes were employed for photo-controlled uptake and release of a cargo molecule from NC interfaces and light-induced ZnO NCs aggregation.

Further research on ultrafine engineering of the OEG-capped ZnO NCs included the incorporation of a natural pigment obtained from beetroot, betanin, and a selected  $H_2$ -evolving catalyst. As a result, a hybrid nanosystem based on abundant and inexpensive materials (ZnO NCs, a beetroot extract, and a hydrogenase mimic) was assembled and successfully employed for the photocatalytic generation of  $H_2$ . In the final part of the thesis, the OEG-capped ZnO NCs were employed as electron transporting layers in conventional planar perovskite solar cells (PSCs). The excellent reproducibility of ZnO-based PSCs' fabrication procedure and the high-power conversion efficiencies make the constructed devices highly promising in the context of developing efficient methods of harvesting solar energy.

In summary, the results of this thesis show the great potential of organometallic chemistry as a base for developing new colloidal ZnO nanostructures prospective for energy, catalysis, electronic, and sensing technologies, where the efficiency of charge separation at the interface is essential for successful applications. The presented work also provides unprecedented in-depth insights into the structure and composition of the organic ligand shell of the ZnO NCs in both the solid-state and colloidal systems. The presented findings unlock new pathways to control dynamic processes and molecular engineering involving colloidal ZnO NCs.