

LANTHANIDE DOPED ZnO NANOCRYSTALS: SYNTHESIS, SURFACE MODIFICATION AND OPTICAL BEHAVIOUR

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Quantum dots (QDs) have been extensively investigated during the past decades. Their unique optical properties due to quantum confinement effects are of interest for application in optoelectronics, such as in display monitors but also as optical biomarkers [1]. A great interest arises from the optical properties of doped semiconductor nanocrystals namely lanthanide (Ln) doped zinc oxide. While doping in bulk semiconductors is now habitual, the doping of semiconductor nanocrystals is not straightforward. The small dimensions of the colloidal QDs guides the way to new difficulties not stumbled upon in bulk materials. Once the QD doping is achieved, an additional dilemma is encountered. The dopant may be likely to diffuse towards the surface or into the solution due to thermodynamic driving forces, since the dopant atoms are always only a few lattice constants from the QDs surface [2].

Lanthanide ions are excellent candidates for luminescent centers due to their 4f intra-shell transitions, e.g. the characteristic narrow emission bands make Ln-doped materials bright colored luminescent materials. Here the incorporation of foreign ions in a host, in particular for ZnO nanocrystals, does not mean necessarily replacement of ions in the crystalline lattice. Regardless the type of incorporation of Ln ions in semiconductor nanocrystals, optical properties of nanocrystals are anticipated to be remarkably modified. However, it is also true that this task poses several challenges namely due to size and charge constrains.

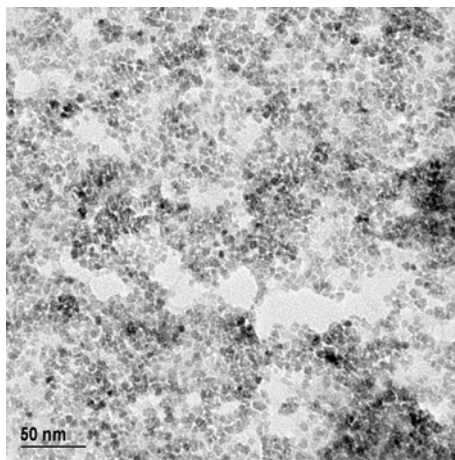


Fig.1 – TEM image of ZnO nanocrystals

We report here our attempts on the incorporation of Ln cations in ZnO quantum dots using a wet colloidal method previously applied for d-metal doping of ZnO nanostructures.[3,4] Several experimental parameters have been investigated in order to vary the morphological features of ZnO quantum dots. The average size and monodispersity of the colloids, and hence the optical band gap, could be controlled by a rigorous adjustment of the temperature of synthesis as shown in Fig.2. The spectra shown in Fig.2 are characteristic of quantum sized ZnO particles obtained in the presence of Tb^{3+} and are similar to those of pure ZnO, i.e. prepared in the absence of the lanthanide. For each temperature of synthesis, the ZnO optical band gap is shifted to higher energies when compared to the typical bulk band gap value ($E_g \sim 3.3$ eV at RT). Surface modification methods were investigated as the path to develop core-shell ZnO heterostructures.[4] In some cases such surface modification was surveyed to evidence the location of the foreign cations in the host. These studies were complemented with a detailed analysis of the photoluminescence properties of the starting dots and the resulting core-shell nanostructures.

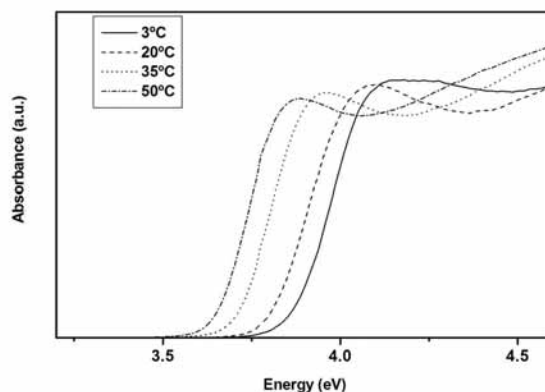


Fig. 2 - Room temperature absorption spectra of Tb^{3+} doped ZnO colloids synthesised at distinct temperatures.

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