Nanosized Mn- and Cu-doped luminescent ZnS particles

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The conjugation of luminescent nano-sized doped ZnS particles with various polymeric and biochemical substrates requires particle surfaces with well defined chemical characteristics and covalently bonded anchor groups. Huge progress has been made in this respect recently, but still the interplay between luminescent properties and surface chemistry remains a delicate theoretical and preparational task. A specific problem with ZnS is the large band gap of this material, widening even more when approaching particle sizes well below 10 nm. The short wavelength of the UV light needed for band-band excitation in such a material does interfere with the requirements of e.g. in vivo investigations of cells. A possible solution is the development of doping schemes making use of states within the band gap in order at least to fine tune the excitation characteristics. On the other hand, employing the donor-acceptor type of luminescence relies on a multiple step mechanism including quite mobile charge carriers (electron-hole pairs may have diffusion lengths up to several nm in ZnS).Therefore, precise control of the surface chemistry is needed in order to avoid excessive surface quenching of the excitation energy.

In this work, the ratio of room temperature luminescence from (bulk) defect sites and Mn^{2+} sites (bulk and surface) has been used in a series of particles with varying particle size to study the influence of ligands present on the surface. Coupling of the ligands to the particle surface has been achieved by thio groups. Although most of the preparation of the nano-particles has been performed in aqueous solution, redispersability and transfer into non-aqueous solvents has been investigated as well. In a second series of experiments, Cu-doped nanoparticles of ZnS have been prepared by several preparational routes, again using thioligands for precipitation and size control. The resulting nanodispersions and nanopowders exhibit bright luminescence on the same level as the Mn-doped material, provided the right combination of doping scheme and surface passivation is used. In order to explore possible applications, the materials are characterized by optical spectroscopy, dynamic light scattering, XRD, surface titration and electron microscopy, combined with tests on stability and dispersability.