Remarks to growth mechanism and doping of II-VI-semiconductor clusters

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The mechanistic exploration of growing inorganic nanocolloids belong to the increasingly popular research subjects of the modern materials science. This contribution focuses on structural and optical properties of tetrahedral precursor clusters and nanocrystals. The possible path of their primary nucleation is discussed in terms of the so-called two step feedback machine with memory - an approach used in the general chaos theory to construct certain fractal geometries.
This mechanistic hypothesis enables us to predict several interesting properties of the growing semiconductor nanoparticles and it also allows us to interpret the experimental data:

1 Doubling periods and changes in stoichiometry in the growth process
Theoretical and experimental HRTEM-, SAXS- and XRD-investigations proved the size and the tetrahedral cluster shape. The experimentally determined cluster stoichiometries as for example $\mathbf{Zn_4O(OAc)_6}$, $\mathbf{Zn_{10}O_4(OAc)_{12}}$, $\mathbf{Cd_{10}}Se_4\mathbf{(OAc)_{12}}$ and $\mathbf{Cd_{34}}Se_{19}(OAc)_{25}(OH)_5(TBP)_{7.5}$ coincide with the stoichiometries of the fractal Sierpinski Tetrahedron: $\mathbf{M_4EL_{12}}$, $\mathbf{M_{10}E_4L_{24}}$, $\mathbf{M_{34}E_{16}L_{72}}$.

2 Structural correlation of the optical absorption spectra
The optical absorption spectra of the II-VI-semiconductor clusters (ZnS, ZnSe, CdS, CdSe) grown in the presence of different stabilizer molecules and solvents exhibit sharp single- or double-peaks. The single peaks are attributed to the electronic transitions in highly symmetrical tetrahedrons whereas the doublets indicate the presence of asymetrical ellipsoid-like tetrahedron dimers.

3 Metal liberation during the growth process
The proposed fractal model predicts liberation of 6 metal cations accompanying the transition from the lower tetrahedron to the next higher hierarchy level (assuming a metal terminated cluster core). In our nucleation studies, the coalescence of CdSe clusters could be induced either thermally or chemically. The experimental results proved the liberation of metal atoms during colloid growth. The liberated metal cations can either be detected in polarographic experiments or they deliver new clusters after reacting with chalcogen source.

4 Functionalization of tetrahedral nanoparticles with foreigner atoms
Based on the Sierpinski Tetrahedron model, the semiconductor nanostructures offer different kinds of cages (primary octahedral, secondary cuboctahedral and so on). The secondary cages, apparently memorized in the condensed systems, offer up to 12 coordination sites for the inclusion of foreigner atoms as for example trivalent Er or tetravalent Si. Certain synthesis routes deliver 1.5 - 2 nm large oxo-chalcogenide clusters (ZnS, CdS, CdSe) or larger nanocrystals (ZnO) and due to existing internal OH-groups, a doping with foreigner atoms becomes possible. An Er-inclusion activates the characteristic Er^{3+}- NIR-fluorescence (located at 1.54 m) whereas the Si-inclusion produces a strong high field shift in the detected ^{29}Si-NMR spectra (presence of interstitial penta- or hexa-coordinated Si-atoms).