# MULTIPRO - 2nd Year Highlights

This document outlines the main highlights and achievements in the second year (1.11.07-31.10.08) of the MULTIPRO project. It is recommended that the accompanying 1st Year Highlights document be read before this report.

The second years work involved:

1. Molecular Modelling - to enable a fundamental basis for the Nano-composite materials to be developed.
2. Developing New Materials – draws on the modelling work to design, develop and manufacture the novel composite-composite materials.
3. Developing the reactive deposition technology based on M3D - accurately deposit a layer of the newly designed material which is then cured.
4. Multifunctional materials for LED packaging with chip on board technology

## 1. Molecular Modelling – the Fundamental Science.

Hala Laboratory of Thermodynamics and Università degli Studi di Trieste

The materials studied in the second year have been divided in two categories:

1. Hybrid Inorganic-Organic Matrices with embedded Nano-particles and
2. Nano-particles dispersed in a solvent (Nano-particle ink) to be used as printing conductive ink.

A multiscale approach[1], which combines molecular, mesoscale and microscale modeling, was developed to efficiently represent and model these systems. This was a challenging process due to the complexity of the composite materials structures and their interaction during processing.

The modeling was carried out by considering both the physical and chemical interactions, including chemical reaction at equilibrium for the polymer matrix, particularly for the system (1).

Interaction energies for the systems were obtained from Molecular Dynamics atomistic simulations and the results were used to derive the corresponding mesoscale simulation parameters. Mesoscopic calculations were performed to validate the models in the case of functionalized and un-functionalized Nano-particles. The effect of cross-linking of the matrix on the mechanical properties has also been investigated and results show a good agreement with experiments. Multiscale simulation was performed for the particle-particle system with full coating for determining the influence of the solvent for the dispersion of the particles-particles. Results of the mesoscale simulation is shown in **Fig.1**:

An important result obtained in the second year has been the production and test of a reactive mesoscale code, able to describe chemical reaction (in the polymer phase) at the mesoscale. The results of this work include prediction of the effects of the system density and isolated-polymer material properties on the polydispersity. The simulation protocol and code has been tested on a real system and the results obtained compared very well with experimental evidence.

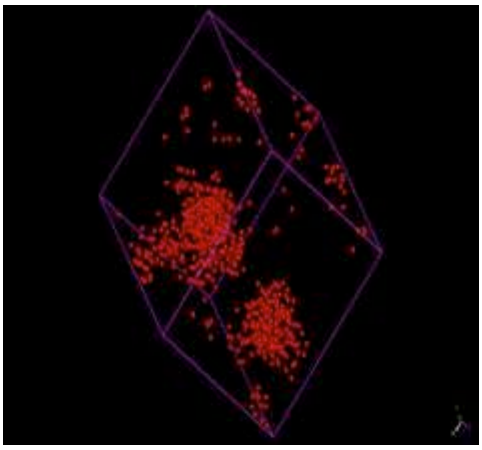

**Figure 1. Simulation of particle-particle dispersion.**
**(Nano-particles marked in red)**

Another important result of the simulations is related to optical properties and in particular the refractive index and the transmittance of loaded matrices.

[1] A full description of the modelling process, theory and the time evolution particle-particle composite system is shown on the MULTIPRO website Modelling web page.

## 2. Developing New Materials

Università degli Studi di Padova (University of Padova)

The Nano-composite route to high refractive index materials has been further exploited by focusing on Titania Nano-particle composites. Titania Nano-crystals in the 4-5 nm diameter range have been synthesised in acidic media with good colloidal stability and high concentration, **Fig. 2.** These particles were homogeneously introduced in a hybrid matrix material obtained through sol-gel processing of glycidoxypropyltrimethoxisilane, obtaining thin films deposition with easily tuneable refractive index in the 1,5-1,89 range, **Fig. 3,** and good transparency.

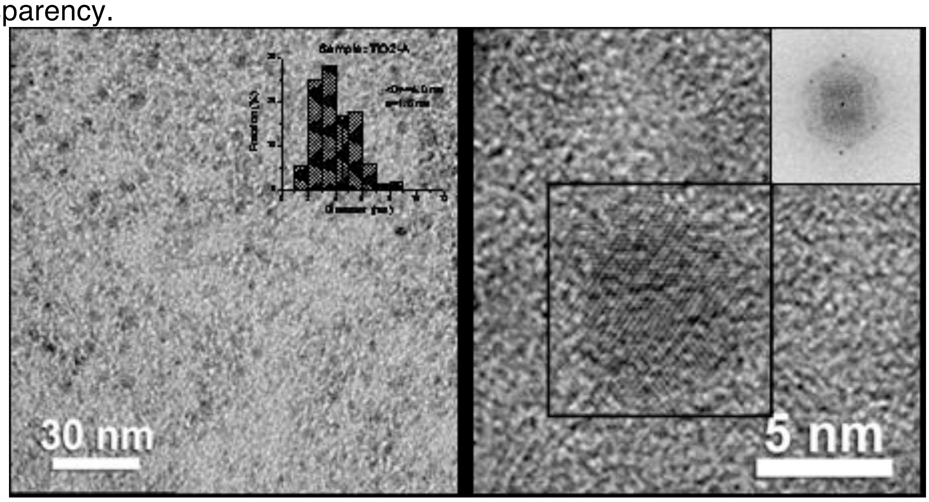


**Figure 2. High Resolution Transmission Electron Microscope (HR TEM) images of Titania particles obtained in acidic media.**

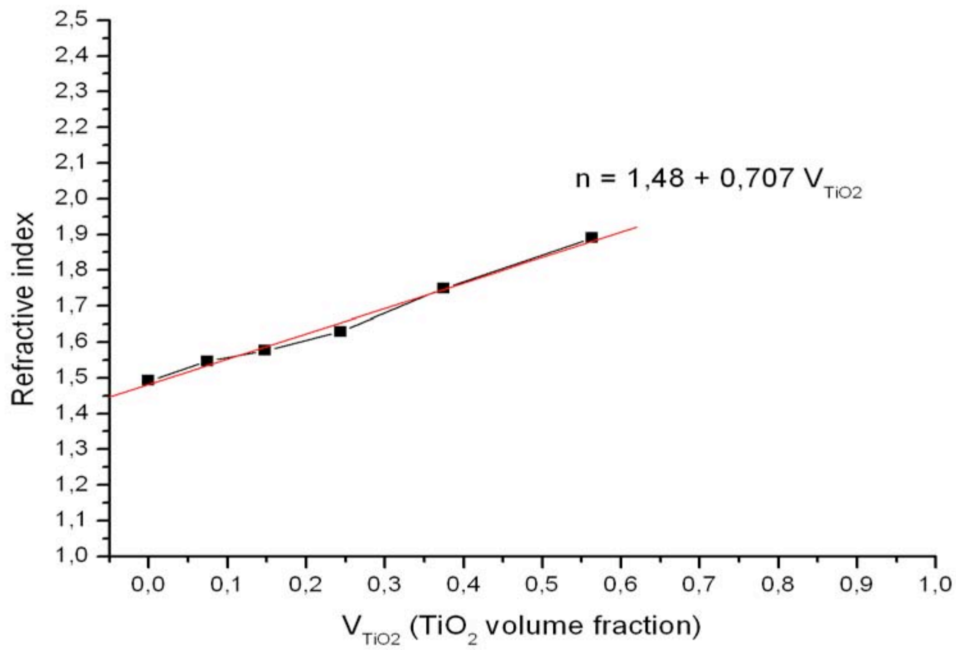


**Figure 3. Refractive Index values dependency on $TiO_2$ volume fraction.**

However, these materials encountered some difficulties when processed with the deposition techniques involved in the project. The materials cracked on post deposition curing of the materials and it was difficult to achieve the correct shape of deposit (a hemisphere LED glob top is required).

Thus, a different synthesis for Titania crystals-crystals in basic media with organic capping has been developed, **Fig. 4**, and hybrid materials with more organic content or purely organic polymers were chosen as matrices. Materials with a refractive index almost 1.8 have been obtained. This allowed a consistent improvement of material processing during deposition. Nevertheless, some aspects have still to be refined.

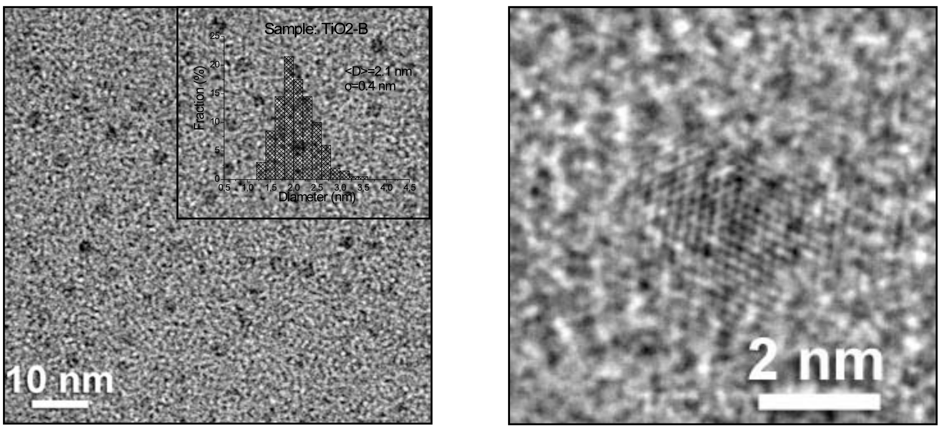


**Figure 4. HR TEM image of Titania particles synthesised in basic media.**

Purely hybrid material based on phenyl containing organosilanes for refractive index enhancement, without inorganic particles, have also been tried due to better processing behaviour. Material with refractive index up to 1,62 has been obtained.

To add a second level of functionality to the new materials, the project considered particles-particles for wavelength conversion to produce tailored white light from standard LEDs. Fluorescent crystal-crystal synthesis based on cadmium selenide core/shell particles has been developed. These particles consist of a CdSe core covered by a shell of graded composition composed of CdS, CdZnS and Zns, in order to guarantee high luminescence and optical property stability, **Fig. 5**.

These particles were properly functionalised in order to achieve homogeneous dispersion in the matrix materials described above with good results. The exact wavelength emission for white light can be tailored by varying the dimension of CdSe core. The synthesis for the right colour emitting particles has to be refined. Additional steps include the mixing both particle-particle types in the same matrix to give a multifunctional material.

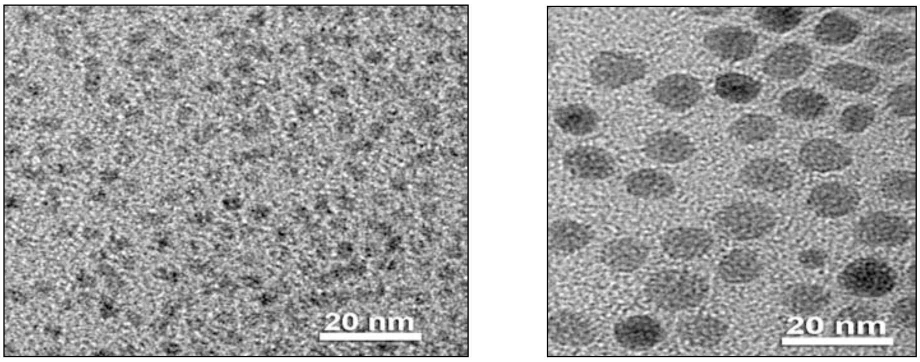


**Figure 5. HR TEM image of CdSe particles before and after shell deposition procedure**

**Figure 6. Photoluminescence under UV illumination of the core-shell particles in solution and incorporated in an inorganic film.**

## 3. Reactive Deposition Technology.

Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung.

IFAM successfully deposited sol gel materials filled with particles-particles for LED encapsulation, which had a RI of up to 1.72 (Project Goal 1.8). Università degli Studi di Padova prepared these solutions. Fig. 7 shows the deposited and cured materials.

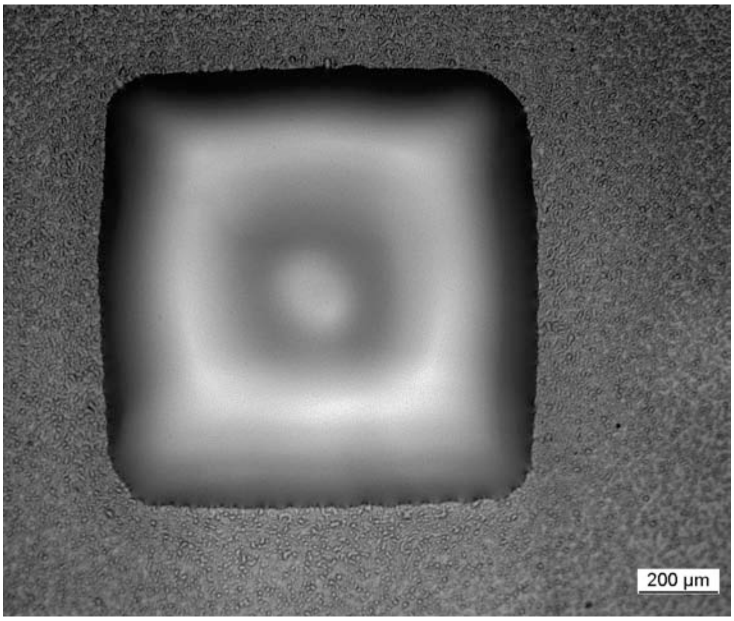


**Figure 7: M$^3$D deposited and furnace cured sol gel material filled with particles-particles to increase the refractive index. Height ca 30$\mu$m**

In addition IFAM printed conductive circuits based on silver and gold inks where CRP could successfully apply LED chips by flip chip bonding, Fig. 8-9. All LED chips could be illuminated via the printed paths.

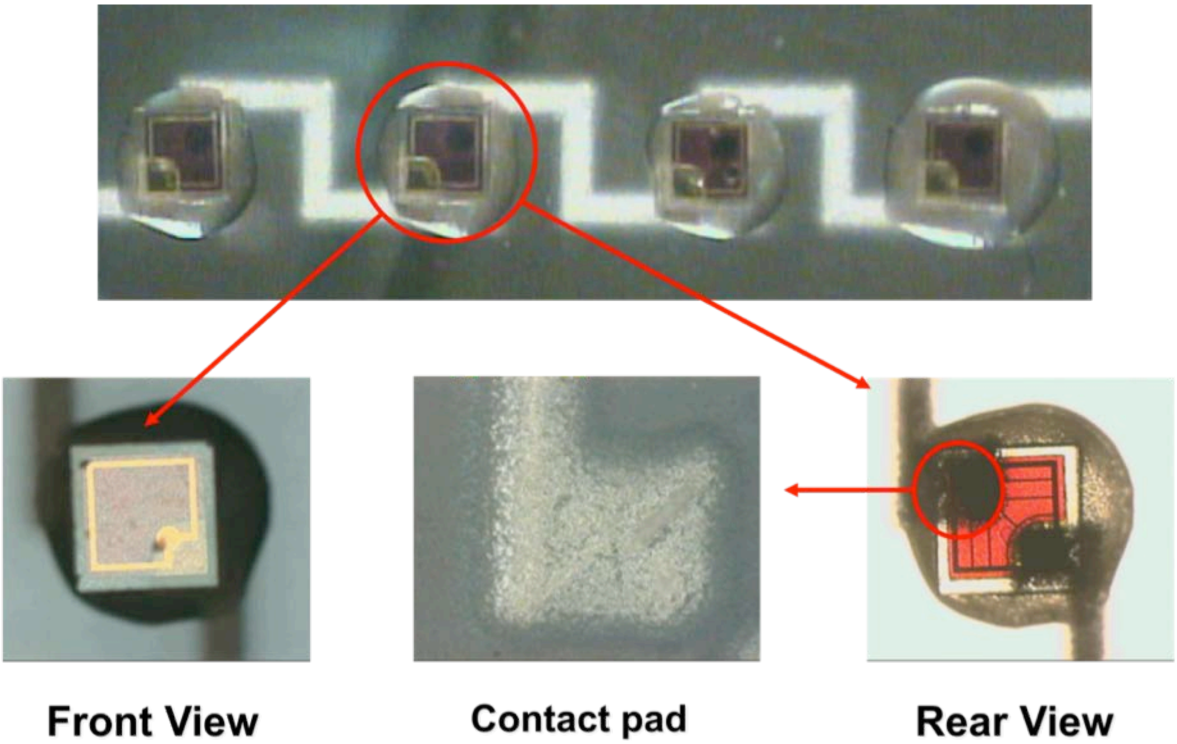


**Figure 8. LED Chips (14mm x 14mm) on Silver Circuit.**

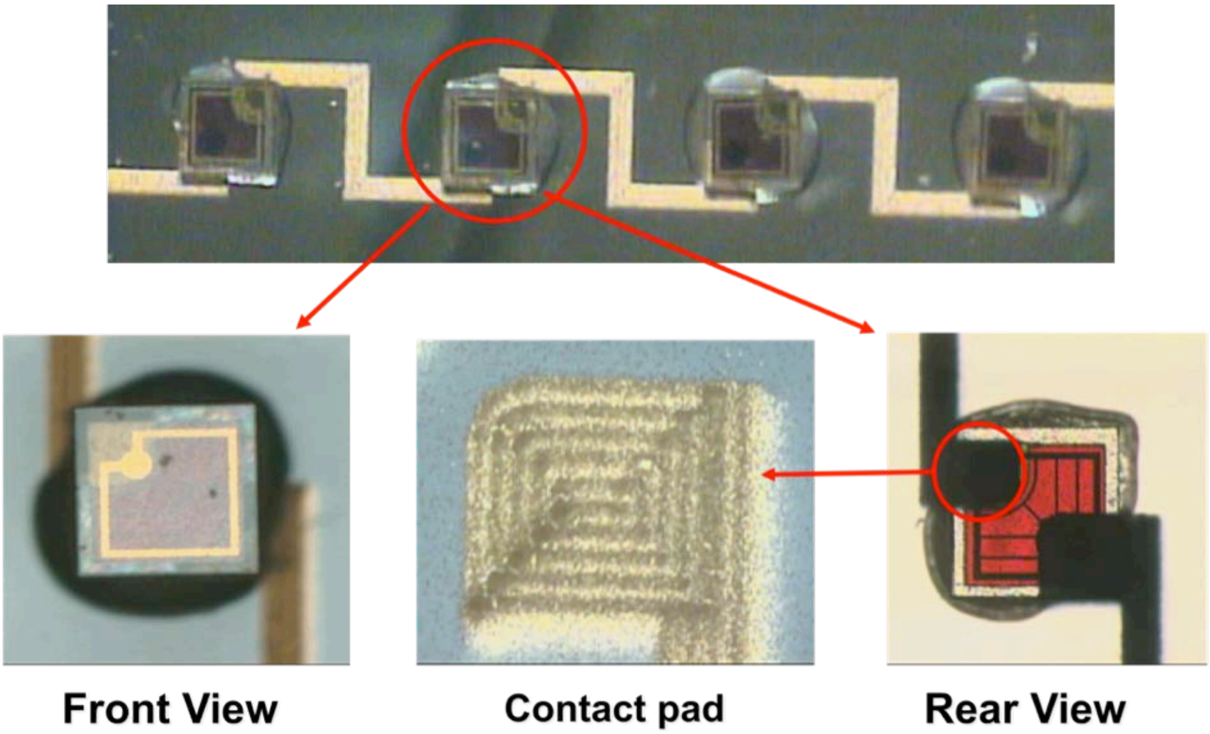


**Figure 9. LED Chips (14mm x 14mm) on Gold Circuit.**

The assembled LED devices exhibited:

- Good adhesion of chip-LEDs on both printed structures
- Good alignment between chip-LEDs contacts and printed structures
- All LEDs series switch on at nominal power
- Silver Ink Printed structures present some voids that need to be eliminated by process optimization.

## 4. Multifunctional materials for LED packaging with chip on board technology

Centro Ricerche Plast-Optica

Multifunctional materials developed in the framework of MULTIPRO project have been applied with chip on board (COB) technology at CRP, Fig. 10.

The hybrid transparent material doped with CdSe, developed by UNIDP, has been employed for LED encapsulation to create white LED light. A blue LED chip has been encapsulated with down-converting material. The results, Fig. 11 show that conversion of blue wavelength has been achieved. However, low wavelength emission nano-particles (which emit in yellow range) must be prepared for true white light production.

Flip chip contacting was exploited for the realization of transparent display on glass. The chip-LED has been attached on the printed line with M$^3$D printer by IFAM. The conductivity achieved was enough in order to drive the red chip LED, as showed in Fig. 12.


**Figure 10. COB automatic assembling line at CRP labs.**

**Figure 11. “White” LED realised by coupling blue LED with down-converter material.**

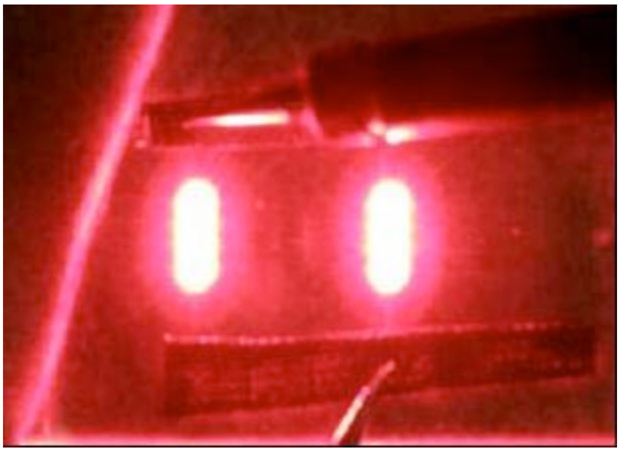

**Figure 12. Red chip LED on glass.**