Deliverable D1.3:

“InP/ZnS core-shell quantum dots growth using non-toxic precursors”

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Summary

Growth of InP/ZnS core-shell quantum dots growth using non-toxic precursors for intended use as fosfors have been carried out at Forschungszentrum Jülich, the main results are:

- Synthesis of InP/ZnS NCs emitting between 505 nm and 650 nm.

- Least toxic phosphorus precursor allowing nanocrystals formation identified as tris trimethyl silyl phosphine (PTMS).

- Efficiency of nanocrystals emitting at 530 nm (green colour) measured to be 60% and at 615 nm (red colour) to be 3-5% although there is evidence that it can be increased.
Colloidal semiconductor nanocrystals as colour convertors for white light LEDs have many advantages which include absorption spectrum matching the emission wavelengths of the LEDs and tunable emission wavelength. This potential has been commercialized in companies such as Nanosys Inc, and 3M, USA. Their small size (less than 10 nm) makes them suitable for incorporation into nanostructured LEDs.

Figure 1 shows a chromaticity diagram with marked emission wavelengths of the nanocrystals considered for white light generation from blue LEDs (450nm peak emission) as a starting point of this project. We have restricted the analysis to the correlated colour temperatures (CCTs) in the range from 2500 K to 6500 K, with chromaticity distance of less than 10⁻⁴ and colour rendering index (CRI) above 80. Simple analysis showed that nanocrystals emitting at 530nm are essential for white light as is one set of nanocrystals emitting in the red part of the light spectrum (615 nm, 630 nm or 650 nm). Examples of spectral composition of white light based on a blue 450 nm LED with 530 nm and 615 nm nanocrystals are shown in the table. The highest CCT that can be achieved is 4500 K and in order to extend it while maintaining high CRI, one should either add nanocrystals emitting at 570 nm or 630 nm. In both cases the full useful CCT range can be achieved with CRI above 80 and efficacies of at least 300 lm/W.

<table>
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<tr>
<th>450nm</th>
<th>530nm</th>
<th>615nm</th>
<th>CCT</th>
<th>CRI</th>
<th>Efficacy (lm/W)</th>
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Table 1. Spectral composition of white light generated from 450nm LED and nanocrystals emitting at 530nm and 615nm.

Figure 1. Black squares mark LED spectrum (450nm) and spectra of considered nanocrystals on the chromaticity diagram. Circles on Planckian locus mark the range of considered CCTs.
For the synthesis of InP/ZnS nanocrystals we have studied two methods: a one-pot method and a hot injection method. We have limited ourselves to less toxic precursors for In and Zn (indium acetate and zinc undecylenate). We have used dodecanethiol as a sulphur precursor.

We have studied a wide range of phosphorus precursors as we found them to be reaction controlling. Only three types precursors resulted in formation of nanocrystals: PH3 (and relater RPH2, R= carbonylic group) and tris trimethyl silyl phosphine (PTMS) and we used the last one (PTMS) due to its lowest toxicity.

In the one-pot method all the precursors are mixed at room temperature and then heated rapidly to the reaction temperature at which nanocrystals form. We have found that one-pot method using standard precursors can produce high quality nanocrystals emitting between 450 and 570nm. The efficiency of the nanocrystals emitting at 530nm and 570nm was 60% and 15% (see Figure 2a), respectively. Since this method allows for scaling up for industrial production as well as allows good reproducibility, we believe that this is a method of choice for the synthesis of nanocrystals emitting in green range of the visible light spectrum. While we plan to improve the efficiency of these nanocrystals further, we have concentrated on developing synthesis methods of nanocrystals emitting in the red range of the visible light spectrum.

Figure 2 a) Quantum efficiency for the studied nanocrystal batches. Open symbol marked the best batch with emission at red spectrum range. B): Time resolved photoluminescence for the nanocrystals shown with closed symbols in a).

Figure 3. Examples of emission spectra of nanocrystals synthesised using one-pot synthesis (green line – emission in green wavelength range) and hot-injection method (red line – emission in red wavelength range). Note the emission from defects at wavelengths above 750nm for red line, which is marked in black (modulation of the signal is caused by optical filter).
Since one-pot method did not allow extending the emission wavelength range, we used a hot injection method, which relies on rapid injection of a room temperature solution of precursors into an extremely hot reaction medium in the presence of surfactants or ligands. We have varied phosphorus precursors (chosen on the basis of their reactivity), temperature of reactants and ligands. We found that we needed to employ multiple injections to produce larger nanocrystals with emission at 630 nm (see Figure 3). Apart from the desired emission from the nanocrystals’ cores we observe an emission from the defects at longer wavelengths (beyond about 750 nm). As a result the efficiency of the reproducible nanocrystals with emission wavelength between 615 and 650 nm was between 3-5% (Figure 2a). Correlation between time resolved photoluminescence (which was very similar for the studied set of samples as shown in Figure 2b) and quantum yield measurements suggests that the efficiency
drop is caused by large fraction of nanocrystals not emitting light at all. Transmission electron microscopy (Figure 4) revealed that the shape of the nanocrystals becomes irregular often the nanocrystals look clustered when the emission wavelength is extended, suggesting surface as a source of defects.

One batch of nanocrystals emitting at 630nm had emission efficiency of 15% although it decayed to 9% over a period of two months (most likely due to insufficient ZnS shell or loss of ligands). We have, however, not yet been able to reproduce this synthesis so we are currently studying the reaction mechanism of InP nanocrystal formation at a molecular level to establish the limiting factor and eliminate the defects. Similarly the growth of ZnS shell is also under investigation.

In conclusion, we found that the one-pot synthesis can be used to produce high quality InP/ZnS nanocrystals emitting in the green range of the visible light spectrum. In order to shift the emission to longer wavelengths, the hot-injection method has to be used. The resulting nanocrystals have wider size distribution and higher number of defects resulting in lower efficiency. We are currently studying the reactions during nanocrystals formation and preparing to improve the passivation with better ZnS shell. At the same time we are trying to correlate different experimental techniques (structural and optical) to find an effective characterization procedure for the nanocrystals.